Federal Ministry
Republic of Austria
Agriculture, Regions
and Tourism

State of the Art for Surface Treatment of Metals and Plastics by an Electrolytic or Chemical Process (Galvanic Industry)

Description of Austrian plants

Vienna, 2021

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1 Stand der Technik (BVT)

1.1 Allgemeine BvT Schlußfolgerungen – Oberflächenbehandlung von Metallen und Kunststoffen durch ein elektrolytisches oder chemisches Verfahren (Galvanikindustrie)

Ausgehend von erhobenen Emissions- und Verbrauchsdaten der österreichischen Galvanikindustrie wurden die folgenden Techniken und Emissionswerte als Stand der Technik abgeleitet. Der Begriff „Stand der Technik" ist dem Begriff „Beste verfügbare Technologie" (BvT) gleichbedeutend.

1.1.1 Allgemeine BvT Umweltmanagementsystem

Es ist BvT, ein Umweltmanagementsystem zu erstellen oder ein international anerkanntes System einzuführen wie z. B. EMAS oder ISO 14001.

Es ist BvT, im Rahmen des Umweltmanagementsystems regelmäßig Kennzahlen zu Energieverbrauch, Wasserverbrauch, Rohstoffverbrauch, Auswahl der Betriebsmittel, Emissionen in die Atmosphäre, Emissionen ins Wasser und zur Abfallerzeugung zu erheben.

1.1.2 Allgemeine BvT Lagerung von Chemikalien

Die folgenden Techniken (in entweder individueller Anwendung oder in einer passenden Kombination) werden als BvT zur Lagerung von Chemikalien angesehen:

- Getrennte Lagerung von Säuren und Basen;
- Getrennte Lagerung von brennbaren und oxidierenden Stoffen (um das Risiko eines Brands zu verringern);
- Lagerung von flüssigen Chemikalien in Auffangbecken/Auffangtassen um eine angemessene interne und externe Behandlung und Entsorgung zu gewährleisten. Es darf zu keiner Kontamination der Umwelt kommen;
- Chemikalien, die unter Feuchtigkeit selbstentzündlich sind, müssen in einem Trockenbereich und getrennt von oxidierenden Stoffen gelagert werden. Der Lagerbereich ist

entsprechend zu kennzeichnen, damit kein Wasser im Fall einer Brandbekämpfung eingesetzt wird;
- Kontamination des Bodens oder des Grundwassers durch Verschütten der Chemikalien, Leckagen oder Überlaufen von Auffangbecken/Auffangtassen muss verhindert werden;
- Die Beschädigung von Lagertanks, Rohrleitungen, Förder- und Überwachungssystemen durch mechanische oder chemische Einflüsse ist zu verhindern (etwa durch bautechnische Maßnahmen, regelmäßige Wartung und Kontrollen);
- Getrennte Lagerung von Säuren und Cyanid (Bildung von Cyanwasserstoff).

1.1.3 Allgemeine BvT Überwachung

Die folgenden Techniken (in entweder individueller Anwendung oder in einer passenden Kombination) werden als BvT zur Überwachung von Abwasser- und Luftemissionen angesehen:

1.1.3.1 Abwasseremissionen

Die Bestimmung von Emissionsparametern an Hand von mengenproportionalen nicht abgesetzten homogenisierten Tagesmischproben ist für die Mehrheit der Parameter BvT. Eine Tagesmischprobe ist die über die tatsächliche Abwasserablaufzeit innerhalb eines Zeitraumes von 24 Stunden mengenproportional gezogene Mischprobe (Abweichung von 24 Stunden Mischprobe gem. Bescheid, z.B. chargenbezogen, kann vorkommen).

Bestimmte Parameter sind kontinuierlich zu messen (wie etwa Abwassermenge, Temperatur und pH-Wert), wobei andere Parameter (aus analytischen Gründen) an Hand von Stichproben bestimmt werden (wie etwa abfiltrierbare Stoffe, Gesamtchlor).

Überwachung durch den Betrieb

Die Implementierung eines Überwachungssystems durch den Betrieb zur Optimierung des Produktionsprozesses und zur Kontrolle der Abwasserreinigungsanlage ist BvT. Dies schließt die Überwachung der Bescheidparameter und zusätzlicher Parameter nach Bedarf (e.g. Messung von Emissionsparametern vor und nach der Behandlung des Abwassers, Abwassermenge, Temperatur, Schlammvolumen, Leitfähigkeit,…), ein, sowie die Setzung kürzerer Überwachungsintervalle.

Externe, unabhängige Überwachung

Eine externe, unabhängige Überwachung durch authorisierte Experten, Institutionen oder Firmen ist BvT.

BvT für eine externe, unabhängige Überwachung umfasst:

- Überwachung von Emissionsparametern;
- Überprüfung der Betriebsparameter (Betriebstagebuch der Abwasseranlage);
- Beurteilung des Zustands der Abwasserreinigungsanlage einschließlich des Probenahmegeräts zur Überwachung durch den Betrieb und des Abwassermengenmessungsgeräts;
- Gegenüberstellung der externen, unabhängigen Überwachungsergebnisse mit den Überwachungsergebnissen durch den Betrieb;
- Gegenüberstellung der Überwachungsergebnisse mit den jeweiligen Emissionsgrenzwerten;
- Überprüfung der Betriebsbedingungen und der Produktionsmenge während der Überwachung;
- Überwachung von zusätzlichen Parametern (siehe "Überwachung durch den Betrieb";
- Dokumentation über die angewandten Messmethoden;
- Externe, unabhängige Überwachung muss an repräsentativen Produktionstagen durchgeführt werden (dabei sind auch Produktionstage mit einer hohen Belastung der Abwasserreinigungsanlage einzubeziehen).

Parameterauswahl

Abwasser aus der Behandlung von Oberflächen kann sich auf Grund der Vielzahl eingesetzter Roh-, Arbeits- und Hilfstoffe, sowie der Bestandteile der bearbeiteten Werkstücke voneinander unterscheiden. Zur Überwachung gilt es die relevanten Parameter zu identifizieren. Relevante Parameter ergeben sich aus den jeweils verwendeten Roh-, Arbeits- und Hilfstoffen, sowie aus den bearbeiteten Werkstücken. Die Parameterauswahl ist von der Wasserrechtsbehörde zu treffen gem. §4(1) Allgemeine Abwasseremissionsverordnung (AAEV).

Es ist BvT, im Allgemeinen folgende Parameter zur Überwachung der Abwasserbeschaffenheit einzusetzen – Table 1 präsentiert den Stand der Technik für die Überwachung allgemeiner Parameter, deren Messmethode und die Mindesthäufigkeiten der Eigen- und

Fremdüberwachung. Die Begriffe Eigen- und Fremdüberwachung sind gem. AAEV §1(3)Z8 und Z9 zu verstehen. AAEV §1(3)Z8 „Eigenüberwachung: Kontrolle der Beschaffenheit des Abwassers, die durch den Wasserberechtigten selbst oder durch einen von ihm Beauftragten durchgeführt wird.“ AAEV §1(3)Z9 „Fremdüberwachung: Kontrolle der Beschaffenheit des Abwassers gemäß § 134 WRG 1959 oder im Einzelfall durch die Gewässeraufsicht oder die Behörde.“

Gemäß Methodenverordnung Wasser gilt im Rahmen der Eigenüberwachung eine Analysemethode als gleichwertig, wenn ihre Bestimmungsgrenze bei höchstens 30% der zu überwachenden Emissionsbegrenzung liegt (Methoden-VO §4(4)1).

Eine werktägliche Eigenüberwachung bedeutet, dass die Eigenüberwachung an Tagen an denen am Standort produziert wird zu erfolgen hat. Bei großen Bandverzinkungsanlagen ist die Mindesthäufigkeit der Eigenüberwachung wöchentlich an versetzten Tagen. Große Bandverzinkungsanlagen sind Anlagen mit einer Produktionskapazität größer 100.000 t/a.

Für die Fremdüberwachung (FÜ) gilt, dass in der Regel eine Mindesthäufigkeit der FÜ von allen 6 Monaten (2xjährlich) Stand der Technik ist. Eine externe Überwachung (Fremdüberwachung) kann im Einzelfall jährlich stattfinden, sofern die Emissionswerte nachweislich ausreichend stabil sind und z.B. der Prozess kontinuierlich abläuft. Im Bedarfsfall (bei geringem Automatisierungsgrad der Abwasserbehandlung, hoher Belastung und stark schwankende Zusammensetzung des Abwassers, bei häufigen Grenzwertüberschreitungen) kann aber auch eine häufigere FÜ vorgeschrieben werden (z.B. 3xjährlich, 4x jährlich oder 6xjährlich).

Table 1: Stand der Technik der allgemeinen Parameter zur Überwachung der Abwasserbeschaffenheit und die, Mindesthäufigkeiten der Eigen- und Fremdüberwachung

Parameter	Norm	Mindesthäufigkeit – EÜ[1]	Mindesthäufigkeit – FÜ[2] [3]
Temperatur	DIN 38404-4 (DEV C 4)	kontinuierlich	halbjährlich
Abfiltrierbare Stoffe	ÖNORM EN 872	–	halbjährlich
pH-Wert	ÖNORM EN ISO 10523	kontinuierlich	halbjährlich
Bakterientoxizität GL	ÖNORM EN ISO 11348-1	–	halbjährlich
Fischeitoxizität GF,Ei	ÖNORM EN ISO 15088	–	halbjährlich

Es ist BvT, Metalle oder Metalloide im Abwasser zu überwachen. Metalle oder Metalloide stammen aus in Lösung gegangenen Werkstückanteilen (Hauptmetalle, Legierungsbestandteile), aus Arbeits- und Hilfsstoffen (Bäder und deren Zusätze), sowie aus Chemikalien, die in der Abwasserreinigung eingesetzt werden (Eisen, Aluminium) – Table 2 präsentiert den Stand der Technik für die Überwachung von Metallen oder Metalloiden, deren Messmethode und die Mindesthäufigkeiten der Eigen- und Fremdüberwachung.

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[1] Bei großen Bandverzinkungsanlagen ist die Mindesthäufigkeit der Eigenüberwachung wöchentlich an versetzten Tagen

[2] Eine externe Überwachung (Fremdüberwachung) kann im Einzelfall jährlich stattfinden, sofern die Emissionswerte nachweislich ausreichend stabil sind und z.B. der Prozess kontinuierlich abläuft

[3] Im Bedarfsfall (bei geringem Automatisierungsgrad der Abwasserbehandlung, hoher Belastung und stark schwankende Zusammensetzung des Abwassers, bei häufigen Grenzwertüberschreitungen) kann aber auch eine häufigere FÜ vorgeschrieben werden

Table 2: Stand der Technik der Metalle und die, Mindesthäufigkeiten der Eigen- und Fremdüberwachung

Parameter	Norm	Mindesthäufigkeit – EÜ[4]	Mindesthäufigkeit – FÜ[5] [6]
Aluminium	ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	werktags	halbjährlich
Arsen	ÖNORM EN ISO 15586; ÖNORM EN ISO 11969; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	werktags	halbjährlich
Barium	ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	werktags	halbjährlich
Blei	ÖNORM ISO 8288; ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	werktags	halbjährlich
Cadmium	ÖNORM ISO 8288; ÖNORM EN ISO 5961; ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	werktags	halbjährlich
Chrom-Gesamt	ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2;	werktags	halbjährlich
Chrom-VI	ÖNORM M 6288; DIN 38405-4 (DEV D 4); ÖNORM EN ISO 10304-3	werktags	halbjährlich
Cobalt	ÖNORM ISO 8288; ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	werktags	halbjährlich

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[4] Bei großen Bandverzinkungsanlagen ist die Mindesthäufigkeit der Eigenüberwachung wöchentlich an versetzten Tagen

[5] Eine externe Überwachung (Fremdüberwachung) kann im Einzelfall jährlich stattfinden, sofern die Emissionswerte nachweislich ausreichend stabil sind und z.B. der Prozess kontinuierlich abläuft

[6] Im Bedarfsfall (bei geringem Automatisierungsgrad der Abwasserbehandlung, hoher Belastung und stark schwankende Zusammensetzung des Abwassers, bei häufigen Grenzwertüberschreitungen) kann aber auch eine häufigere FÜ vorgeschrieben werden

Parameter	Norm	Mindesthäufigkeit – EÜ[4]	Mindesthäufigkeit – FÜ[5] [6]
Eisen	ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	werktags	halbjährlich
Kupfer	ÖNORM ISO 8288; ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	werktags	halbjährlich
Nickel	ÖNORM ISO 8288; ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	werktags	halbjährlich
Selen	ÖNORM EN ISO 15586; DIN 38405 – D 23-2 (DEV D 23-2); ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	werktags	halbjährlich
Silber	ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	werktags	halbjährlich
Zink	ÖNORM ISO 8288; ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	werktags	halbjährlich

Es ist BvT, Fluorid, Phosphor, Sulfat, Ammonium und Nitrit im Abwasser zu überwachen. F, P, SO_4, NH_4 und NO_2 stammen aus dem Einsatz von Arbeitschemikalien. Table 3 präsentiert den Stand der Technik für die Überwachung von F, P, SO_4, NH_4 und NO_2, deren Messmethode und die Mindesthäufigkeiten der Eigen- und Fremdüberwachung.

Table 3: Stand der Technik F, P, SO_4, NH_4 und NO_2 und die, Mindesthäufigkeiten der Eigen- und Fremdüberwachung

Parameter	Norm	Mindesthäufigkeit – EÜ[7]	Mindesthäufigkeit – FÜ[8] [9]
Fluorid	ÖNORM EN ISO 10304-1; DIN 38405-D4-1 (DEV D 4-1)	werktags	halbjährlich
Phosphor	ÖNORM EN ISO 6878; ÖNORM EN ISO 15681-1; ÖNORM EN ISO 15681-2; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	wöchentlich	halbjährlich
Sulfat	ÖNORM EN ISO 10304-1	wöchentlich	halbjährlich
Ammonium ber. als N (NH_4-N)	ÖNORM EN ISO 14911; ÖNORM EN ISO 11732; ÖNORM ISO 7150-1; ÖNORM ISO 5664; DIN 38406-5 (DEV E 5)	werktags	halbjährlich
Nitrit ber. als N (NO_2-N)	ÖNORM EN 26777; ÖNORM EN ISO 10304-1; ÖNORM EN ISO 13395	werktags	halbjährlich

Es ist BvT, freies Chlor und Ammonium im Abwasser zu überwachen, wenn Cyanid- oder Nitritoxidation in der Abwasserbehandlung eingesetzt wird. Table 4 präsentiert den Stand der Technik für die Überwachung von freiem Chlor und Ammonium.

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[7] Bei großen Bandverzinkungsanlagen ist die Mindesthäufigkeit der Eigenüberwachung wöchentlich an versetzten Tagen

[8] Eine externe Überwachung (Fremdüberwachung) kann im Einzelfall jährlich stattfinden, sofern die Emissionswerte nachweislich ausreichend stabil sind und z.B. der Prozess kontinuierlich abläuft

[9] Im Bedarfsfall (bei geringem Automatisierungsgrad der Abwasserbehandlung, hoher Belastung und stark schwankende Zusammensetzung des Abwassers, bei häufigen Grenzwertüberschreitungen) kann aber auch eine häufigere FÜ vorgeschrieben werden

Table 4: Stand der Technik – freies Chlor und Ammonium und die, Mindesthäufigkeiten der Eigen- und Fremdüberwachung

Parameter	Norm	Mindesthäufigkeit – EÜ	Mindesthäufigkeit – FÜ[10] [11]
freies Chlor	ÖNORM EN ISO 7393-1; ÖNORM EN ISO 7393-2	–	halbjährlich
Ammonium ber. als (NH_4-N)	ÖNORM EN ISO 14911; ÖNORM EN ISO 11732; ÖNORM ISO 7150-1; ÖNORM ISO 5664; DIN 38406-5 (DEV E 5)	werktags	halbjährlich

Es ist BvT, Cyanid im Abwasser zu überwachen, wenn Cyanid als Arbeitsstoff verwendet wird. Cyanid kann als freies Cyanid und als komplex gebundenes Cyanid vorliegen. Table 5 präsentiert den Stand der Technik für die Überwachung von Cyanid.

Table 5: Stand der Technik – Cyanid und die, Mindesthäufigkeiten der Eigen- und Fremdüberwachung

Parameter	Norm	Mindesthäufigkeit – EÜ[12]	Mindesthäufigkeit – FÜ[13] [14]
Cyanid – leicht freisetzbar	ÖNORM EN ISO 14403-1; ÖNORM EN ISO 14403-2; DIN 38405-13 (DEV D 13); ÖNORM M 6285	werktags	halbjährlich
Cyanid gesamt	ÖNORM EN ISO 14403-1; ÖNORM EN ISO 14403-2; ÖNORM M 6285; DIN 38405-13 (DEV D 13)	werktags	halbjährlich

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[10] Eine externe Überwachung (Fremdüberwachung) kann im Einzelfall jährlich stattfinden, sofern die Emissionswerte nachweislich ausreichend stabil sind und z.B. der Prozess kontinuierlich abläuft

[11] Im Bedarfsfall (bei geringem Automatisierungsgrad der Abwasserbehandlung, hoher Belastung und stark schwankende Zusammensetzung des Abwassers, bei häufigen Grenzwertüberschreitungen) kann aber auch eine häufigere FÜ vorgeschrieben werden

[12] Bei großen Bandverzinkungsanlagen ist die Mindesthäufigkeit der Eigenüberwachung wöchentlich an versetzten Tagen

[13] Eine externe Überwachung (Fremdüberwachung) kann im Einzelfall jährlich stattfinden, sofern die Emissionswerte nachweislich ausreichend stabil sind und z.B. der Prozess kontinuierlich abläuft

[14] Im Bedarfsfall (bei geringem Automatisierungsgrad der Abwasserbehandlung, hoher Belastung und stark schwankende Zusammensetzung des Abwassers, bei häufigen Grenzwertüberschreitungen) kann aber auch eine häufigere FÜ vorgeschrieben werden

Es ist BvT, Sulfid im Abwasser zu überwachen, wenn Sulfid zur Fällung in der Abwasserbehandlung eingesetzt wird. Table 6 präsentiert den Stand der Technik für die Überwachung von Sulfid.

Table 6: Stand der Technik – Sulfid und die, Mindesthäufigkeiten der Eigen- und Fremdüberwachung

Parameter	Norm	Mindesthäufigkeit – EÜ[15]	Mindesthäufigkeit – FÜ[16] [17]
Sulfid	ÖNORM M 6615; DIN 38405-27 (DEV 27)	wöchentlich	halbjährlich

Es ist BvT, zur Überwachung der organischen Inhaltsstoffe im Abwasser die Parameter CSB, AOX, schwerflüchtige lipophile Stoffe, Kohlenwasserstoffindex, Summe anionische und nichtionische Tenside und POX einzusetzen. Alternativ zum Parameter CSB kann der Parameter TOC eingesetzt werden. Halogenorganische Verbindungen gelangen durch Roh-, Arbeits- oder Hilfsstoffe ins Abwasser, entstehen aber auch im Abwasser selbst (Cyanidoxidation mit Natriumhypochlorit-Lösung) und werden durch den Parameter AOX erfasst. Der Parameter POX ist nur in jenen Fällen anzuwenden, in denen leichtflüchtige halogenierte Kohlenwasserstoffe in der Fertigung eingesetzt werden. Die Parameter Kohlenwasserstoffindex und schwerflüchtige lipophile Stoffe erfassen Fette, Öle, Kohlenwasserstoffe und sonstige hydrophobe Roh-, Arbeits- und Hilfsstoffe im Abwasser. Table 7 präsentiert den Stand der Technik für die Überwachung von organischen Inhaltsstoffen im Abwasser.

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[15] Bei großen Bandverzinkungsanlagen ist die Mindesthäufigkeit der Eigenüberwachung wöchentlich an versetzten Tagen

[16] Eine externe Überwachung (Fremdüberwachung) kann im Einzelfall jährlich stattfinden, sofern die Emissionswerte nachweislich ausreichend stabil sind und z.B. der Prozess kontinuierlich abläuft

[17] Im Bedarfsfall (bei geringem Automatisierungsgrad der Abwasserbehandlung, hoher Belastung und stark schwankende Zusammensetzung des Abwassers, bei häufigen Grenzwertüberschreitungen) kann aber auch eine häufigere FÜ vorgeschrieben werden

Table 7: Stand der Technik – organische Inhaltsstoffe im Abwasser und die Mindesthäufigkeiten der Eigen- und Fremdüberwachung

Parameter	Norm	Mindesthäufigkeit – EÜ[18]	Mindesthäufigkeit – FÜ[19] [20]
CSB	ÖNORM M 6265; DIN 38409-41 (DEV H 41); DIN 38409-44 (DEV H 44); ÖNORM ISO 15705	werktags	halbjährlich
AOX	ÖNORM EN ISO 9562	–	halbjährlich
Schwerflüchtige lipophile Stoffe	DIN ISO 11349 (DEV H 56)	–	halbjährlich
Kohlenwasserstoffindex	ÖNORM EN ISO 9377-2	–	halbjährlich
Summe anionische und nichtionische Tenside	DIN 38405-D23	–	halbjährlich
Anionische Tenside	ÖNORM EN 903	–	halbjährlich
Nichtionische Tenside	DIN 38409-H23	–	halbjährlich
POX	DEV-H 25	–	halbjährlich

1.1.3.2 Luftemissionen

Soweit nicht anders angegeben, beziehen sich die BvT assoziierten Emissionswerte für Emissionen in die Luft auf Konzentrationen, ausgedrückt als Masse emittierter Stoffe bezogen auf das Abgasvolumen im Normzustand (trockenes Gas bei einer Temperatur von 273,15 K und einem Druck von 101,3 kPa) ohne Korrektur für den Sauerstoffgehalt, ausgedrückt in mg/Nm³.

Der Mittelungszeitraum von BvT assoziierten Emissionen in die Luft ist ein Mittelwert über drei aufeinanderfolgende Messungen von jeweils 30 Minuten. Für Parameter, bei denen

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[18] Bei großen Bandverzinkungsanlagen ist die Mindesthäufigkeit der Eigenüberwachung wöchentlich an versetzten Tagen

[19] Eine externe Überwachung (Fremdüberwachung) kann im Einzelfall jährlich stattfinden, sofern die Emissionswerte nachweislich ausreichend stabil sind und z.B. der Prozess kontinuierlich abläuft

[20] Im Bedarfsfall (bei geringem Automatisierungsgrad der Abwasserbehandlung, hoher Belastung und stark schwankende Zusammensetzung des Abwassers, bei häufigen Grenzwertüberschreitungen) kann aber auch eine häufigere FÜ vorgeschrieben werden

eine 30-minütige Probenahme aus Gründen der Probenahme oder Analyse nicht sinnvoll ist, kann ein besser geeigneter Messzeitraum gewählt werden.

Wird die Abluft aus zwei oder mehreren Quellen über einen gemeinsamen Abluftkanal abgeleitet, so gelten die BvT assoziierten Emissionswerte für den kombinierten Ausstoß aus dem Abluftkanal.

Parameterauswahl

Abluft aus der Behandlung von Oberflächen kann sich auf Grund der Vielzahl angewandter Verfahren, eingesetzter Roh-, Arbeits- und Hilfstoff, sowie der Bestandteile der bearbeiteten Werkstücke voneinander unterscheiden. Zur Überwachung gilt es, die relevanten Parameter zu identifizeren. Relevante Parameter ergeben sich aus den angewendeten Verfahren, den jeweils verwendeten Roh-, Arbeits- und Hilfstoffen, sowie aus den bearbeiteten Werkstücken.

Es ist BvT, im Allgemeinen folgende Parameter zur Überwachung der Emissionen in die Luft einzusetzen. Table 8 präsentiert den Stand der Technik für die Überwachung allgemeiner Parameter, deren Messmethode und die Mindesthäufigkeiten.

Table 8: Mindesthäufigkeit der Überwachung – Stand der Technik allgemeiner Parameter zur Überwachung der Abluftbeschaffenheit

Parameter	Norm	Mindesthäufigkeit
Staub	EN 13284-1	3 Jahre
HCl	EN 1911	3 Jahre

Tabelle 9: Mindesthäufigkeit der Überwachung – Stand der Technik prozessspezifische Parameter zur Überwachung der Abluftbeschaffenheit

Parameter	Norm	Mindesthäufigkeit
Cr – total	EN 14385	3 Jahre
Cr(VI)	DIN 38405 D24	3 Jahre

Parameter	Norm	Mindesthäufigkeit
Cu	EN 14385	3 Jahre
Ni	EN 14385	3 Jahre
Zn	EN 14385	3 Jahre
CN	EN 14403-2	3 Jahre
HCN	EN 14403-2	3 Jahre
H_2SO_4	EN 14791:2017	3 Jahre
HF	EN 15713	3 Jahre
TVOC	EN 12619	3 Jahre

1.1.4 Allgemeine BvT Energieverbrauch und Reduzierung der Wärmeverluste

Die folgenden Techniken (in entweder individueller Anwendung oder in einer passenden Kombination) werden als BvT zur Verminderung von Energieverbrauch und Reduzierung der Wärmeverluste angesehen:

- Implementierung eines Energie Management Systems;
- Weitestgehende Reduktion des Spannungsabfalls zwischen Stromquelle und Verbraucher durch die Verringerung des Abstands zwischen Gleichrichter und Anode bzw. Kathode (Leitrollen bei Bandanlagen) – auf Grund von Korrosionsgefahr können die Gleichrichter nicht immer in unmittelbarer Nähe der Arbeitsstationen installiert werden;
- Ausstattung jeder Arbeitsstation mit einem eigenen Gleichrichter, um den Galvanisierstrom je nach Warenoberfläche einstellen und regeln zu können (bei der elektrolytischen Oberflächenbehandlung);
- Möglichkeiten zur Wärmerückgewinnung wahrnehmen;
- Wärmeisolierung von beheizten Bädern (doppelwandige Behälter, vorisolierte Behälter);
- Isolierabdeckung der Lösungsoberfläche durch geeignete Abdeckungen;
- Lufteinblasung zur Elektrolytbewegung von beheizten Elektrolyten ist nicht BvT, da durch die erhöhte Verdunstung Energieverluste auftreten.

1.1.5 Allgemeine BvT Wasserverbrauch und Abwasseranfall

Die folgenden Techniken (in entweder individueller Anwendung oder in einer passenden Kombination) werden als BvT zur Verminderung von Wasserverbrauch und Abwasseranfall angesehen:

- Überwachen der Wasser- und Stoffverbrauchsstellen innerhalb einer Anlage und regelmäßiges Aufzeichnen der Verbrauchswerte, die relevant für den Betrieb (Prozess) sind. Die aufgezeichneten Werte dienen dem Umweltmanagementsystem;
- Reduzierung des Eintrags von Verunreinigungen durch effizientes Spülen;
- Reduzierung des Eintrags von Spülwasser durch geeignete Maßnahmen wie Abquetschen, Abblasen oder entsprechende Abtropfzeiten der Werkstücke;
- Reduzierung von Verschleppungsverlusten durch Abtropfen, Abblasen, Abquetschen, Abstreifen, Abschleudern, Rütteln (bei Gestellware), Trommeldrehung über dem Bad;
- Reduzierung von Verschleppungsverlusten durch (wenn möglich) fertigungsgerechte Konstruktion der Werkstücke zur Vermeidung von Sacklöchern, Falzen und Spalten;
- Reduzierung von Verschleppungsverlusten durch sachgerechte Teileaufhängung bei Gestellware (Schrägaufhängung, Auslaufmöglichkeit bei Hohlkörpern), entsprechende Perforation oder Kantenbohrung bei Trommeln;
- Reduzierung von Verschleppungsverlusten bei Cr(VI) Beschichtung (insbesondere bei automatischen Anlagen) durch chemisches Spülen mit sauren hydrogensulfithaltigen Lösungen;
- Mehrfachnutzung von Spülwasser durch Kaskadenspülung (Gegenstromprinzip), Spritzspülen (Spritzregister über Tauchspüle, wenn anwendbar, Hohlteile Gestell nicht anwendbar, Trommel nicht anwendbar), Kreislaufspülung mittels Ionentauscher;
- Verwendung von Standspülen, somit können Verdunstungs – und/oder Verschleppungsverluste des vorgeschalteten Wirkbads ergänzt werden (Ausnahme Wirkbäder die bei Raumtemp. Arbeiten)
- Wenn verfahrenstechnisch möglich Rückführung des Spülwasseraustrags aus der ersten Spülstufe in den Prozess (wirkt Wasser- und Chemikalienverlust entgegen);
- Weitestgehender Verzicht auf den Einsatz von Arbeits- oder Hilfsstoffen mit wassergefährdenden Eigenschaften, soweit auf Grund der eingesetzten Produktionsverfahren möglich und weitestgehender Verzicht auf den Einsatz von halogenhaltigen oder halogenabspaltenden Chemikalien;
- Bei der Neutralisationsfällung können saure bzw. alkalische Abwässer zur pH-Wert Einstellung verwendet werden.

1.1.6 Allgemeine BvT Abfallmanagement und Badlebensdauer

Die folgenden Techniken (in entweder individueller Anwendung oder in einer passenden Kombination) werden als BvT zur Vermeidung oder Verminderung von Abfallerzeugung und zur Verbesserung der Badlebensdauer (Standzeit) angesehen:

- Behandlung von Prozessbädern mittels geeigneter Verfahren wie Membranfiltration, Ionentausch, Elektrolyse, thermische Verfahren etc. zur weitestgehenden Verlängerung der Standzeiten der Prozessbäder;
- Retardation zum Regenerieren von schwefelsauren Anodisierelektrolyten (Konstanthalten des Aluminiumgehalts durch Adsorption mittels Ionentauscherharzen);
- Einsatz von Verfahren zur sortenreinen Rückgewinnung von Roh-, Arbeits- oder Hilfsstoffen aus Prozessbädern oder Spülwässern (z. B. Dialyse oder Elektrodialyse für Nickel, Eindampfung oder Verdunstung für Glanz- oder Hartchrom, Fällung für Zink);
- Vorbereitung zur Wiederverwendung, Recycling oder Verwerten fester oder flüssiger Rückstände (AWG, BGBl. I Nr. 102/2002);
- Stoffe extern zurückzugewinnen (z. B. Phosphorsäure, Chromsäure, verbrauchte Ätzlösungen);
- Rückgewinnung von Metallen durch Elektrolyse;
- Rückgewinnung von Metallen durch Adsorption auf Ionentauscherharzen;
- Rückhalt von Badinhaltsstoffen mittels verschleppungsarmer Warentransportmethoden, Spritzschutz und optimierter Badzusammensetzung;
- Reduzierung von Verschleppungsverlusten durch Abtropfen, Abquetschen, Abstreifen, Abschleudern, Rütteln (bei Gestellware), Trommeldrehung über dem Bad;
- Reduzierung von Verschleppungsverlusten durch fertigungsgerechte Konstruktion der Werkstücke zur Vermeidung von Sacklöchern, Falzen und Spalten;
- Reduzierung von Verschleppungsverlusten durch sachgerechte Teileaufhängung bei Gestellware (Schrägaufhängung, Auslaufmöglichkeit bei Hohlkörpern), Kantenbohrungen bei Trommeln;
- Reduzierung von Verschleppungen durch Badpflege und geeignete Badzusammensetzung (Oberflächenspannung, Konzentration der Inhaltsstoffe, rechtzeitiges Nachschärfen etc.);
- Rückgewinnung oder Rückführung dafür geeigneter Badinhaltsstoffe aus Spülbädern in die Prozessbäder.

1.1.7 Allgemeine BvT Chemikalienverbrauch und Stoffverluste

Die folgenden Techniken (in entweder individueller Anwendung oder in einer passenden Kombination) werden als BvT zur Reduktion des Chemikalienverbrauchs und von Stoffverlusten angesehen:

- Überwachung und Aufzeichnung des Chemikalienverbrauchs;
- Bevorzugte analytische Überwachung und bedarfsorientierte Dosierung der Chemikalien;
- Gezielter Einsatz von Hilfsstoffen (durch die ersten beiden Maßnahmen) zur Vermeidung der organischen Belastung des Abwassers;
- Rückgewinnung von Metallen durch Elektrolyse;
- Rückgewinnung von Metallen durch Adsorption auf Ionentauscherharzen;
- Verringerung der Stoffverluste und des Chemikalienverbrauchs durch die Verringerung von Verschleppungsverlusten (siehe 1.1.5);
- Rückführung des Spülwasseraustrags aus der ersten Spülstufe in den Prozess (wenn verfahrenstechnisch möglich);
- Den Stoffkreislauf für Prozesschemikalien weitestgehend zu schließen mit einer Kombination von passenden Techniken, wie Gegenstromspülen, Ionentausch, Membrantechniken und Verdunstung;
- Adsorption von Säuren durch Ionentauscherharze für verbrauchte Beizlösungen (z. B. Schwefelsäurebeizen und Ätzlösungen für Kupfer; Flusssäurebeize für Edelstahlbehandlung; Phosphor-, Schwefelsäurebeize für Edelstahl oder Elektropolieren von Aluminium, Schwefel-, Salzsäurebeizen für Stahl).

1.1.8 Allgemeine BvT Luftemissionen

Es ist BvT, Abluft mittels Randabsaugungen (Wannenabsaugung) zu sammeln. Jedenfalls ist die Abluft der folgenden Prozesse abzusaugen:

- Cyanidhaltige Elektrolyte;
- Kadmiumhaltige Elektrolyte;
- Hartverchromen (Cr(VI));
- Nickelelektrolyte;
- Lösungen aus denen Ammoniak entweicht;
- Verwendung löslicher Anoden (wirkt der Knallgasbildung entgegen);
- Prozesse der Metalloberflächenbehandlung, aus denen voraussichtlich säurebildende Stickoxide jeglicher Art in die Atmosphäre entweichen (z. B. chemisches Glänzen von

Aluminium, Kupferlegierungen, Salpetersäurebeizen, Reinigungen mit Salpetersäure, chemisches Strippen mit Salpetersäure);
- Beizen und Strippen mit Salzsäure – vor allem bei erhöhten Temperaturen (über Raumtemp.) und Konzentrationen >15 % (Bildung von Chlorwasserstoff und Salzsäuredämpfen – Korrosionsgefahr am Arbeitsplatz);
- Beizen und Strippen mit Schwefelsäure – vor allem bei Temperaturen >60 °C (Säure-aerosole);
- Flusssäurebeizen;
- Alkalische Reinigungslösungen >60 °C (Wasserdampf).

Es ist BvT, Abluft aus stauberzeugenden Tätigkeiten wie Polieren und Schleifen abzusaugen.

Es ist nicht BvT, Lufteinblasung zur Badbewegung cyanidischer Elektrolyte zu verwenden (Förderung der Karbonatbildung).

Table 10 zeigt end of pipe Techniken zur Verringerung von Luftemissionen. Es ist BvT die folgenden Techniken einzeln oder in einer geeigneten Kombination einzusetzen. Die genannten Techniken sind weder normativ noch erschöpfend.

Table 11 zeigt den Stand der Technik für Abluftemissionen aus der Galvanikindustrie und vergleicht diese mit den BvT-assoziierten Emissionswerten des STM BREF (2006). Die Parameterauswahl ist gem. 1.1.3.2 zu treffen.

Table 10: End-of pipe Techniken zur Verringerung von Luftemissionen

Technik	Schadstoffe	Anwendungsbereich
Gewebefilter, Zyklon	Staub	Mechanische Behandlungsschritte, z. B. Vorbehandlung zur Oberflächenbehandlung (z. B. Schleifen), Bohren bei Leiterplattenherstellung
Aerosolabscheider (Tröpfchenabscheider)	Aerosole	Oberflächenbehandlung von Metallen und Kunststoffen durch ein elektrolytisches oder chemisches Verfahren mitsamt Vorbehandlung (Beizbäder) und Nachbehandlung (Passivieren)
Absorption (Säurewäscher, Laugenwäscher)	Säurenebel, gasförmige oder partikuläre Schadstoffe (Salze, Staub)	Oberflächenbehandlung von Metallen und Kunststoffen durch ein elektrolytisches oder chemisches Verfahren mitsamt Vor- und Nachbehandlung

Technik	Schadstoffe	Anwendungsbereich
Thermische Nachverbrennung	TVOC	Katalytisches Tauchlackieren (KTL), Pulverbeschichtung (insbesondere Einbrennöfen)

Table 11: Abluftemissionen – Stand der Technik, STM BREF 2006

Parameter	Einheit	Stand der Technik	STM BREF 2006
Staub	mg/Nm³	0,2–5	<5–30
HCl	mg/Nm³	0,1–9	<0,3–30
Cr – total	mg/Nm³	<0,01–0,09	<0,1–0,2
Cr(VI)	mg/Nm³	<0,01	< 0,01–0,2
Cu	mg/Nm³	<0,01–0,02	< 0,01–0,02
Ni	mg/Nm³	0,002–0,01[21]	< 0,01–0,1
Zn	mg/Nm³	0,02–0,05[22]	< 0,01–0,5[22]
CN	mg/Nm³	0,5–1,0	–
HCN	mg/Nm³	0,1–1,0	0,1–3,0
H_2SO_4	mg/Nm³	0,1–1,2	–
HF	mg/Nm³	0,5–0,8	<0,1–2,0
TVOC	mg/Nm³	0,7–5 (TNV)	
5–25 (andere Technologien)	–		
Stickoxide (gesamt säurebildend als NO_2)	mg/Nm³	–	5–500
NH_3	mg/Nm³	–	0,1–10

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[21] In der Ableitung des Wertebereichs ist nur eine großflächige autokatalytische Nickel-Beschichtungsanlage enthalten

[22] Das obere Ende liegt bei Großbandverzinkungsanlagen bei 0,5 mg/Nm³

1.1.9 Allgemeine BvT Abwasseremissionen

Die folgenden Techniken (in entweder individueller Anwendung oder in einer passenden Kombination) werden als BvT zur Verminderung von Abwasseremissionen angesehen:

- Einsatz von Pufferbecken oder anderen gleichwertigen Maßnahmen zur Abminderung von Abwassermengen- und Schmutzfrachtspitzen;
- Gesonderte Erfassung und Behandlung von komplexbildnerhaltigen (starke oder harte Komplexbildner) und komplexbildnerfreien Abwässern und Spülwässern (zur Verhinderung der Bildung schwer zerstörbarerer Schwermetallverbindungen);
- gesonderte Erfassung und Reinigung saurer, basischer, chromat-, cyanid-, nitrit-, komplexbildner- und sulfathaltiger Abwasserteilströme;
- Einsatz physikalischer, physikalisch-chemischer oder chemischer Abwasserreinigungsverfahren für einzelne Teilströme (z. B. Oxidation/Reduktion, Fällung, Flockung, Emulsionsspaltung, Extraktion, Membrantechnik, Elektrolyse) und für das Gesamtabwasser (z. B. Neutralisation, Sedimentation, Filtration, Fällung/Flockung, Ionentausch);
- Einsatz biologischer Abwasserreinigungsverfahren bei der Direkteinleitung von Abwasser zur Reduktion von CSB, BSB, TOC, Stickstoffverbindungen und Phosphorverbindungen;
- bevorzugter Einsatz physikalischer oder physikalisch-chemischer Verfahren zur Zerstörung (Zersetzung, Oxidation) von Komplexbildnern oder zur Cyanid- und Nitritoxidation; bei Einsatz chemischer Verfahren bevorzugte Anwendung von Ozon, Wasserstoffperoxid oder anderer Persauerstoffverbindungen – Wasserstoffperoxid oxidiert lediglich freies Cyanid (keine Metallcyanidkomplexe);
- Vorbedingung für die Metallfällung (Neutralisationsfällung) ist die Oxidation/ Reduktion der einzelnen Teilströme (z. B. Chromatreduktion, Cyanidoxidation etc.) und dass keine harten Komplexbildner im Abwasser vorhanden sind;
- Eine verbesserte Aggregation kann durch den Einsatz von Flockungshilfsmitteln (z.B. Eisen(III)- oder Aluminiumsalze) erreicht werden;
- Sulfidfällung ist nur als Nachreinigung nach der Neutralisationsfällung bedarfsweise einzusetzen, da jene zu schlecht sedimentierbaren und filtrierbaren Reduktionsprodukten führt und freies Sulfid zu einer Verblockung der Ionentauscherharze führt;
- vom Abwasser gesonderte Erfassung und Verwertung der bei der Produktion oder bei der Abwasserreinigung anfallenden Rückstände;
- Implementierung von Maßnahmen, in Chemikalien-, Säure-, Laugelager und Produktionsräumen, zur Vermeidung direkter Einleitung größerer Abwassermengen in die Kanalisation im Fall von Unfällen (mittels z. B. Puffer-, Rückhaltesystemen);

- Einsetzen von Maßnahmen zur Verhinderung des direkten Eintritts von Chemikalien oder kontaminierten Löschwasser in die Kanalisation oder in die Umwelt bei Unfällen oder Feuer durch technische oder operative Vorbeugemaßnahmen (Löschwasserrückhalt, ÖWAV Regelblatt 37) unter Beachtung der Brandschutzmaßnahmen;
- Redundanzen kritischer Prozessteile (z. B. Belüftungssystem, Pumpensystem, Pufferbecken, Notfallüberfluss) zur Verfügung zu stellen;
- Durchführung von Dichtheitsüberprüfungen des Kanal- und Abwasserbehandlungssystems (e.g. alle 5 bis 10 Jahre) oder regelmäßige Videoüberwachung bzw. visuelle Kontrolle des Kanal- und Abwasserbehandlungssystems.

Die folgenden Techniken werden als BvT zur Verminderung von AOX Emissionen angesehen:

- Die eingesetzten Hydrauliköle, Befettungsmittel, Wasserverdränger und Kühlschmiermittel enthalten nachweislich keine halogenorganischen Verbindungen;
- Die in der Produktion und in der Abwasserreinigung eingesetzte Salzsäure weist nachweislich keine höhere Verunreinigung durch halogenorganische Verbindungen, als es nach ÖNORM EN 939 „Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch – Salzsäure“ (Jänner 2000) zulässig ist, auf;
- Die in der Abwasserreinigung eingesetzten Aluminium- oder Eisensalze weisen nachweislich keine höhere Belastung mit halogenorganischen Verbindungen als 100 Milligramm AOX pro Kilogramm Aluminium oder Eisen im jeweiligen Behandlungsmittel auf.

1.1.10 BvT zum Betrieb der Abwasserreinigungsanlage ist

- Eine verantwortliche Person für die Bedienung und Instandhaltung der Abwasserreinigungsanlage und der Kanalisation zu nominieren;
- Die für die Bedienung und Instandhaltung der Abwasserreinigungsanlage verantwortliche Belegschaft auszubilden und zu schulen;
- Eine Betriebsanweisung zu erstellen und aktualisieren, welche eine Beschreibung der gesamten Abwasserreinigungsanlage, deren Funktionen, Anlagenteile und die jeweiligen Überwachungs- und Instandhaltungsoperationen beinhaltet;
- Ein Betriebstagebuch über den Betrieb der Abwasserreinigungsanlage (z. B. laut ÖWAV-Regelblatt 13) zu führen, das alle relevanten Messungen, Kalibrierungen, Instandhaltungs- und Wartungsarbeiten, Übergabe an einen befugten Sammler oder Behandler von Abfällen aus der Abwasserbehandlung, Beobachtungen, Störungen und

Änderungen des Betriebs sowie der Belegschaft, Normalbetriebvoraussetzungen um die Abwasserreinigungsanlage in Betrieb zu nehmen sowie für den Betrieb der Abwasserreinigungsanlage unter gewissen Betriebsvorraussetzungen beinhaltet;

- Alarmsysteme und Notfallpläne für wesentliche Einheiten/Schlüsselparameter zu installieren;
- Ein Informationssystem für die unmittelbare Meldung von Fehlfunktionen (z. B. unmittelbar die externe Abwasserreinigungsanlage zu informieren; sofern relevant).

Table 12 zeigt prozessintegrierte und End-of-Pipe-Techniken zur Verringerung der Abwasseremissionen. Es ist BvT, eine geeignete Kombination der folgenden Techniken einzusetzen. Die genannten Techniken sind weder normativ noch erschöpfend.

Table 14 zeigt den Stand der Technik für direkt abgeleitetes Abwasser aus der Galvanikindustrie und vergleicht diesen mit den BvT-assoziierten Emissionswerten des STM BREF (2006) und der AEV Oberflächenbehandlung.

Table 15 zeigt den Stand der Technik für indirekt abgeleitetes Abwasser aus der Galvanikindustrie und vergleicht diesen mit den BvT-assoziierten Emissionswerten des STM BREF (2006) und der AEV Oberflächenbehandlung.

Table 12: Prozessintegrierte und End-of-Pipe-Techniken zur Verringerung der Abwasseremissionen

Technik	Schadstoffe	Anwendungsbereich
Verdampfung	Vorbehandlung vor der Entfernung von Schadstoffen	Aufkonzentrierung von Spülwasser und Rückgewinnung der ausgeschleppten Prozesslösung bei ggf. gleichzeitiger Nutzung der Überschusswärme. Alternativ kann ein Vakuumverdampfer eingesetzt werden. Das Konzentrat der Verdampfung wird der Prozesslösung zugeführt, das Destillat dem Spülwasserkreislauf. Die Stoffkreisläufe können mit einem Verdampfer geschlossen werden, da er eine nahezu vollständige Elektrolytrückführung mit Spülwasser ermöglicht. Die Prozesslösungen müssen thermisch stabil sein.
Elektrolytische Metallrückgewinnung	Metalle	Spülwasser; Schwefelsaure Regenerate von Kationenaustauschern der Spülwasserbehandlung, die Nichteisenmetalle enthalten; Prozesslösung der chemischen Metallabscheidung; Konzentrate der Umkehrosmose. Je edler das Metall und je konzentrierter die Lösung, desto besser funktioniert die elektrolytische Metallrückgewinnung. Bei der elektrolytischen Metallabscheidung aus zyanidischen Lösungen findet parallel dazu eine anodisch-oxidative Zerstörung des Zyanids statt. Elektrolysezellen mit Wirbelbett erhöhen den Wirkungsgrad des Verfahrens.
Ionentauscherharze	Siehe Table 13	Ionentauscherharze können sowohl in der Wasseraufbereitung (Enthärten oder VE-Wasser), in der Spülwasserrückgewinnung, in der Abwasserreinigung, als auch zur Metallrückgewinnung angewendet werden. Abhängig vom verwendeten Ionentauscherharz werden unterschiedliche Schadstoffe entfernt. Der kombinierte Einsatz ist möglich. Ionentauscherharze werden üblicherweise als kationische oder anionische Harze klassifiziert. In Kationentauschern werden positiv geladene Ionen wie Nickel, Kupfer und Natrium mit Wasserstoffionen oder Natriumionen getauscht. In Anionentauschern werden negativ geladene Ionen wie Chromate, Sulphate und Chloride mit Hydroxidionen getauscht. Eine detaillierte Auflistung der mittels Ionentauscherhazen entfernbaren Schadstoffe ist im Anschluss zu dieser Tabelle dargestellt.

Technik	Schadstoffe	Anwendungsbereich
		Eine effektive Sedimentation (Verringerung der abfiltrierbaren Stoffe) erhöht die Leistung und Lebensdauer der Ionentauscherharze, sowie das Einstellen auf den für das jeweilige Harz optimalen pH-Wert. Ionentauscherharze können mittels Regenerationslösungen regeneriert werden. Die Anfallenden Lösungen können in den Prozess rückgeführt werden (siehe Retardation), der Metallrückgewinnung zugeführt werden oder außerhalb des Betriebs verwertet werden.
Säure-(Harz-)Sorption oder Retardation	Metalle, Rückgewinnung von Prozesslösungen	Regeneration verbrauchter Beizen; Konstanthalten des Aluminiumgehalts beim Anodisieren.
Diffusionsdialyse	Metalle	Zum Warten oder Rückgewinnen verbrauchter Säuren (Beizlösungen, Anodisierlösungen, Ätzlösungen, Stripperlösungen) mittels Anionentauschermembran. Zur Diffusionsdialyse wird VE-Wasser benötigt. Es wird das Konzentrationsgefälle zwischen verunreinigter Beize und entsalztem Wasser (getrennt durch Anionentauschermembran) genutzt. Metalle werden wegen ihrer elektrischen Ladung und der Selektivität der Membran zurückgehalten. Zwischen den Zellen muss kein elektrisches Potenzial angelegt werden. Die Beizsäure muss vor der Behandlung gefiltert werden.
Membranelektrolyse	Metalle	Standzeitverlängerung von Ätzlösungen (einschließlich Kunststoffätzen), Beiz- und Stripperlösungen
Elektrodialyse	anorganische Abbauprodukte, Metalle	Metallrückgewinnung. Instandhaltung von chemischen Nickelelektrolyten
Oxidationsverfahren		
Oxidation	Komplexbildner (werden aufgebrochen), Nitrite	Komplexbildnerhaltige Abwässer; Nitrithaltige Abwässer Bevorzugte Oxidationsmittel: Ozon, Wasserstoffperoxid oder andere Persauerstoffverbindungen. Natriumhypochlorit führt zur Bildung organischer Chlorverbindungen (AOX) während der Oxidation.
Strahlungsunterstützte Oxidation	Cyanide, EDTA	Cyanidhaltiges Abwasser; EDTA-haltiges Abwasser; Oxidation mittels Wasserstoffperoxid unter UV-Strahlung.

Technik	Schadstoffe	Anwendungsbereich
		Bevor diese Technik angewendet wird, muss das Kupfer elektrolytisch aus der Lösung abgeschieden werden. Nach der Zerstörung des Cu-EDTA Komplexes kann das Restkupfer gefällt werden.
Elektrolytische (anodische) Oxidation	Cyanide	Cyanidhaltiges Abwasser
Reduktion		
Reduktion mit Natriumdithionit	Kupferkomplexe, Sechswertige Chromatverbindungen	Abwasser mit Kupferkomplexen: Ein Überschuss an Dithionit löst Kupfer aus dem Hydroxid und verhindert die Fällung. Cr(VI)-haltige Abwässer: Cr(VI) lässt sich nur schwer fällen, weshalb eine Reduktion zu Cr(III) notwendig ist, welche als Cr(III) Hydroxide gefällt werden können. Die Reduktion erfolgt bei hohen pH-Werten (im Gegensatz zur Reduktion mit Hydrogensulfit).
Reduktion mit Hypophosphit	Nickel, Zinn	Abwasser mit Nickel- oder Zinnkomplexen
Reduktion mit Amidosulfonsäure	Nitrite	Nitrithaltige Abwässer: Reduzierung der Nitrite zu Stickstoff und Schwefelsäure. pH-Wert Absenkung und hohe Nitritkonzentration führt zur Bildung nitroser Gase. Luftabsaugung mit Wäscher erforderlich.
Reduktion mit Bisulfit (Natriumhydrogensulfit)	Sechswertige Chromatverbindungen	Cr(VI)-haltige Abwässer: Cr(VI) lässt sich nur schwer fällen, weshalb eine Reduktion zu Cr(III) notwendig ist, welche als Cr(III) Hydroxide gefällt werden können. Die Reduktion erfolgt bei pH-Wert unter 2,5.
Fällung		
Neutralisationsfällung /Hydroxidfällung	Metalle	Prozessabwasser: Das Verfahren lässt sich üblicherweise am besten kontrollieren, wenn alle Metalle getrennt gefällt werden (Anpassen des pH-Werts auf den für das jeweilige Metall optimalen Wert). Bei einem Abwassergemisch lässt sich ein für die Fällung aller Metalle optimaler pH-Wert schwerer einhalten. Die Schwermetalle werden durch Neutralisation und anschließende Fällung bei pH-Werten von 9–11 (entsprechend der Fällungstabelle) aus dem Abwasser entfernt. Beim Fällen entsteht ein Wasser-Feststoffgemisch (Galvanikschlamm). Sofern nach vorhergehender Oxidation oder Reduktion Komplexbildner die Hydroxidfällung behindern, kann Calciumhydroxid statt

Technik	Schadstoffe	Anwendungsbereich
		Natronlauge bei der Fällung verwendet werden, bzw. Calcium- oder Magensiumchlorid zugegeben werden.
Sulfidfällung	Metalle	Komplexbildnerhaltige Abwässer. Aus harten Komplexen können Metalle als Sulfide gefällt werden. Fällungsmittel sind Natriumsulfidlösungen. Ein Überschuss kann mit Eisen(III)Salzen zurückgenommen werden. Sulfidfällung ist nur als Nachreinigung nach der Neutralisationsfällung bedarfsweise einzusetzen, da jene zu schlecht sedimentierbaren und filtrierbaren Reduktionsprodukten führt und freies Sulfid zu einer Verblockung der Ionentauscherharze führt.
Fluoridfällung	Fluorid	Fluoridhaltige Abwässer (Aluminiumbeizen, Glanzbäder, Edelstahlbeizen, Chromatierbäder, Phosphatierbäder). Freies Fluorid kann mit Kalziumverbindungen, z. B. mit Kalkmilch, in Verbindung mit Neutralisation gefällt werden. (Calziumchloridlösung kann zur Unterstützung beigegeben werden) Fluoridkomplexe, wie z. B. BF_4, AlF_6 oder SiF_6, lassen sich mit Kalziumverbindungen nicht vollständig fällen.
Phosphatfällung	Phosphate	Die Eliminierung des Phosphates ist in der Abwasserbehandlung der galvanischen Industrie ein seltenes Problem, da fast immer ausreichend Metallionen zur Phosphatfällung anwesend sind. Ist dies nicht der Fall, müssen Eisen- oder Aluminiumverbindungen zugesetzt werden. Die Fällung lässt sich auch mit Kalkmilch bei pH-Werten über 10 durchführen.
Sulfatfällung	Sulfat	Die Sulfatfällung ist selten notwendig, obwohl eine Überwachung des Sulfatgehaltes für Indirekteinleiter zum Schutz des Kanalnetzes wichtig sein kann. Sulfat lässt sich als Kalziumsulfat auf 1 g/l fällen.
Flockung	Erhöhte Flockungsrate, verbessertes Absetzverhalten	Die Zugabe von Flockungsmittel verbessert die Sedimentation nach der Fällung.
Feststoffabscheidung		
Sedimentation	Feststoffe	Vorbehandelter Gesamtabwasserstrom
Flotation	Feststoffe, Öle, Fette	Vorbehandelter Gesamtabwasserstrom
Filtration (z.B. Kiesfilter, Sandfilter)	Feststoffe	Vorbehandelter Gesamtabwasserstrom

Technik	Schadstoffe	Anwendungsbereich
Membrantechnik	Feststoffe, Öle und Fette	Speisewasserversorgung Entfernen von Ölen und Fetten aus Entfettungslösungen Warten der Prozesslösungen Vorbehandelter Gesamtabwasserstrom
Adsorptionstechniken – Aktivkohle	leichtflüchtige halogenierte Kohlenwasserstoffe, Metalle, organische Abbauprodukte	Vorbehandelter Gesamtabwasserstrom Beim Einsatz leichtflüchtiger Kohlenwasserstoffe (z.B. Entfettung) Entfettungsbad, Spülbäder Warten der Prozesslösung
Biologische Abwasserreinigung		
Biologische Abwasserreinigung (z.b.: Belebtschlammverfahren, Nitrifikation und De-Nitrifikation, Bio-Membran Filtration, etc.)	BSB, CSB, TOC, TN, TP, KW-Index	Direkteinleitung Kohlenwasserstoffe werden im Klärschlamm teilweise adsorbiert

Ionentauscherharze – Selektivität unterschiedlicher Schadstoffe:

Ionen sind nach absteigender Selektivität gelistet.

Table 13: Selektivität unterschiedlicher Ionentauscherharze, absteigend gelistet

Stark saure Kationentauscher	Schwach saure Kationentauscher	Stark basische Anionentauscher	Komplexbildner Harze (Iminodiacetate)	Komplexbildner Harze (Aminophosphonate)
Barium	Kupfer	Iodide	Kupfer	Blei
Blei	Blei	Nitrat	Quecksilber	Kupfer
Strontium	Eisen	Hydrogesulfit	Blei	Zink
Calcium	Zink	Chlorid	Nickel	Nickel
Nickel	Nickel	Cyanid	Zink	Kadmium
Kadmium	Kadmium	Hydrogencarbonat	Kadmium	Cobalt
Kupfer	Kalzium	Hydroxide	Cobalt	Kalzium
Zink	Magnesium	Fluoride	Eisen	Magnesium

Stark saure Kationentauscher	Schwach saure Kationentauscher	Stark basische Anionentauscher	Komplexbildner Harze (Iminodiacetate)	Komplexbildner Harze (Aminophosphonate)
Eisen	Strontium	Sulphate	Mangan	Strontium
Magnesium	Barium		Kalzium	Barium
Mangan	Alkalien		Magnesium	Alkalien
Alkalimetalle			Strontium	
Wasserstoff			Barium	

Quelle: STM BREF, 2006

Kationische Metallkomplexe mit Ammoniak, Aminen, Triethanolamin, Quadrol lassen sich mit Iminodiacetat-Harzen entfernen.

In Verbindung mit Citrat, EDTA und NTA ist eine Vorbehandlung notwendig, da die ausschließliche Behandlung mit Ionenaustauschern hier nicht möglich ist.

Zur Entfernung von 6:2 FTS haben sich schwach basische Anionenaustauscherharze ggf. in Kombination mit stark basischen Anionenaustauscherharzen bewährt. (Blepp, Willand, Weber, 2020)

Der untere Wertebereich für Emissionen von Metallen und Cyanid in der Spalte „Stand der Technik“ bezieht sich auf Anlagen, in denen die jeweiligen Stoffe im Verfahren nicht eingesetzt werden, außer es werden zwei getrennte Wertebereiche (mit und ohne Einsatz) angegeben.

Table 14: Abwasseremissionen Direkteinleitung – Stand der Technik, STM BREF 2006, AEV Oberflächenbehandlung

Parameter	Einheit	Stand der Technik Direkteinleitung	STM BREF 2006	AEV Oberflächenbehandlung
Temperatur	° C	30		30
Bakterientoxizität GL		8		8

Parameter	Einheit	Stand der Technik Direkteinleitung	STM BREF 2006	AEV Oberflächen-behandlung
Fischeitoxizität GF,Ei		4		4
Abfiltrierbare Stoffe	mg/l	3–30	5–30[23]	30
pH-Wert		6,5–9,0		6,5–9,0
Aluminium	mg/l	0,3–1,5	1–10	3
Arsen	mg/l			0,1
Barium	mg/l			5
Blei	mg/l	0,02–0,1[24] 0,02–0,5[25]	0,05–0,5	0,5
Cadmium	mg/l	0,0005–0,01[24]	0,1–0,2	0,1
Cadmium – prod. Spez. Fracht [26]	g/kg			0,2
Chrom-Gesamt	mg/l	0,001–0,01[24] 0,01–0,5[25]	0,1–2,0[27]	0,5
Chrom-VI	mg/l	0,01–0,1	0,1–0,2[28]	0,1
Cobalt	mg/l			1
Eisen	mg/l	0,02–1,0	0,1–5[29]	2
Kupfer	mg/l	0,1–0,3[24] 0,2–0,5[25]	0,2–2,0	0,5
Nickel	mg/l	0,01[30]–0,5	0,2–2,0	0,5
Selen	mg/l			0,5
Silber	mg/l	<0,001–0,025[24] <0,01–0,1[25]	0,1–0,5	0,1

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[23] Große Bandanlagen (Sn oder ECCS, elektrochemisches Verchromen) 4–40 mg/l

[24] Bei Abwasser aus dem Galvanisieren ohne Einsatz des jeweiligen Metalls

[25] Bei Abwasser aus dem Galvanisieren mit Einsatz des jeweiligen Metalls

[26] Bei Abwasser aus dem Galvanisieren mit Einsatz von Cadmium

[27] Große Bandanlagen (Sn oder ECCS, elektrochemisches Verchromen) 0,03–1,0 mg/l

[28] Große Bandanlagen (Sn oder ECCS, elektrochemisches Verchromen) 0,0001–0,01 mg/l

[29] Große Bandanlagen (Sn oder ECCS, elektrochemisches Verchromen) 2–10 mg/l

[30] Werte von 0,001 mg/l bis 0,01 mg/l wurden gemeldet von einigen Anlagen wo keine Ni-Beschichtung stattfindet

Parameter	Einheit	Stand der Technik Direkteinleitung	STM BREF 2006	AEV Oberflächenbehandlung
Zink	mg/l	0,01–2,0[31]	0,2–2,0[32] [33]	2
Zinn	mg/l	0,03–1,0	0,2–2[34]	1
Freies Chlor	mg/l			0,2
Ammonium ber. als N (NH_4-N)	mg/l	0,5–10,0		50
Ammoniak ber. als N (NH_3-N)	mg/l	0,02–0,4		0,5
Cyanid, leicht freisetzbar	mg/l	0,01–0,06	0,01–0,2	0,1
Cyanid – Gesamt	mg/l	1,5		2
Fluorid	mg/l	3–20	10–20	20
Nitrit ber. als N (NO_2-N)	mg/l	0,1–1,0		1,5
Phosphor – Gesamt	mg/l	0,02–1,0	0,5–10	2
Sulfat	mg/l			–
Sulfid	mg/l			0,1
CSB	mg/l	100–150[35]	100–500[36]	200[37]
AOX	mg/l	0,04–1,0[38]		1[39]

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[31] Große Bandverzinkungsanlagen 0,3 – 1,0 mg/l; in-house Galvaniken können 1,5 mg/l erreichen

[32] Große Bandanlagen (Sn oder ECCS, elektrochemisches Verchromen) 0,02–0,2 mg/l

[33] Große Bandanlagen (Zn oder Zn-Ni) 0,2–2,2 mg/l

[34] Große Bandanlagen (Sn oder ECCS, elektrochemisches Verchromen) 0,03–1,0 mg/l

[35] 250 mg/l bei Abwasser aus dem Herstellen von Leiterplatten

[36] Große Bandanlagen (Sn oder ECCS, elektrochemisches Verchromen) 120–200 mg/l

[37] 300 mg/l bei Abwasser aus dem Herstellen von Leiterplatten

[38] Bei Einsatz von Natriumhypochlorit (in der CN-Entgiftung) oder unlöslichen Anoden mit Chlorid im Wirkbad (Chlorid durch Einschleppung oder im Wirkbad) liegen die AOX Emissionen im oberen Wertebereich

[39] Bei Abwasser aus dem Galvanisieren oder Mechanischen Bearbeiten (§ 1 Abs. 2 Z 1 oder 13) gilt die Emissionsbegrenzung für AOX auch als eingehalten, wenn
1. die eingesetzten Hydrauliköle, Befettungsmittel, Wasserverdränger und Kühlschmiermittel nachweislich keine halogenorganischen Verbindungen enthalten und
2. die in der Produktion und in der Abwasserreinigung eingesetzte Salzsäure nachweislich keine höhere Verunreinigung durch halogenorganische Verbindungen aufweist, als es nach ÖNORM EN 939 „Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch – Salzsäure“ Jänner 2000 zulässig ist und
3. die in der Abwasserreinigung eingesetzten Aluminium- oder Eisensalze nachweislich keine höhere

Parameter	Einheit	Stand der Technik Direkteinleitung	STM BREF 2006	AEV Oberflächenbehandlung
Schwerflüchtige lipophile Stoffe	mg/l	2–15		20
Kohlenwasserstoff-Index	mg/l	0,1–3,0	1–5	5
Summe anionische und nichtionische Tenside	mg/l	1,0–5,0		
POX	mg/l		0,1–0,5	0,1[40]

Der untere Wertebereich für Emissionen von Metallen und Cyanid in der Spalte „Stand der Technik“ bezieht sich auf Anlagen, in denen die jeweiligen Stoffe im Verfahren nicht eingesetzt werden, außer es werden zwei getrennte Wertebereiche (mit und ohne Einsatz) angegeben.

Belastung mit halogenorganischen Verbindungen aufweisen, als 100 Milligramm AOX pro Kilogramm Aluminium oder Eisen im jeweiligen Behandlungsmittel und
4. soweit auf Grund der geforderten Produktqualität und des angewandten Produktionsprozesses möglich cyanideinsetzende Technologien durch cyanidfreie Technologien ersetzt werden und
5. bei unvermeidbarer Anwendung einer cyanideinsetzenden Technologie die Cyanide durch nicht halogenhaltige oder -abspaltende Chemikalien zerstört werden oder bei Anwendung von halogenhaltigen oder -abspaltenden Chemikalien der Zuwachs des AOX-Gehaltes im Abwasserteilstrom aus der Cyanidoxidation nicht größer ist als 0,5 mg/l.

[40] Die Emissionsbegrenzung für POX ist nur bei Einsatz von leichtflüchtigen halogenierten Kohlenwasserstoffen (LHKW) vorzuschreiben; sie ist im Abwasserteilstrom aus der Anwendung dieser Stoffe einzuhalten. Anstelle des Parameters POX kann die Summe von Dichlormethan, 1-1-1-Trichlorethan, 1-2-Dichlorethan, Trichlorethen, Tetrachlorethen und eines sonst eingesetzten LHKW`s (ber. als Cl) bestimmt werden, sofern der Wasserrechtsbehörde bei der wasserrechtlichen Bewilligung der Abwassereinleitung bekannt gegeben wird, welche dieser LHKW eingesetzt werden. Die Bestimmung der LHKW Einzelsubstanzen erfolgt gemäß den Methodenvorschriften der Anlage A Abschnitt II der MVW.

Table 15: Abwasseremissionen Indirekteinleitung – Stand der Technik, STM BREF 2006, AEV Oberflächenbehandlung

Parameter	Einheit	Stand der Technik Indirekteinleitung	STM BREF 2006	AEV Oberflächen-behandlung
Temperatur	° C	35		35
Bakterientoxizität GL				
Fischeitoxizität GF,Ei				
Abfiltrierbare Stoffe	mg/l	10–50[41]		150
pH-Wert		6,5–10,0		6,5–10,0
Aluminium	mg/l	0,3–1,5		durch AFS begrenzt
Arsen	mg/l			0,1
Barium	mg/l			5
Blei	mg/l	0,02–0,1[42] 0,02–0,5[43]	0,05–0,5	0,5
Cadmium	mg/l	0,0005–0,01[44]	0,1–0,2	0,1
Cadmium – prod. Spez. Fracht	g/kg			0,2
Chrom-Gesamt	mg/l	0,001–0,01[44] 0,01–0,5[45]	0,1–2,0[46]	0,5
Chrom-VI	mg/l	0,01–0,1	0,1–0,2[47]	0,1
Cobalt	mg/l			1
Eisen	mg/l	0,02–1,0	[48]	durch AFS begrenzt

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[41] Der obere Wertebereich kann 100 mg/l betragen, sofern sichergestellt ist, dass es nicht zu Ablagerungen auf Grund der Einleitung kommt, die den Betrieb der öffentlichen Kanalisations- oder Abwasserreinigungsanlage stören.

[42] Bei Abwasser aus dem Galvanisieren ohne Einsatz des jeweiligen Metalls

[43] Bei Abwasser aus dem Galvanisieren mit Einsatz des jeweiligen Metalls

[44] Bei Abwasser aus dem Galvanisieren ohne Einsatz des jeweiligen Metalls

[45] Bei Abwasser aus dem Galvanisieren mit Einsatz des jeweiligen Metalls

[46] Große Bandanlagen (Sn oder ECCS, elektrochemisches Verchromen) 0,03–1,0 mg/l

[47] Große Bandanlagen (Sn oder ECCS, elektrochemisches Verchromen) 0,0001–0,01 mg/l

[48] Große Bandanlagen (Sn oder ECCS, elektrochemisches Verchromen) 2–10 mg/l

Parameter	Einheit	Stand der Technik Indirekteinleitung	STM BREF 2006	AEV Oberflächenbehandlung
Kupfer	mg/l	0,1–0,3[42] 0,2–0,5[43]	0,2–2,0	0,5
Nickel	mg/l	0,01[49]–0,5	0,2–2,0	0,5
Selen	mg/l			0,5
Silber	mg/l	<0,001–0,025[44] < 0,01–0,1[45]	0,1–0,5	0,1
Zink	mg/l	0,01–2,0[50]	0,2–2,0[51] [52]	2
Zinn	mg/l	0,03–1,0	0,2–2[53]	1
Freies Chlor	mg/l			0,2
Ammonium ber. als N (NH_4-N)	mg/l			200
Ammoniak ber. als N (NH_3-N)	mg/l			20
Cyanid, leicht freisetzbar	mg/l	0,01–0,06	0,01–0,2	0,1
Cyanid – Gesamt	mg/l			2
Fluorid	mg/l	3–20		20
Nitrit ber. als N (NO_2-N)	mg/l	0,1–8,0		10
Sulfat	mg/l			–[54]
Sulfid	mg/l			1

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[49] Werte von 0,001 mg/l bis 0,01 mg/l wurden gemeldet von einigen Anlagen wo keine Ni-Beschichtung stattfindet

[50] Große Bandverzinkungsanlagen 0,3 – 1,0 mg/l; in-house Galvaniken können 1,5 mg/l erreichen

[51] Große Bandanlagen (Sn oder ECCS, elektrochemisches Verchromen) 0,02–0,2 mg/l

[52] Große Bandanlagen (Zn oder Zn-Ni) 0.2–2.2 mg/l

[53] Große Bandanlagen (Sn oder ECCS, elektrochemisches Verchromen) 0,03–1,0 mg/l

[54] Die Emissionsbegrenzung ist im Einzelfall bei Korrosionsgefahr für zementgebundene Werkstoffe im Bereich der öffentlichen Kanalisations- oder Abwasserreinigungsanlage festzulegen (technische Norm betreffend „Ausführung von Kanalanlagen“ gemäß Anlage A Abschnitt IV der MVW)

Parameter	Einheit	Stand der Technik Indirekteinleitung	STM BREF 2006	AEV Oberflächenbehandlung
AOX	mg/l	0,04–1,0[55]		1[56]
Schwerflüchtige lipophile Stoffe	mg/l	2–50		100[57]
Kohlenwasserstoff-Index	mg/l	0,1–5,0		15
POX	mg/l			0,1[58]

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[55] Bei Einsatz von Natriumhypochlorit (in der CN-Entgiftung) oder unlöslichen Anoden mit Chlorid im Wirkbad (Chlorid durch Einschleppung oder im Wirkbad) liegen die AOX Emissionen im oberen Wertebereich

[56] Bei Abwasser aus dem Galvanisieren oder Mechanischen Bearbeiten (§ 1 Abs. 2 Z 1 oder 13) gilt die Emissionsbegrenzung für AOX auch als eingehalten, wenn

1. die eingesetzten Hydrauliköle, Befettungsmittel, Wasserverdränger und Kühlschmiermittel nachweislich keine halogenorganischen Verbindungen enthalten und
2. die in der Produktion und in der Abwasserreinigung eingesetzte Salzsäure nachweislich keine höhere Verunreinigung durch halogenorganische Verbindungen aufweist, als es nach ÖNORM EN 939 „Produkte zur Aufbereitung von Wasser für den menschlichen Gebrauch – Salzsäure“ Jänner 2000 zulässig ist und
3. die in der Abwasserreinigung eingesetzten Aluminium- oder Eisensalze nachweislich keine höhere Belastung mit halogenorganischen Verbindungen aufweisen als 100 Milligramm AOX pro Kilogramm Aluminium oder Eisen im jeweiligen Behandlungsmittel und
4. soweit auf Grund der geforderten Produktqualität und des angewandten Produktionsprozesses möglich cyanideinsetzende Technologien durch cyanidfreie Technologien ersetzt werden und
5. bei unvermeidbarer Anwendung einer cyanideinsetzenden Technologie die Cyanide durch nicht halogenhaltige oder -abspaltende Chemikalien zerstört werden oder bei Anwendung von halogenhaltigen oder -abspaltenden Chemikalien der Zuwachs des AOX-Gehaltes im Abwasserteilstrom aus der Cyanidoxidation nicht größer ist als 0,5 mg/l.

[57] Bei Abwasser aus dem Mechanischen Bearbeiten (§ 1 Abs. 2 Z 13) gilt eine Emissionsbegrenzung von 250 mg/l

[58] Die Emissionsbegrenzung für POX ist nur bei Einsatz von leichtflüchtigen halogenierten Kohlenwasserstoffen (LHKW) vorzuschreiben; sie ist im Abwasserteilstrom aus der Anwendung dieser Stoffe einzuhalten. Anstelle des Parameters POX kann die Summe von Dichlormethan, 1-1-1-Trichlorethan, 1-2-Dichlorethan, Trichlorethen, Tetrachlorethen und eines sonst eingesetzten LHKW`s (ber. als Cl) bestimmt werden, sofern der Wasserrechtsbehörde bei der wasserrechtlichen Bewilligung der Abwassereinleitung bekannt gegeben wird, welche dieser LHKW eingesetzt werden. Die Bestimmung der LHKW Einzelsubstanzen erfolgt gemäß den Methodenvorschriften der Anlage A Abschnitt II der MVW.

1.1.11 Allgemeine BvT Boden- und Grundwasserschutz

Die folgenden Techniken (in entweder individueller Anwendung oder in einer passenden Kombination) werden als BvT zur Vorbeugung von Boden- und Grundwasseremissionen angesehen:

- Ausschließliches Laden und Verladen von Roh- und Hilfsstoffen in dazu ausgewiesenen Bereichen. Bei Roh- und Hilfsstoffe mit boden- oder gewässerschädlichen Eigenschaften sind die Lade- und Verladebereiche gegen den ungewollten Austritt von Leckagen zu sichern (etwa durch Bodenversiegelung oder ausreichend Abdeck- und Aufsaugmaterial);
- Sammlung und Zwischenlagerung aller Materialien in dazu ausgewiesenen Bereichen, während auf deren Entsorgung gewartet wird. Bei Materialien mit boden- oder gewässerschädlichen Eigenschaften sind jene Bereiche gegen den Austritt von Leckagen zu sichern;
- Ausstatten aller Pumpensümpfe oder anderer Zwischenspeicher umweltgefährdender Flüssigkeiten mit einem Alarmsystem, welches durch ein hohes Flüssigkeitsniveau ausgelöst wird;
- Erstellen und Implementierung eines Systems zur Prüfung und Inspektion von Becken und Rohrleitungen, welche Rohmaterialien, Additive und andere Substanzen befördern;
- Durchführung von Leckagen-Überprüfungen (optische Sichtprüfung) aller Flanschen und Ventilen an Rohren die zum Transport von Materialien verwendet werden und die Aufrechterhaltung eines Betriebstagebuchs jener Überprüfungen;
- Ein Staumengensystem zur Sammlung jeglicher Austritte aus Flanschen und Ventilen von Rohren, die zum Transport von Materialien verwendet werden, zur Verfügung zu stellen, außer wenn die Konstruktion der Flanschen und Ventile technisch dicht ist;
- Eine adäquate Menge an Sicherheitsbehältern und passende Absorbierer zur Verfügung zu stellen;
- Vermeidung unterirdischer Rohrleitungen zum Transport von Substanzen (außer Wasser);
- Sichere Sammlung und Entsorgung aller Löschwasser (im Brandfall);
- Errichtung impermeabler Böden in Becken oder anderer Container für Oberflächenwässer oder anderer Abwasserströme, um einen ungewollten Austritt zu verhindern.

1.2 Spezifische BvT

Zusätzlich zu den in 1.1 beschriebenen Techniken werden die folgenden Techniken (in entweder individueller Anwendung oder in einer passenden Kombination) als BvT angesehen:

1.2.1 EDTA

Ethylendiamintetraessigsäure (EDTA) bildet starke Komplexe und ist biologisch nur schwer abbaubar. Komplexbildner können die Fällung von Metallen bei der Abwasserbehandlung beeinträchtigen oder bereits gefällte Metalle in aquatischem Milieu rücklösen. EDTA ist in der Galvanikindustrie weit verbreitet, etwa in Entfettungsbädern. EDTA wird auch in der Herstellung von gedruckten Leiterplatten verwendet, etwa in Ätzbädern.

Es ist BvT:

- Den Einsatz von EDTA durch biologisch abbaubare Ersatzstoffe (etwa auf Glukolsäurebasis oder Weinsäurebasis) zu substituieren;
- Auf den Einsatz von EDTA durch die Anwendung alternativer Fertigungsverfahren zu verzichten (etwa Direktmetallisierung bei der Leiterplattenherstellung).

Wo auf den Einsatz von EDTA nicht verzichtet werden kann, ist es BvT

- Das Ausbringen von EDTA in die Umwelt durch Stoff- und Wassersparmaßnahmen zu verringern (z. B. Wiederverwertung des Spülwassers im Prozessbad zum Ausgleichen von Verschleppungs- und Verdampfungsverlusten ggf. nach Vorbehandlung);
- EDTA und ihre Salze aus chemischen Kupferbädern und deren Spülwässern rückzugewinnen;
- EDTA im Abwasser durch UV-Strahlung und Wasserstoffperoxid zu zerstören (siehe 1.1.9).

1.2.2 Cyanide

Cyanide sind toxische Stoffe, die mit manchen Metallen (z. B. Nickel) Komplexe bilden und somit die Metallfällung in der Abwasserbehandlung erschweren. Cyanide bilden im sauren Milieu Cyanwasserstoff.

Es ist BvT:

- Cyanide nicht in der Entfettung zu verwenden;
- Cyanidisch Zink durch saures Verzinken oder alkalisch-cyanidfreies Verzinken zu ersetzen;
- Cyanidisch Kupfer durch saures Verkupfern oder Kupfer-Pyrophosphat zu ersetzen (ausgenommen bei: Anschlagverkupferung (strike platig) auf Stahl, Zinkdruckguss, Aluminium und Aluminiumlegierungen).

Wo auf den Einsatz von Cyanid nicht verzichtet werden kann, ist es BvT

- Abluft aus cyanidhaltigen Prozessbädern abzusaugen und mit Luftwäschern zu behandeln;
- Auf Badumwälzung mittels Lufteinblasung zu verzichten, da dadurch die Carbonatbildung erhöht wird;
- Das Ausbringen von Cyanid in die Umwelt durch Stoff- und Wassersparmaßnahmen zu verringern;
- Cyanidhaltiges Abwasser mittels Oxidationsverfahren zu behandeln (siehe 1.1.9).

1.2.3 PFOS und PFAS

Perflurooctansulfonsäure (PFOS) gehört der Stoffgruppe der Poly- und perfluorierten Alkylsubstanzen (PFAS) an. Zu PFAS zählen mehr als 4.700 künstliche Chemikalien. PFAS sind persistent, bioakkumulativ, ubiquitär und teilweise[59] toxisch. PFOS und verwandte Stoffe sind seit 2009 durch das Stockholmer Übereinkommen beschränkt.

PFOS wurde als Netzmittel bzw. Sprühnebelunterdrücker bei der Cr(VI) Beschichtung verwendet, sowie im Bereich der Kunststoffgalvanik (Kunstoffbeize), um die Bildung von Chromsäureaerosole zu verringern und die Arbeitnehmerschutzauflagen bzgl. Cr(VI) in der Umgebungsluft einhalten zu können, da Cr(VI) krebserregend ist. Chromsäure ist hoch oxidativ, eine Vielzahl an Netzmitteln würde dementsprechend schnell in Cr(VI) Bädern oxidieren. PFOS Salze hingegen können den Belastungen im Chrombad Stand halten.

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[59] Auf Grund der Vielzahl an PFAS können nicht alle Chemikalien im Einzelnen auf ihre toxische Wirkung untersucht werden. Unter jenen PFAS die im genaueren betrachtet wurden, konnte beobachtet werden, dass die meisten moderat bis hochtoxisch sind (EEA, 2020)

Gemäß der Verordnung über persistente organische Schadstoffe (POP-VO (EU) 2019/1021[60]) ist der Einsatz von PFOS bei Hartverchromen (Cr(VI) Beschichtung) nur in geschlossenen Kreisläufen erlaubt (derzeit Frist: bis 7.9.2025). Die Substitution von PFOS durch 6:2-Fluortelomersulfonsäure (6:2-FTS) ist nach aktuellem Kenntnisstand vollständig erfolgt. 6:2-FTS ist ein polyfluoriertes Netzmittel und kommt über den Abwasserpfad in die Umwelt. Polyfluorierte Verbindungen mit C-H Bindungen sind weniger stabil als perfluorierte Verbindungen mit außergewöhnlich stabilen C-F Bindungen. Daher bedarf es einer 2–5-mal höheren Zudosierung von 6:2-FTS im Vergleich zu PFOS. (Blepp, Willand, Weber, 2017; Blepp, Willand, Weber, 2020)

6:2 FTS wird in der Umwelt zu persistenten kurzkettigen perfluorierten Verbindungen abgebaut, die eine hohe Mobilität aufweisen (Nachweise in Oberflächenwasser, Grundwasser, Trinkwasser, Anreicherung in Pflanzen, Exposition des Menschen über Umweltpfad). Zurzeit wird geprüft, ob kurzkettige perfluorierte Substanzen und ihre Vorläuferverbindungen (wie 6:2 FTS) als „besonders besorgniserregende Stoffe“ (SVHCs) unter REACH reguliert werden sollen. (Blepp, Willand, Weber, 2020; Brendel et al. 2018)

Sofern auf die Verwendung von PFOS-haltigen Netzmitteln aus produktionstechnischen Gründen nicht verzichtet werden kann, ist es BvT, den Stoffkreislauf zu schließen. Ein Stoffkreislauf gilt als geschlossen, wenn folgende Punkte erfüllt sind:

- Prozesswannen mit effizienter Absaugung zur Minimierung der Belastung der Umgebung mit Chromsäureaerosolen;
- Sortenreiner Abluftwäscher mit Rückführung der Waschlösung in die Prozesslösung;
- Ausschließlich dokumentierte durchsatz- bzw. bedarfsbezogene Dosierung von PFOS;
- Rückführung des PFOS-haltigen Chromelektrolyten durch Abspülen der Werkteile direkt über dem Prozessbad;
- Mehrstufiges Kaskadenspülsystem zur weitgehenden Rückführung des ausgeschleppten PFOS zur Erzielung eines hohen Spülkriteriums ohne großen Wasserüberhang;

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[60] Im Jahr 2021 wurden auch Perfluoroctansäure (PFOA), ihre Salze und verwandte Verbindungen in die POP-Verordnung aufgenommen. Im Weiteren steht auch eine Beschränkung des Einsatzes von Perfluorhexansulfonsäure, ihren Salzen und verwandten Verbindungen im Rahmen des Stockholmer Übereinkommens zu persistenten organischen Schadstoffen bevor. Ab 2023 bestehen unter REACH Verbote und Beschränkungen für C9-C14-PFCA (perfluorierte Carbonsäuren mit 9 bis 14 Kohlenstoffatomen in der Kette), ihre Salze und C9-C14-PFCA-verwandte Stoffe.

- Einsatz eines Verdunsters zur Aufkonzentrierung von Spülwasser und Rückgewinnung der ausgeschleppten Prozesslösung bei gleichzeitiger Nutzung der Überschusswärme – bedingt durch die schlechte Stromausbeute des Verchromungsprozesses;
- Rückführung von aufkonzentrierten Spülwasserkonzentraten zum Ausgleich von Verdunstungsverlusten der Elektrolyten;
- Standzeitverlängerung der PFOS-haltigen Chromelektrolyte durch Einsatz der Kationenaustauschertechnik zur Abtrennung von Fremdmetallen und Chrom(III) aus Spülwasserkonzentraten; Regenerierung der Kationenaustauscherharze mit Schwefelsäure und deren Wiederverwendung im Abwasserbehandlungsprozess;
- Behandlung von PFOS-haltigen Abwasserteilströmen mittels PFOS-spezifischen Ionenaustauschern.

Sofern auf die Verwendung von 6:2-FTS-haltigen Netzmitteln aus produktionstechnischen Gründen nicht verzichtet werden kann, ist es BvT den Gesamtabwasserstrom mittels 6:2-FTS-spezifischen Ionentauschern zu behandeln.

Zur „Behandlung von 6:2-FTS-haltigen Abwasserströmen mittels 6:2-FTS-spezifischen Ionentauschern“:

Gemäß der Fallstudie in Blepp, Willand, Weber (2020) zum Verbleib des eingesetzten 6:2-FTS in Cr(VI)-Beschichtungsanlagen, wird die zusätzliche Behandlung des Gesamtabwasserstroms auf 6:2-FTS empfohlen. „Aufgrund der festgestellten Verschleppung des 6:2 FTS im Galvanikautomat durch Ad- und Desorptionsvorgänge muss davon ausgegangen werden, dass allein eine Teilstrombehandlung des Chrom(VI)-haltigen Abwasserteilstromes auf 6:2 FTS nicht ausreichend ist.“ (Blepp, Willand, Weber, 2020)

Zur Entfernung von 6:2 FTS haben sich schwach basische Anionenaustauscherharze ggf. in Kombination mit stark basischen Anionenaustauscherharzen bewährt. In Verbindung mit einem Verdampfer können die benötigten Ionentauscher signifikant kleiner dimensioniert werden.

Durch den Einsatz veränderter nasschemischer Prozesse oder technologischer Alternativen zum nasschemischen Verchromen, kann auf die Verwendung von PFAS verzichtet werden. Table 16 zeigt eine Übersicht von alternativen Verfahren. Das dekorative Beschichten auf Cr(III), das funktionelle Verchromen auf Cr(III) Basis, Nickel-Kombinationsschichten werden in Österreich angewendet wendet. Die restlichen Technologien sind in Österreich noch nicht in Anwendung. Die aufgelisteten Technologien sind jedoch bereits in anderen Ländern in Verwendung. Die Technologien sind in Kapitel 1.3 beschrieben. Im Gegensatz zur Cr(VI) Elektrolyten handelt es sich bei den aufgelisteten Technologien nicht um eine „one fits all“ Lösung. Auf die möglichen Anwendungsgebiete (Grenzen der Anwendbarkeit) wird in Kapitel 1.3 eingegangen.

Table 16: Alternative nasschemische Prozesse und technologische Alternativen zum nasschemischen Verfahren

Nasschemische Prozesse	Technologische Alternativen zum nasschemischen Verfahren
Dekoratives Verchromen auf Cr(III) Basis	Hochgeschwindigkeits-Flammspritzen (High Velocity Oxygen Fuel, HVOF-Verfahren)
Funktionelles Verchromen auf Cr(III) Basis	Physikalische Gasphasenabscheidung (Physical Vapour Deposition – PVD)
Ersatz von funktionellem Verchromen durch Nickel-Kombinationsschichten	Plasmanitrieren
Funktionelles Verchromen im geschlossenen Reaktor bei Unterdruck	Laserauftragsschweißen (Laser Metal Deposition – LMD) und extremes Hochgeschwindigkeitslaserauftragsschweißen (EHLA)

Quelle: Blepp, Willand, Weber, 2020

1.2.4 Sechswertiges Chrom

Es ist BvT Cr(VI) Beschichtung mit Cr(III) Beschichtung zu ersetzen, sofern die Anforderungen an die Schichteigenschaften dies zulassen.

Schichteigenschaften sind:

- Korrosionsschutz
- Abriebbeständigkeit
- Verschleißbeständigkeit
- Hohe Härte
- Haltbarkeit (Lebensdauer)
- Ästhetik
- Metallsicher Charakter
- Porenfreiheit
- Temperaturbeständigkeit
- Antiadhäsion

- Geringe Reibung
- Gute Haftung
- Gleichbleibende Farbqualität
- Mikrorissigkeit
- Glanzvermögen
- Reflexionsvermögen
- Eignung als medizinisches Gerät

Sind Schichteigenschaften wie etwa Korrosionsschutz, Abriebbeständigkeit oder hohe Härte für die Beschichtung nicht vorrangig, kann Cr(VI) durch Cr(III) ersetzt werden (wie etwa im Automobilbereich, Innenausstattung).

Für eine gute Schichtaufbringung von Cr(VI) oder Cr(III) ist eine Unternickelung bzw. Unterkupferung notwendig.

Es ist BvT, bei der Kunststoffmetallisierung chromhaltige Beizlösungen (Chromschwefelbeizlösungen) durch Oxidationsmittel auf Permanganatbasis zu ersetzen.

Bei der Umstellung von Cr(VI) Prozessen zu Cr(III) Prozessen kann es zu einer höheren Belastung an Gesamtchrom im Abwasser kommen.

1.3 Verzicht PFAS-haltiger Netzmittel – Einsatz veränderter nasschemischer Prozesse oder Einsatz technologischer Alternativen zum nasschemischen Verchromen

Im Folgenden sind die in Table 16 aufgelisteten Techniken, die Art der Anwendung und die Grenzen der Anwendung beschrieben.

1.3.1 Nasschemische Prozesse

1.3.1.1 Dekoratives Verchromen auf Cr(III) Basis

Der Einsatz von per- oder polyfluorierten Netzmitteln ist in Chrom(III)elektrolyten nicht erforderlich, da in ihnen nicht dieselben stark oxidativen Bedingungen herrschen, wie in

Chrom(VI)elektrolyten. Meist können herkömmliche Tenside, wie sie auch etwa in Nickelelektrolyten verwendet werden, eingesetzt werden (Blepp, Willand, Weber, 2020).

Cr(III)-Elektrolyte reagieren empfindlicher auf Verunreinigungen, was sich auf das Aussehen und die Qualität der Beschichtung niederschlägt. Sie benötigen daher intensivere Badpflegemaßnahmen als Cr(VI)-Elektrolyte. In der Abwasserbehandlung ist auf die häufig enthaltenen Komplexbildner zu achten. Metallkomplexe sind durch geeignete Verfahren (siehe 1.1.9) zu behandeln. Cr(III) Beschichtungen sind nicht UV-beständig (Schichtverfärbung).

1.3.1.2 Funktionelles Verchromen auf Cr(III) Basis

Eine breite Anwendung von Cr(III)-Verfahren beim funktionellen Beschichten besteht noch nicht, unter anderem auf Grund der nicht ausreichenden Schichtdicken.

Das finnische Unternehmen Savroc Oy hat ein Hartchromverfahren auf Chrom(III)-Basis entwickelt, das nach Firmenangaben seit Jahren erfolgreich in Spanien und Finnland für Verschleißteile, Kugelhähne und Hydraulikstangen eingesetzt wird. Die erreichbare Härte liegt bei 1500 HV bis 1800 HV. Das Verfahren wird laut Entwicklerangaben bereits bei 50 Anlagen erprobt oder bereits seit mehreren Jahren angewendet (z. B. Tecnocrom Industrial S.A.). (Blepp, Willand, Weber, 2020)

Die Schichten haben andere Eigenschaften im Vergleich zu konventionellen Hartchromschichten, da aus Cr(III)-Elektrolyten kein reines elementares Chrom abgeschieden wird, sondern grobkörnige Chromverbindungen. Das Verfahren benötigt das Erhitzen der Werkteile auf 400–700 °C, was den Einsatz der Technologie einschränkt (Werkstückverzug, z.B. Medizintechnik). (Blepp, Willand, Weber,2020) Für große Werkstücke (Pipelinetechnologie, Druckerwalzen, Wellen im Großmaschinenbau) ist das Verfahren nicht anwendbar.

1.3.1.3 Ersatz von funktionellen Verchromen durch Nickel-Kombinationsschichten

1.3.1.3.1 Nickel-Wolfram Legierungsabscheidung

„Duratec NiW“ ist ein Verfahren zur Abscheidung von Nickel-Wolfram-Legierungsschichten mit einer Legierungszusammensetzung 65/35 Prozent Ni/W, ±5 Prozent. Die abgeschiedenen Schichten weisen eine hohe Abrieb- und Korrosionsbeständigkeit auf. Das einfach zu führende Verfahren kann in vielen Fällen Hartchrom ersetzen. (ZVO 2018d)

„Ein besonderer Vorteil ist die Duktilität der Legierung mit bis zu 10 % Dehnung. Dadurch stellen derartige Nickel-Wolfram-Schichten eine Alternative zu funktionellen Chromschichten sowie zu Nickel-Phosphor-Schichten dar. Vor allem bei höheren Einsatztemperaturen schneiden diese Schichten dem Anbieter zufolge bei Verschleißbeanspruchung deutlich besser ab, als Hartchromschichten.” (Meyer 2018)

Die hohen Kosten von Wolfram beschränken den wirtschaftlichen Einsatz. In der Abwasserbehandlung ist auf Komplexbildner zu achten. Auf Grund von Nickelemissionen ist das Verfahren nicht für die Lebensmittel- oder Pharmaindustrie geeignet. Schichteigenschaften: keine Antihafteigenschaften, schlechte Poliereigenschaften, Schichtdicke ist begrenzt, geringer Korrosionsschutz.

1.3.1.3.2 Chemisch Nickel mit Dispersionsschichten

Partikel aus Diamant und Bornitrid, die als Suspension im Elektrolyt vorliegen, werden im chemischen Nickelverfahren abgeschieden. Dadurch werden verschließfeste Schichten erzeugt, die Hartchromschichten bereits in der Textilmaschinenindustrie und im Maschinenbau ersetzen. (Blepp, Willand, Weber, 2020)

In der Abwasserbehandlung ist auf Komplexbildner zu achten. Auf Grund von Nickelemissionen ist das Verfahren nicht für die Lebensmittel- oder Pharmaindustrie geeignet. Keine gute Antihafteigenschaften.

1.3.1.3.3 Nickellegierungsabscheidungen

Bei dieser Nickellegierungsabscheidung handelt es sich um eine Kombinationsschicht aus zwei Legierungen der Metalle Kupfer, Zinn und Nickel, genaugenommen einer Nickel-Zinn-Schicht und einer Zwischenschicht aus Bronze (Kölle 2018). Die Schichten weisen eine hohe Korrosionsbeständigkeit auf und sind meerwasserbeständig. Die maximal erreichbare Härte liegt mit ca. 600HV weit unter den durch Hartchrombeschichtungen erreichbaren Härtegraden(1000 HV). (Blepp, Willand, Weber, 2020) Die Nickellegierungsabscheidungen können nur sehr dünn aufgetragen werden, die Schichtdicke ist mit 5 µ begrenzt.

Die Schichten sind meersalzbeständig. Daher wird das Verfahren in Windkraft-Off-Shore-Anlagen oder für Hydraulikzylinder von Hafenkränen eingesetzt. (Candel-Ruiz A. 2019)

In der Abwasserbehandlung ist auf Komplexbildner zu achten. Auf Grund von Nickelemissionen ist das Verfahren nicht für die Lebensmittel- oder Pharmaindustrie geeignet.

1.3.1.4 Funktionelles Verchromen im geschlossenen Reaktor bei Unterdruck

Die Beschichtung und das Spülen passiert in einem geschlossenen Reaktor sequentiell getrennt. Es kann auf Netzmittel verzichtet werden, da keine Chromsäure Aerosole in die Umgebungsluft abgegeben werden. Ein besonderes Augenmerk muss jedoch auf den Explosionsschutz gelegt werden, da auch beim Verchromen im geschlossenen System Wasserstoff und Sauerstoff frei wird. (Blepp, Willand, Weber, 2020)

Das Verfahren ist seit Jahren im industriellen Einsatz. Durch den hohen Automatisierungsgrad ist es jedoch auf hohe Stückzahlen ausgelegt.

Aktuell keine Anlage in Österreich bekannt.

1.3.2 Technologische Alternativen zum nasschemischen Verfahren

Bei technologischen Alternativen zum nasschemischen Verfahren wird eine umfangreiche Abluftreinigung benötigt (im Gegensatz zu nasschemischen Verfahren, wo eine umfangreiche Abwasserreinigung benötigt wird).

1.3.2.1 Hochgeschwindigkeits-Flammspritzen (High Velocity Oxygen Fuel, HVOF-Verfahren)

Beim HVOF-Verfahren erfolgt eine kontinuierliche Gasverbrennung mit hohen Drücken innerhalb einer Brennkammer, in deren zentraler Achse der pulverförmige Spritzzusatz zugeführt wird.

Mit dem HVOF-Verfahren können extrem dünne Schichten und Schichten ab ca. 50 µm bis zu 0,5 mm dicken Beschichtungen mit hoher Korrosionsbeständigkeit, Verschleißbeständigkeit und hoher Maßgenauigkeit erzeugt werden. Weitere Vorteile des Verfahrens sind die Möglichkeit der Vor-Ort-Reparaturen durch mobile Geräte und dass, anders als beim galvanischen Verchromen, keine Begrenzung der Bauteilgröße gegeben ist. Durch dieses

Verfahren können beispielsweise auch Wolframcarbidschichten (WC Co Cr) abgeschieden werden, die noch härter als Hartchromschichten sind und durch den Chromanteil auch eine sehr gute Korrosionsbeständigkeit haben. (Blepp, Willand, Weiland, 2020) Hierbei kommt es jedoch zur Bildung von Chromoxiden.

Das Verfahren ist bereits weit verbreitet (in Deutschland 450 Anlagen, europaweit 2000 Anlagen) und industriell in vielen Anwendungsbereichen erprobt. Als Alternativverfahren für das Hartverchromen wird das Hochgeschwindigkeits-Flammspritzen (HVOF-Verfahren) von Chromschichten z. B. für Druckwalzen eingesetzt. Weitere Einsatzgebiete sind Flugzeugfahrwerke, Kolben und Walzen, Hydraulik-Kolben und Kolbenstangen, Gleitflächen von Dampfbügeleisen Walzen für die Fotoindustrie, Teile für petrochemische und chemische Maschinen, z. B. Pumpen, Schieber, Kugelventile, mechanische Dichtungen, Reparatur und Standzeiterhöhung bei landwirtschaftlichen Maschinen usw. (Blepp, Willand, Weiland, 2020)

Innenbeschichtungen sind bis zu einem Durchmesser von 100 mm möglich. Für komplexe Geometrien, Werkteile mit und Hinterschneidungen ist es nicht geeignet. Die Prozessparameter beim Hochtemperatur-Flammspritzen von Chrom müssen im optimalen Bereich gehalten werden, sonst ist in Verbindung mit Luftsauerstoff die Bildung von Chrom(VI)-Verbindungen möglich. Vor-Ort-Reperaturen sind mit diesem Verfahren nicht möglich.

1.3.2.2 Physikalische Gasphasenabscheidung (Physical Vapour Deposition – PVD)

Bei der physikalischen Gasphasenabscheidung (englisch; PVD) wird im Vakuum mithilfe physikalischer Verfahren das Ausgangsmaterial durch Verdampfen oder aus Feststoffen atomar z. B. durch Laserbeschuss in die Gasphase überführt. Es scheidet sich anschließend am kälteren Werkstück (Substrat) durch Kondensation wieder ab.

Als Beschichtungen kommen heute vor allem Hartstoffschichten auf Basis von Titannitrid (TiN), Titancarbonitrid (TiCN), Titanaluminiumnitrid (TiAlN) oder Diamant (DLC) zum Einsatz. Für Druckgussteile aus Aluminium und Magnesium werden vor allem chrombasierende Schichtsysteme wie Chromnitrid (CrN), Chromvanadiumnitrid (CrVN) und Chromaluminiumnitrid (CrAlN) eingesetzt. (Blepp, Willand, Weber, 2020)

Schichten der physikalischen Gasphasenabscheidung werden für Werkzeuge aus beschichteten Schneidstoffen eingesetzt. Auch Wälzlager, Fahrwerksteile, Waffentechnologie, Stellglieder, Kugeln in Kugellagern, Laufringe und Zylinder, Klappensysteme und Pumpen werden mit dem Verfahren hergestellt. (Galvanotechnik 9/2019)

Die Verfahren sind nur für Kleinteile im nicht-korrosionsanfälligen Einbaubereichen geeignet. Große Teile wie Hydraulikstangen im Flugzeugbau oder Walzen in der Druckindustrie sind kaum im Hochvakuum zu beschichten.

1.3.2.3 Plasmanitrieren

Das Plasmanitrieren arbeitet mit einem Stickstoff-Wasserstoffgemisch, das in einem geschlossenen Vakuumofen bei Unterdruck durch Anlegen einer Spannung zwischen Behälterwand und Charge ionisiert wird. Der Vorgang erzeugt einen erkennbaren Glimmsaum am Werkzeug. Dadurch können die Gasionen mit dem Eisen von niedrig bis hochlegierten Stählen reagieren und eine harte Nitrierzone ausbilden.

Beim Plasmanitrieren handelt es sich nicht um eine Oberflächenbeschichtung, sondern um einen Diffusionsprozess. Die ionisierte Gasatmosphäre diffundiert in die Randzone von Stahlbauteilen ein. Das Verfahren wird angewandt, um Funktionsflächen eine höhere Oberflächenhärte zu vermitteln (bis 1000 HV). Es erhöht den Verschleißwiderstand und verringert das Korrosionsverhalten. Die Oberflächentemperaturen liegen bei 350–600 °C. Bei diesen Temperaturen kann es zu Werkstückverzug kommen.

Typische Anwendungsgebiete umfassen Getriebe, Kurbelwellen, Nockenwellen, Nockenstößel, Ventilkomponenten, Extruderschnecken, Druck-Form-Guß-Werkzeuge, Schmiedegesenke, Werkzeuge zur Kaltumformung, Einspritzdüsen, Kunststoff-Spritzwerkzeuge, lange Wellen, Achsen, Kupplungen und Motorteile.

Das Verfahren eignet sich auch für sehr große Stahl- oder Gussteile. Die Plasmanitrierung kann auf alle wichtigen Gusseisen- und Stahlgussvarianten angewendet werden, die in Automobilwerkzeugen verwendet werden. (Blepp, Willand, Weber, 2020)

1.3.2.4 Laserauftragsschweißen (Laser Metal Deposition – LMD) und extremes Hochgeschwindigkeitslaserauftragsschweißen (EHLA)

Beim Laserauftragschweißen werden Metallpulver auf die Oberfläche eines Grundwerkstoffs aufgebracht und mittels Laser angeschmolzen. Beim EHLA-Verfahren trifft ein pulverförmiger Zusatzwerkstoff bereits oberhalb des Schmelzbades auf das Laserlicht, welches es noch auf dem Weg zum Bauteil bis nahe an den Schmelzpunkt erhitzt.

Der Einsatz von Materialkombinationen ist möglich zur Erhöhung der Bauteillebensdauer. Eingesetzt werden je nach Anforderungen an die Verschleißschicht Wolframcarbid, Titan- und Chromcarbide, aber auch Pulver auf Eisen-, Nickel- und Cobaltbasis. Die Abscheidungsrate liegt bei bis zu 1000 cm²/min, Beschichtungsdicken bei 10–250 µm und die Vorschubgeschwindigkeit bei >100 m/min. Ohne Schutzgas und Vakuum ist dieses Verfahren jedoch nicht möglich.

Das Verfahren ist z. B. für Bremsscheiben wirtschaftlicher, als das Hartverchromen. Vorteile des Verfahrens sind der Verzicht auf umweltschädliche Chemikalien oder die umfangreiche Auswahl von Zusatzwerkstoffen, sowie eine exzellente Anbindung der Schicht an das Substrat. (Käszmann 2019a)

Mögliche Einsatzfelder: Bremsscheiben, Ventile, Kolbenringe, Wellen in der Automobilindustrie, Dosierwalzen, Druck-, Plattenzylinder in der Druckindustrie, Hydraulikzylinder, Kolben und Stangen im Maschinenbau.

Das Verfahren kann nur bei rotationssymetrischen Werkteilen eingesetzt werden. Komplexe Geometrien und Werkteile mit Hinterschneidungen, Sacklöchern können nicht beschichtet werden. (Blepp, Willand, Weber, 2020) Die resultierende Oberfläche ist hart, rau und schwer mechanisch polierbar.

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2 State of the Art

2.1 General BAT conclusions – surface treatment of metals and plastics by an electrolytic or chemical process (galvanic industry)

Based on emissions and consumption data collected by the Austrian galvanic industry, the following techniques and emission values were derived as state of the art. The term ‘state of the art’ is equivalent to ‘best available technology’ (BAT).

2.1.1 General BAT Environmental Management System

It is BAT to establish an environmental management system or to introduce an internationally recognised system such as EMAS or ISO 14001.

It is BAT to regularly collect indicators of energy consumption, water consumption, raw material consumption, selection of inputs, emissions to the atmosphere, emissions to water and waste generation within the framework of the environmental management system.

2.1.2 General BAT Storage of Chemicals

The following techniques (applied either individually or in an appropriate combination) are considered to be BAT for the storage of chemicals:

- Separate storage of acids and alkalis;
- Separate storage of flammable and oxidising substances (to reduce the risk of fire);
- Storage of liquid chemicals in collection basins/collection trays to ensure adequate (internal and external) treatment and disposal. A contamination of the environment has to be avoided.
- Chemicals that become spontaneously flammable in contact with moisture must be stored in a dry area and separated from oxidising substances. The storage area has to be marked accordingly so that no water is used in the event of a fire;
- Contamination of soil or ground water as a result of chemical spillages, leakages or overflow of collection basins/trays must be prevented;

- Damaging of storage tanks, pipelines, conveying and monitoring systems caused by mechanical or chemical influences has to be prevented (through constructional measures, frequent maintenance and controls);
- Separate storage of acids and cyanide (to prevent the formation of hydrogen cyanide).

2.1.3 General BAT Monitoring

The following techniques (applied either individually or in an appropriate combination) are considered to be BAT for monitoring wastewater and air emissions:

2.1.3.1 Wastewater emissions

The determination of emission parameters on the basis of daily flow-proportional composite samples is BAT for the majority of parameters. A daily composite sample is a composite sample which is taken over the actual time of wastewater discharge within 24 hours (24 hours composite sample deviations according to permit, e.g. batch-related composite samples can take place).

Certain parameters must be measured continuously (such as the quantity of wastewater, temperature and pH), while other parameters (for analytical reasons) are determined on the basis of samples (such as filterable substances, total chlorine).

Monitoring by operator (self-monitoring)

It is BAT to implement a self-monitoring system to optimise the production process and to control the wastewater treatment plant. This includes monitoring of parameters set by permit, if necessary additional parameters (e.g. measurement of emission parameters before and after the treatment of wastewater, wastewater quantity, temperature, sludge volume, conductivity, etc.), setting shorter monitoring intervals.

External independent monitoring

It is BAT to arrange external, independent monitoring by authorised experts, institutions or companies.

BAT for external independent monitoring includes:

- Monitoring of emission parameters;
- Verification of operating parameters (operations diary of the wastewater treatment plant);
- Assessment of condition of the the wastewater treatment plant, including the sampling device for operational monitoring and the effluent quantity measurement device;
- Comparison of the external independent monitoring results with the self-monitoring results;
- Comparison of the monitoring results with the respective emission limit values;
- Verification of the operating conditions and production volumes during monitoring;
- Monitoring of additional parameters (see “Monitoring by operator”;
- Documentation of the measurement methods used;
- External independent monitoring of the wastewater treatment plant must be carried out on representative production days (including production days with high loads for the wastewater treatment plant).

Parameter selection

Wastewater from the treatment of surfaces can vary in its characteristics due to the large number of different raw materials, work materials and auxiliary materials that are used, as well as the different components of the processed workpieces. For monitoring, the relevant parameters need to be identified. Relevant parameters are derived from the raw materials, work materials and auxiliary materials used, as well as from the workpieces that are processed. The parameter selection has to be done by the local authority according to §4(1) General Ordniance on Wastewater Emissions (AAEV).

It is BAT to generally use the following parameters to monitor the quality of wastewater. Table 17 presents the state of the art for the monitoring of general parameters, the measuring method and the minimum frequencies of self- and external monitoring. Self- and external-monitoring is defined according to §1(3)8 & 9 AAEV. AAEV §1(3)8 “Self-monitoring: control of the wastewater condition by the permit holder (operator) or an assigned person/institute.” AAEV §1(3)9 “External-monitoring: control of the wastewater condition according to §134 WRG (water law) 1959 or in individual cases by water regulators or the local authority.”

For self-monitoring an analysis method is equivalent, according to the ordinance on wastewater emission monitoring standards, if the limit of detection is max. 30 % of the respective emission limit value (§4(4)1).

Self-monitoring on every working day means that self-monitoring has to be done on days when production takes place. The minimum self-monitoring frequency for large scale steel coil zinc coating plants is weekly on shifted/different days. Large scale steel coil zinc coating plants are plants with a production capacity above 100,000 t/a.

A minimum external-monitoring frequency of all 6 months (2x per year) is BAT. In individual cases the minimum monitoring frequency can be done annually if the emission values are proven to be sufficiently stable and e.g. the process is continuous. If necessary (low degree of automation of the wastewater treatment plant, high emission load and significant fluctuations in the composition of the wastewater, frequent exceedance of emission limit values) more frequent external-monitoring can be prescribed (e.g. 3x per year, 4x per year, 6x per year).

Table 17: State of the art – general parameters for monitoring the quality of wastewater and minimum frequencies for self- and external monitoring

Parameters	Standard	Minimum frequency – self-monitoring [61]	Minimum frequency – external-monitoring [62] [63]
Temperature	DIN 38404-4 (DEV C 4)	continuous	half-yearly
TSS	ÖNORM EN 872	–	half-yearly
pH value	ÖNORM EN ISO 10523	continuous	half-yearly
Bacteria toxicity G_L	ÖNORM EN ISO 11348-1	–	half-yearly
Fish toxicity G_F,Ei	ÖNORM EN ISO 15088	–	half-yearly

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[61] The minimum self-monitoring frequency for large scale steel coil zinc coating plants is weekly on shifted/different days.

[62] In individual cases the minimum monitoring frequency can be done annually if the emission values are proven to be sufficiently stable and e.g. the process is continuous.

[63] If necessary (low degree of automation of the wastewater treatment plant, high emission load and significant fluctuations in the composition of the wastewater, frequent exceedance of emission limit values) more frequent external-monitoring can be prescribed.

It is BAT to monitor metals or metalloids in the wastewater. Metals or metalloids come from parts that are used in the process solution (the main metals, alloy components), working materials and auxiliary materials (baths and additives), as well as from chemicals used in wastewater treatment (iron, aluminium). Table 18 presents the state of the art for the monitoring of metals or metalloids, their measuring method and the minimum frequency of self- and external monitoring.

Table 18: State of the art – metals, minimum frequencies for self- and external monitoring

Parameters	Standard	Minimum frequency – self-monitoring [64]	Minimum frequency – external-monitoring [65] [66]
Aluminium	ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	working days	half-yearly
Arsenic	ÖNORM EN ISO 15586; ÖNORM EN ISO 11969; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	working days	half-yearly
Barium	ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	working days	half-yearly
Lead	ÖNORM ISO 8288; ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	working days	half-yearly
Cadmium	ÖNORM ISO 8288; ÖNORM EN ISO 5961; ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	working days	half-yearly
Total chromium	ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2;	working days	half-yearly

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[64] The minimum self-monitoring frequency for large scale steel coil zinc coating plants is weekly on shifted/different days

[65] In individual cases the minimum monitoring frequency can be done annually if the emission values are proven to be sufficiently stable and e.g. the process is continuous.

[66] If necessary (low degree of automation of the wastewater treatment plant, high emission load and significant fluctuations in the composition of the wastewater, frequent exceedance of emission limit values) more frequent external-monitoring can be prescribed.

Parameters	Standard	Minimum frequency – self-monitoring [64]	Minimum frequency – external-monitoring [65] [66]
Chromium VI	ÖNORM M 6288; DIN 38405-4 (DEV D 4); ÖNORM EN ISO 10304-3	working days	half-yearly
Cobalt	ÖNORM ISO 8288; ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	working days	half-yearly
Iron	ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	working days	half-yearly
Copper	ÖNORM ISO 8288; ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	working days	half-yearly
Nickel	ÖNORM ISO 8288; ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	working days	half-yearly
Selenium	ÖNORM EN ISO 15586; DIN 38405 – D 23-2 (DEV D 23-2); ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	working days	half-yearly
Silver	ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	working days	half-yearly
Zinc	ÖNORM ISO 8288; ÖNORM EN ISO 15586; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	working days	half-yearly

It is BAT to monitor fluoride, phosphorus, sulphate, ammonium and nitrite in the wastewater. F, P, SO_4, NH_4-N and NO_2-N come from the use of process chemicals. Table 19 presents the state of the art for the monitoring of F, P, SO_4, NH_4-N and NO_2-N, the measurement method and the minimum frequencies for self- and external monitoring.

Table 19: State of the art for P, SO_4, NH_4-N and NO_2-N and minimum frequencies for self- and external monitoring

Parameters	**Standard**	**Minimum frequency – self-monitoring** [67]	**Minimum frequency – external-monitoring** [68] [69]
Fluoride	ÖNORM EN ISO 10304-1; DIN 38405-D4-1 (DEV D 4-1)	working days	half-yearly
Phosphorus	ÖNORM EN ISO 6878; ÖNORM EN ISO 15681-1; ÖNORM EN ISO 15681-2; ÖNORM EN ISO 11885; ÖNORM EN ISO 17294-2	weekly	half-yearly
Sulphate	ÖNORM EN ISO 10304-1	weekly	half-yearly
Ammonium (NH_4-N)	ÖNORM EN ISO 14911; ÖNORM EN ISO 11732; ÖNORM ISO 7150-1; ÖNORM ISO 5664; DIN 38406-5 (DEV E 5)	working days	half-yearly
Nitrite (NO_2-N)	ÖNORM EN 26777; ÖNORM EN ISO 10304-1; ÖNORM EN ISO 13395	working days	half-yearly

It is BAT to monitor free chlorine and ammonium in wastewater when cyanide or nitrite oxidation is used in wastewater treatment. Table 4 presents the state of the art for the monitoring of free chlorine and ammonium.

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[67] The minimum self-monitoring frequency for large scale steel coil zinc coating plants is weekly on shifted/different days

[68] In individual cases the minimum monitoring frequency can be done annually if the emission values are proven to be sufficiently stable and e.g. the process is continuous.

[69] If necessary (low degree of automation of the wastewater treatment plant, high emission load and significant fluctuations in the composition of the wastewater, frequent exceedance of emission limit values) more frequent external-monitoring can be prescribed.

Table 20: State of the art for free chlorine and ammonium and minimum frequencies for self- and external monitoring

Parameters	Standard	Minimum frequency – self-monitoring [70]	Minimum frequency – external-monitoring [71] [72]
free chlorine	ÖNORM EN ISO 7393-1; ÖNORM EN ISO 7393-2	–	half-yearly
Ammonium	ÖNORM EN ISO 14911; ÖNORM EN ISO 11732; ÖNORM ISO 7150-1; ÖNORM ISO 5664; DIN 38406-5 (DEV E 5)	working days	half-yearly

It is BAT to monitor cyanide in wastewater when cyanide is used in the process. Cyanide can be present as free cyanide and as cyanide complex. Table 21 presents the state of the art for the monitoring of cyanide.

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[70] The minimum self-monitoring frequency for large scale steel coil zinc coating plants is weekly on shifted/different days.

[71] In individual cases the minimum monitoring frequency can be done annually if the emission values are proven to be sufficiently stable and e.g. the process is continuous.

[72] If necessary (low degree of automation of the wastewater treatment plant, high emission load and significant fluctuations in the composition of the wastewater, frequent exceedance of emission limit values) more frequent external-monitoring can be prescribed.

Table 21: State of the art for cyanide and minimum frequencies for self- and external monitoring

Parameters	Standard	Minimum frequency – self- monitoring [73]	Minimum frequency – external- monitoring [74] [75]
Cyanide – free	ÖNORM EN ISO 14403-1; ÖNORM EN ISO 14403-2; DIN 38405-13 (DEV D 13); ÖNORM M 6285	working days	half-yearly
Total cyanide	ÖNORM EN ISO 14403-1; ÖNORM EN ISO 14403-2; ÖNORM M 6285; DIN 38405-13 (DEV D 13)	working days	half-yearly

It is BAT to monitor sulphide in wastewater when sulphide is used for precipitation in wastewater treatment. Table 22 presents the state of the art for the monitoring of sulphide.

Table 22: State of the art for sulphide and minimum frequencies for self- and external monitoring

Parameters	Standard	Minimum frequency – self- monitoring [76]	Minimum frequency – external- monitoring [77] [78]
Sulphide	ÖNORM M 6615; DIN 38405-27 (DEV 27)	weekly	Half-yearly

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[73] The minimum self-monitoring frequency for large scale steel coil zinc coating plants is weekly on shifted/different days.

[74] In individual cases the minimum monitoring frequency can be done annually if the emission values are proven to be sufficiently stable and e.g. the process is continuous.

[75] If necessary (low degree of automation of the wastewater treatment plant, high emission load and significant fluctuations in the composition of the wastewater, frequent exceedance of emission limit values) more frequent external-monitoring can be prescribed.

[76] The minimum self-monitoring frequency for large scale steel coil zinc coating plants is weekly on shifted/different days.

[77] In individual cases the minimum monitoring frequency can be done annually if the emission values are proven to be sufficiently stable and e.g. the process is continuous.

[78] If necessary (low degree of automation of the wastewater treatment plant, high emission load and significant fluctuations in the composition of the wastewater, frequent exceedance of emission limit values) more frequent external-monitoring can be prescribed.

It is BAT to use the parameters COD, AOX, low-volatile lipophilic substances, hydrocarbon index, sum of anionic and non-ionic surfactants and POX to monitor organic contents in the wastewater. Alternatively to COD, TOC can be used. Organic halogen compounds enter the wastewater through raw materials, work materials or auxiliary substances, but are also generated in the wastewater itself (cyanide oxidation with sodium hypochlorite) and are determined as AOX. The parameter POX is to be used only in cases where volatile halogenated hydrocarbons are used in manufacturing. Hydrocarbon index and low-volatile lipophilic substances include fats, oils, hydrocarbons and other hydrophobic working materials and auxiliaries that are present in wastewater. Table 23 presents the state of the art for the monitoring of organics in wastewater.

Table 23: State of the art for organic content in wastewater and minimum frequencies for self- and external monitoring

Parameters	Standard	Minimum frequency – self- monitoring [79]	Minimum frequency – external- monitoring [80] [81]
COD	ÖNORM M 6265; DIN 38409-41 (DEV H 41); DIN 38409-44 (DEV H 44); ÖNORM ISO 15705	working days	half-yearly
AOX	ÖNORM EN ISO 9562	–	half-yearly
Low **volatile lipophilic substances**	DIN ISO 11349 (DEV H 56)	–	half-yearly
Hydrocarbon index	ÖNORM EN ISO 9377-2	–	half-yearly
Total anionic and non-ionic surfactants	DIN 38405-D23	–	half-yearly
Anionic surfactants	ÖNORM EN 903	–	half-yearly
Non-ionic surfactants	DIN 38409-H23	–	half-yearly
POX	DEV-H 25	–	half-yearly

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[79] The minimum self-monitoring frequency for large scale steel coil zinc coating plants is weekly on shifted/different days.

[80] In individual cases the minimum monitoring frequency can be done annually if the emission values are proven to be sufficiently stable and e.g. the process is continuous.

[81] If necessary (low degree of automation of the wastewater treatment plant, high emission load and significant fluctuations in the composition of the wastewater, frequent exceedance of emission limit values) more frequent external-monitoring can be prescribed.

2.1.3.2 Air emissions

Unless otherwise specified, the BAT-associated emission levels for emissions to air refer to concentrations expressed as the mass of the substances emitted in relation to the volume of exhaust gases at standard conditions (dry gas at a temperature of 273.15 K and a pressure of 101.3 kPa), without correction for the oxygen content expressed in mg/Nm³.

The averaging period for BAT associated emissions to air is an average over three consecutive measurements of 30 minutes each. For parameters for which 30-minute sampling is not practical, for reasons of sampling or analysis, a more appropriate measurement period may be chosen.

If the exhaust air comes from two or more sources and are emitted via a common exhaust air duct, the BAT-associated emission levels apply to the combined emissions emitted through the exhaust air duct.

Parameter selection

Exhaust air from the treatment of surfaces can vary due to the variety of processes used, the variety of raw materials, work and auxiliary materials and the different components of the workpieces processed. For monitoring, it is necessary to identify the relevant parameters. Relevant parameters are selected on the basis of the processes used, the raw materials, work materials and auxiliary materials used, as well as the processed workpieces.

It is BAT to generally use the following parameters to monitor emissions to the air. Table 24 presents the state of the art for the monitoring of parameters, the measurement method and the minimum frequencies.

Table 24: Minimum frequencies for monitoring emissions to air – state of the art general parameters

Parameters	Standard	Minimum frequency
Dust	EN 13284-1	3 years
HCl	EN 1911	3 years

Tabelle 25: Minimum monitoring frequency emissions to air – state of the art process specific

Parameter	Standard	Minimum frequency
Cr – total	EN 14385	3 Years
Cr(VI)	DIN 38405 D24	3 Years
Cu	EN 14385	3 Years
Ni	EN 14385	3 Years
Zn	EN 14385	3 Years
CN	EN 14403-2	3 Years
HCN	EN 14403-2	3 Years
H_2SO_4	EN 14791:2017	3 Years
HF	EN 15713	3 Years
TVOC	EN 12619	3 Years

2.1.4 General BAT Energy consumption and reduction of heat losses

The following techniques (applied either individually or in an appropriate combination) are considered to be BAT for reducing energy consumption and heat losses:

- Implementation of an energy management system;
- As far as possible, reduction of voltage drop between power source and consumer by reducing the distance between rectifier and anode/cathode (wire belt rollers for belt systems) – due to the risk of corrosion, rectifiers cannot always be installed in the immediate vicinity of the workstations;
- Equip each workstation with its own rectifier to regulate the electroplating current and adjust it to the product surface (in case of electrolytic surface treatment);
- Consider possibilities for heat recovery;
- Thermal insulation of heated process baths (double-walled containers, pre-insulated containers);
- Insulation of process solution by appropriate covers;
- Air injection to increase the movement of heated electrolytes is not BAT, as energy losses occur due to increased evaporation.

2.1.5 General BAT Water consumption and wastewater discharge

The following techniques (applied either individually or in an appropriate combination) are considered to be BAT for reducing water consumption and wastewater discharged:

- Monitor of points of water and materials usage in an installation and regularly record consumption levels which are relevant for the process. The recorded values are used for the environmental management system;
- Reduce the input of impurities through efficient rinsing;
- Reduce the input of rinsing water through suitable measures such as squeezing, blowing off (air spray) or appropriate draining time;
- Reduce drag-out losses by draining, blowing off (air spray), squeezing, wiping, centrifuging, shaking (rack lines), drum rotation over the bath;
- Reduce drag-out losses by (if possible) appropriate design of workpieces to avoid cup-shaped recesses, notches and fissures;
- Reduce drag-out losses by appropriate positioning of workpieces in rack lines (angular positioning, outlet possibilities for hollow bodies), appropriate perforation or edge drillings for drums;
- For Cr(VI) coating (especially automatized plants), reduce drag-in by chemical rinsing with acidic hydrogen sulfite containing solutions;
- Multiple use of rinsing water through cascade rinsing (counter current principle), spray rinsing, circulation rinsing using ion exchanger;
- Use of eco-rinses, evaporation losses and/or drag-out losses can be added to the process bath (except for process baths operated at room temperature)
- If possible, recirculate rinsing water from the first rinsing stage back to the process (to prevent water and chemical losses);
- As far as possible, avoid usage of chemical substances with hazardous properties for the aquatic environment; as far as possible, avoid usage of halogen-containing or halogen-releasing chemicals;
- Acidic or alkaline effluent can be used for pH adjustment in neutralisation.

2.1.6 General BAT Waste Management and Process Bath Lifetime

The following techniques (applied either individually or in an appropriate combination) are considered to be BAT for the purpose of preventing or reducing waste generation and improving process bath lifetime:

- Treatment of process baths by means of appropriate procedures such as membrane filtration, ion exchange, electrolysis, thermal processes, etc. for the widest possible extension of process bath life span;
- Retardation for the regeneration of sulphuric-acid anodising electrolytes (keeping the aluminium content constant by adsorption using ion exchanger resins);
- Use of methods for the recovery of raw materials, working materials or auxiliaries from process baths or rinsing water (e.g. dialysis or electrodialysis for nickel, evaporation chromium, precipitation of zinc);
- Preparation for reuse or recycling of solid or liquid residues (Waste Management Act, Federal Law Gazette I No 102/2002);
- External recovery of materials (e.g. phosphoric acid, chromic acid, spent etching solutions);
- Recovery of metals by electrolysis;
- Recovery of metals by adsorption on ion exchange resins;
- Retaining of process bath ingredients by means of transporting methods that reduce or prevent carry-over, by spray protection and optimised bathroom composition;
- Reduction of drag-out losses by to dripping, squeezing, centrifuging, shaking (rack lines), drum rotation over the bath;
- Reduction of drag-out losses by (if possible) appropriate design of workpieces to avoid cup-shaped recesses, notches and fissures;
- Reduction of drag-out losses by appropriate positioning of workpieces in rack lines (angular positioning, outlet possibilities for hollow bodies), appropriate perforation or edge drillings for drums;
- Reduction of drag-out losses through bath monitoring and appropriate bath composition (surface tension, concentration of process chemicals, timely adjustment, etc.);
- Recovery or recycling of suitable ingredients from the rinsing baths for reuse in the process baths.

2.1.7 General BAT Chemical Consumption and Substance Losses

The following techniques (applied either individually or in an appropriate combination) are considered to be BAT for reducing chemical consumption and material losses:

- Monitoring and recording of chemicals consumption;
- Analytical monitoring and demand-based dosing of chemicals;

- Targeted use of auxiliaries (by applying the two measures above) to avoid organic pollution of wastewater;
- Recovery of metals by electrolysis;
- Recovery of metals by adsorption on ion exchange resins;
- Reducing material losses and chemical consumption by reducing drag-out losses (see 2.1.5);
- Recirculation of rinsing water from the first rinsing stage back to the process (if possible);
- Close the material loop for process chemicals as far as possible by using a combination of appropriate techniques such as cascade rinsing, ion exchange, membrane techniques and evaporation;
- Adsorption of acids on ion exchange resins for used pickling solutions (e.g. sulphuric acid pickling solutions and copper etching solutions; hydrofluoric acid pickling baths used for stainless steel; phosphoric or sulphuric acid baths for stainless steel or electropolishing of aluminium, sulphuric or hydrochloric acid baths for steel treatment).

2.1.8 General BAT Air emissions

It is BAT to extract exhaust air by means of edge extraction. In any case, exhaust air must be extracted from the following processes:

- Cyanide containing electrolytes;
- Cadmium containing electrolytes;
- Hard chromium plating (Cr(VI));
- Nickel electrolytes;
- Solutions from which ammonia escapes;
- Use of soluble anodes (to counteract the formation of oxyhydrogen);
- Processes of metal surface treatment from which acid-forming nitrogen oxides of any kind are expected to escape into the atmosphere (e.g. chemical brightening of aluminium, copper alloys, nitric acid pickling, nitric acid cleaning, chemical stripping with nitric acid);
- Hydrochloric acid pickling and stripping– especially at elevated temperatures (above room temperature) and concentrations >15 % (formation of hydrogen chloride and hydrochloric acid vapours – risk of corrosion);
- Sulphuric acid pickling and stripping – especially at temperatures >60 °C (acidic aerosols);

- Hydrofluoric acid pickles;
- Alkaline cleaning solutions >60 °C (water vapour).

It is BAT to extract exhaust air from activities such as polishing and grinding.

It is not BAT to use air injection for cyanide electrolyte agitation (carbonate formation).

Table 26 shows end of pipe techniques to reduce air emissions. It is BAT to use the following techniques either individually or in an appropriate combination. This list is not normative or exhaustive.

Table 27 shows the state of the art for exhaust air emissions from the electroplating industry and compares them with the BAT-associated emission levels of the STM BREF (2006). The parameter selection is to be made in accordance with 1.1.3.2.

Table 26: End-of-pipe techniques for reducing air emissions

Technology	Pollutants	Application
Fabric filter, cyclone	Dust	Mechanical treatment steps, e.g. pre-treatment for surface treatment (e.g. grinding), drilling in PCB manufacturing
Aerosol separator (droplet separator)	Aerosols	Surface treatment of metals and plastics using an electrolytic or chemical process, including pre-treatment (pickling baths) and post-treatment (passivation)
Absorption (acid scrubber, alkaline scrubber)	Acid mists or gaseous pollutants or particulate matter (salts, dust)	Surface treatment of metals and plastics using an electrolytic or chemical process including pre- and post-treatment
Thermal post-combustion (thermal oxidation – TO)	TVOC	Catalytic dip-paint coating (CDC), powder coating (especially curing ovens)
Bio-filter	TVOC	PCB manufacturing

Table 27: Exhaust air emissions – state of the art, STM BREF 2006

Parameter	Unit	State of the art	STM BREF 2006
Dust	mg/Nm³	0.2–5	<5–30
HCl	mg/Nm³	0.1–9	<0.3–30
Cr – total	mg/Nm³	< 0.01–0.09	<0.1–0.2
Cr(VI)	mg/Nm³	< 0.01	< 0.01–0.2
Cu	mg/Nm³	< 0.01–0.02	< 0.01–0.02
Ni	mg/Nm³	0.002–0.01[82]	< 0.01–0.1
Zn	mg/Nm³	0.02–0.05[83]	< 0.01–0.5[84]
CN	mg/Nm³	0.5–1.0	–
HCN	mg/Nm³	0.1–1.0	0.1–3.0
H_2SO_4	mg/Nm³	0.1–1.2	–
HF	mg/Nm³	0.5–0.8	<0.1–2.0
TVOC	mg/Nm³	0.7–5 (TO) 5–25 (other technique)	
Nitrogen oxides (total acid-forming as NO_2)	mg/Nm³	–	5–500
NH_3	mg/Nm³	–	0.1–10

2.1.9 General BAT Wastewater emissions

The following techniques (applied either individually or in an appropriate combination) are considered to be BAT for reducing wastewater emissions:

- Use of buffer tanks or other equivalent measures to reduce wastewater and emisison load peaks;
- Separate collection and treatment of complexing agent (strong complexing agent) containing and complexing agent free effluent and rinsing water (to prevent the formation of hard-to-destruct heavy metal compounds);

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[82] For deriving the State of the Art emission range only one autocatalytic Ni coating plant was included

[83] The upper end is 0.5 mg/Nm³ for large scale steel coil zinc coating plants

[84] Large scale steel coil pants, zinc or zinc-nickel process 0.2 – 2.5 mg/Nm³

- Separate collection and purification of acidic, basic, chromatic, cyanide, nitrite, complexing agents and sulphate-containing wastewater streams;
- Use of physical, physico-chemical or chemical wastewater treatment methods for partial streams (e.g. oxidation/reduction, precipitation, flocculation, extraction, membrane technology, electrolysis) and for the total volume of wastewater (e.g. neutralisation, sedimentation, filtration, precipitation/flocculation, ion exchange);
- Use of biological wastewater treatment processes for direct discharge of wastewater to reduce COD, BOD, TOC, nitrogen compounds and phosphorus compounds;
- Giving preference to the use of physical or physico-chemical processes for the destruction (decomposition, oxidation) of complexing agents or for cyanide and nitrite oxidation; in the case of chemical processes, using ozone, hydrogen peroxide or other peroxygen compounds – hydrogen peroxide oxidises only free cyanide (no metal cyanide complexes);
- The pre-condition for metal precipitation (neutralisation) is the oxidation/reduction of the individual partial streams (e.g. chromate reduction, cyanide oxidation, etc.) and that no strong complexing agents are present in the wastewater;
- Increased aggregation can be achieved by using flocculation agents (e.g. iron(III) or aluminium salts);
- Sulphide precipitation should only be used for post-treatment after neutralisation, as it leads to poorly settleable and filterable reduction products and free sulphide leads to blocking of ion exchanger resins;
- Separate collection and recovery of residues resulting from production or the treatment of wastewater;
- Implementation of measures in chemicals, acid, alkalis storage and production areas, to avoid direct discharge of large amounts of wastewater into the sewer in the event of accidents (e.g. buffer, restrain systems);
- Implementation of measures to prevent the direct entry of chemicals or contaminated fire extinguisher water into the sewer system or the environment in the event of accidents or fires through technical or operational preventive measures (fire extinguishing restrain systems) considering fire precautionary measures;
- Provide redundancy of critical parts of the process (e.g. ventilation system, pump system, buffer basin, emergency overflow);
- Conduct leakproofness checks of the sewer- and wastewater treatment system (e.g. every 5 to 10 years) or conduct regular video surveillance or visual controls of the sewer and wastewater treatment system.

The following techniques are BAT for the reduction of AOX emissions:

- Used hydraulic oils, greasing agents, solvents and lubricants contain no halogenorganic compounds;
- Used hydrogen chlorides (in the production or in wastewater treatment) do not contain significant amounts of halogenorganic compounds Conduct (according to ÖNORM EN 939 “products for water treatment for human consumption – hydrogen chloride” (January 2000)
- Aluminium or iron salts for wastewater treatment do not contain a higher amount of halogenorganic compounds than 100 mg AOX per kg aluminium or iron

2.1.10 BAT for the operation of the wastewater treatment plant is to

- Nominate a person responsible for the operation and maintenance of the wastewater treatment plant and the sewer system;
- Train the staff responsible for the operation and maintenance of the wastewater treatment plant;
- Establish and update operating instructions containing a description of the entire wastewater treatment plant, its functions, sub-installations and the respective monitoring and maintenance operations;
- Keep an operational diary recording the operations carried out at the wastewater treatment plant (e.g. according to ÖWAV Regulation Sheet 13), which includes all relevant measurements, calibrations, maintenance and maintenance work, disposals of waste to an authorised company from wastewater treatment, observations, disruptions and changes to the plant and staff, normal operating conditions to put the wastewater treatment plant into operation, and for the operation of the wastewater treatment plant under certain operating conditions;
- Install alarm systems and emergency plans for essential units/key parameters;
- An information system for the immediate reporting of malfunctions (e.g. informing the external wastewater treatment plant directly; where relevant).

Table 28 shows process-integrated and end-of-pipe techniques to reduce wastewater emissions. It is BAT to use a suitable combination of the following techniques. This list is not normative or exhaustive.

Table 30 shows the state of the art for directly discharged wastewater from the electroplating industry and compares it with the BAT-associated emission values of the STM BREF (2006) and the Wastewater Emissions Ordinance (AEV) for surface treatment.

Table 31 shows the state of the art for indirect discharged wastewater from the electroplating industry and compares it with the BAT-associated emission levels of the STM BREF (2006) and the AEV surface treatment.

Table 28: Process-integrated and end-of-pipe techniques to reduce wastewater emissions

Technology	Pollutants	Application
Evaporation	Pre-treatment before removal of pollutants	Concentration of rinsing water and recovery of the extracted process solution with possible simultaneous use of excess heat. Alternatively, a vacuum evaporator can be used. The concentrate of the evaporation is fed into the process solution, the distillate to the rinsing water cycle. The material loop can be closed with an evaporator. The process solutions must be thermally stable.
Electrolytic metal recovery	Metals	Rinsing water; Sulphur-acid regenerates of cation exchangers from rinsing water treatment containing non-ferrous metals; Process solution of chemical metal separation; Concentrates of reverse osmosis. The nobler the metal and the more concentrated the solution, the better electrolytic metal recovery works. Electrolytic metal separation from cyanide solutions is accompanied by anodic-oxidative destruction of the cyanide. Fluidised bed cells increase the process efficiency.
Ion exchanger resins	See: Table 29	Ion exchanger resins can be used in water treatment (deionized water), rinsing water recovery, wastewater treatment, and metal recovery. Depending on the ion exchanger resin used, different pollutants are removed. Combined uses are possible. Ion exchanger resins are usually classified as cationic or anionic resins. In cation exchangers positively charged ions such as nickel, copper and sodium are exchanged with sodium ions or hydrogen ions. In anion exchangers negatively charged ions such as chromates, sulphates and chlorides are exchanged with hydroxide ions. A detailed list of pollutants that can be removed by means of ion exchangers is shown below. Effective sedimentation (reduction of the filterable substances) increases the performance and life-span of

Technology	Pollutants	Application
		ion exchanger resins, as well as adjusting to the optimal pH value for the respective resin. Ion exchanger resins can be regenerated using regeneration solutions. The resulting solutions can be returned to the process (see retardation), sent to metal recovery or be recovered off-site.
Acid (resin) sorption or retardation	Metals, recovery of process solutions	Regeneration of spent pickling solutions; keeping the aluminium content constant in anodising.
Diffusion dialysis	Metals	Treating or recovering consumed acids (pickling solutions, anodising solutions, etching solutions, stripper solutions) by anion exchanger membrane. For diffusion dialysis, deionised water is required. The difference in concentration between polluted pickling and desalinated water (separated by anion exchanger membrane) is used. Metals are retained because of their electrical charge and the selectivity of the membrane. No electric current between the cells is required. Pickling acids must be filtered before treatment.
Membrane electrolysis	Metals	Extension of bath life-span of etching solutions (including plastic etching), pickling and stripper solutions
Electrodialysis	inorganic degradation products, metals	Metal recovery. Maintenance of electroless nickel electrolytes
Oxidation processes		
Oxidation	Complexing agents (are broken up), nitrites	Effluents containing complexes; Nitrite-containing wastewater Preferred oxidising agents: ozone, hydrogen peroxide or other peroxygen compounds. Sodium hypochlorite leads to the formation of organic chlorine compounds (AOX) during oxidation.
Radiation-assisted oxidation	Cyanide, EDTA	Cyanide-containing wastewater; Wastewater containing EDTA; Oxidation using hydrogen peroxide under UV radiation. Before this technique is applied, the copper must be removed from the solution. After the destruction of the Cu-EDTA complex, the residual copper can be precipitated.
Electrolytic (anodic) oxidation	Cyanide	Cyanide-containing wastewater
Reduction		
Reduction with sodium dithionite	Copper complexes, hexavalent chromate compounds	Wastewater with copper complexes: An excess of dithionite releases copper from the hydroxide and prevents precipitation. Cr(VI)-containing effluents:

Technology	Pollutants	Application
		Cr(VI) is difficult to precipitate and therefore reduction to Cr(III) is necessary, which can be precipitated as Cr(III) hydroxide. The reduction takes place at high pH values (as opposed to the reduction with bisulphite).
Reduction with hypophosphite	Nickel, tin	Wastewater with nickel or tin complexes
Reduction with amidosulfonic acid	Nitrites	Nitrite-containing effluents: Reduction of nitrites to nitrogen and sulphuric acid. pH reduction and high nitrite concentration leads to the formation of nitrous gases. Air extraction with scrubber required.
Reduction with bisulphite (sodium hydrogen sulphite)	Hexavalent chromate compounds	Cr(VI)-containing effluents: Cr(VI) is difficult to precipitate and therefore reduction to Cr(III) is necessary, which can be precipitated as Cr(III) hydroxide. The reduction takes place at pH below 2.5.
Precipitation		
Neutralisation and precipitation /Hydroxide precipitation	Metals	Process wastewater: The method is usually best controlled when all metals are precipitated separately (adjusting the pH value to the optimal value for the respective metal). In the case of a wastewater mixture, an optimal pH value for the precipitation of all metals is more difficult to maintain. The heavy metals are removed from the wastewater by neutralisation and subsequent precipitation at pH values of 9-11 (according to the precipitation table). A mixture of water and solids (galvanic sludge) is produced during precipitation. If, after previous oxidation or reduction, complexing agents hinder hydroxide precipitation, calcium hydroxide may be used instead of sodium hydroxide in precipitation, or calcium or magnesium chloride may be added.
Sulphide precipitation	Metals	Effluents containing complexing agents. Metals can be precipitated as sulphides from hard complexes. Precipitation agents are sodium sulfide solutions. An excess can be recovered by adding iron(III)salts. Sulphide precipitation should only be used as an additional cleaning step after neutralisation, as it leads to poorly settleable and filterable reduction products and free sulphide leads to blocking of ion exchanger resins.
Fluoride precipitation	Fluoride	Fluoride-containing effluents (aluminium stains, gloss baths, stainless steel stains, chromatite baths, phosphate baths). Free fluoride can be precipitated with calcium compounds, e.g. with calcium hydroxide, in combination with neutralisation. Fluoride complexes, such as BF_4, AlF_6

Technology	Pollutants	Application
		or SiF_6, cannot be fully precipitated with calcium compounds.
Phosphate precipitation	Phosphates	The elimination of phosphate is a rare problem in wastewater treatment in the galvanic industry, as there are almost always enough metal ions for phosphate precipitation. If this is not the case, iron or aluminium compounds must be added. Precipitation can also be carried out with calcium hydroxide at pH values above 10.
Sulphate precipitation	Sulphate	Sulphate precipitation is rarely necessary, although monitoring of the sulphate content may be important for indirect dischargers to protect the channel network. Sulphate is easy to precipitate as calcium sulphate (can be precipitated to 1 g/l).
Flocculation	Increased flocculation rate, improved sedimentation behaviour	The addition of flocculants improves sedimentation after precipitation.
Solid separation		
Sedimentation	Solids	Pre-treated total wastewater stream
Flotation	Solids, oils, fats	Pre-treated total wastewater stream
Filtration (e.g. gravel filter, sand filter)	Solids	Pre-treated total wastewater stream
Membrane technology	Solids, oils, fats	Feed water supply Removal of oils and fats from degreasing solutions Maintenance of process solutions Pre-treated wastewater stream
Adsorption techniques – activated carbon	volatile halogenated hydrocarbons, metals, organic degradation products	Pre-treated wastewater stream When using volatile hydrocarbons (e.g. degreasing) Degreasing baths, rinsing baths Maintenance of the process solution
Biological wastewater treatment		
Biological wastewater treatment (e.g.: Activated sludge process, nitrification and de-nitrification, bio-membrane filtration, etc.)	BOD, COD, TOC, TN, TP, hydrocarbons	Direct discharge Hydrocarbons are partly adsorbed in the sludge

Ion exchange resins – selectivity of different pollutants

Ions are listed in descending order by selectivity.

Table 29: Selectivity of different ion exchanger resins, listed in descending order.

Strong acid (cation) resin selectivity	Weak acidic (cation) resin selectivity	Strong base (anion) resin selectivity	Chelating resin selectivity (iminodiacetate)	Chelating resin selectivity (aminophosphonic)
Barium	Copper	Iodide	Copper	Lead
Lead	Lead	Nitrate	Mercury	Copper
Strontium	Iron	Bisulphite	Lead	Zinc
Calcium	Zinc	Chloride	Nickel	Nickel
Nickel	Nickel	Cyanide	Zinc	Cadmium
Cadmium	Cadmium	Bicarbonate	Cadmium	Cobalt
Copper	Calcium	Hydroxide	Cobalt	Calcium
Zinc	Magnesium	Fluorides	Iron	Magnesium
Iron	Strontium	Sulphates	Manganese	Strontium
Magnesium	Barium		Calcium	Barium
Manganese	Alkalis		Magnesium	Alkalis
Alkali metals			Strontium	
Hydrogen			Barium	

Source: STM BREF, 2006

Cationic metal complexes with ammonia, amines, triethanolamine, quadrol can be removed with iminodiacetate resins.

In combination with citrate, EDTA and NTA, pre-treatment is necessary as treatment with ion exchangers alone is not possible here.

For the removal of 6:2 FTS, weak base anion exchange resins may have proved to be effective in combination with strong base anion exchange resins. (Blepp, Willand, Weber, 2020)

The lower ranges of values for emissions of metals and cyanide in the column ‘State of the art’ refer to installations where the respective substances are not used in the process, except where two separate ranges of values (with and without use) are indicated (see footnote).

Table 30: Wastewater emissions Direct discharge – State of the art, STM BREF 2006, National Ordinance Surface treatment

Parameter	Unit	State of the art Direct discharge	STM BREF 2006	National Ordinance
Temperature	°C	30		30
Bacteria toxicity G_L		8		8
Fish toxicity $G_{F,Ei}$		4		4
TSS	mg/l	3–30	5–30[85]	30
pH value		6.5–9.0		6.5–9.0
Aluminium	mg/l	0.3–1.5	1–10	3
Arsenic	mg/l			0.1
Barium	mg/l			5
Lead	mg/l	0.02–0.1[86] 0.02–0.5[87]	0.05–0.5	0.5
Cadmium	mg/l	0.0005–0.01[86]	0.1–0.2	0.1
Cadmium – prod. Specific load [88]	g/kg			0.2
Total chromium	mg/l	0.001–0.01[86] 0.01–0.5[87]	0.1–2.0[89]	0.5
Chromium VI	mg/l	0.01–0.1	0.1–0.2[90]	0.1
Cobalt	mg/l			1

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[85] Large scale steel coil coating (Sn or ECCS, electrochemical chromium plating) 4–40 mg/l

[86] For wastewater from electroplating without the use of the respective metal

[87] For wastewater from electroplating with the use of the respective metal

[88] For wastewater from electroplating with the use of cadmium

[89] Large scale steel coil coating (Sn or ECCS, electrochemical chromium plating) 0.03–1.0 mg/l

[90] Large scale steel coil coating (Sn or ECCS, electrochemical chromium plating) 0.0001–0.01 mg/l

Parameter	Unit	State of the art Direct discharge	STM BREF 2006	National Ordinance
Iron	mg/l	0.02–1.0	0.1–5[91]	2
Copper	mg/l	0.1–0.3[86] 0.2–0.5[87]	0.2–2.0	0.5
Nickel	mg/l	0.01[92]–0.5	0.2–2.0	0.5
Selenium	mg/l			0.5
Silver	mg/l	<0.001–0.025[86] <0.01–0.1[87]	0.1–0.5	0.1
Zinc	mg/l	0.01–2[93]	0.2–2.0[94] [95]	2
Tin	mg/l	0.03–1.0	0.2–2[96]	1
Free chlorine	mg/l			0.2
Ammonium (NH_4-N)	mg/l	0.5–10.0		50
Ammonia (NH_3-N)	mg/l	0.02–0.4		0.5
Cyanide – free	mg/l	0.01–0.06	0.01–0.2	0.1
Cyanide – total	mg/l	1.5		2
Fluoride	mg/l	3–20	10–20	20
Nitrite (NO2-N)	mg/l	0.1–1.0		1.5
Phosphorus – Total	mg/l	0.02–1.0	0.5–10	2
Sulphate	mg/l			–
Sulphide	mg/l			0.1
COD	mg/l	100–150[97]	100–500[98]	200[99]

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[91] Large scale steel coil coating (Sn or ECCS, electrochemical chromium plating) 2–10 mg/l

[92] Values from 0.001 mg/l to 0.01 mg/l were reported from installations without Ni coating

[93] Large scale steel coil zinc coating plants 0.3–1.0 mg/l; in-house electroplating plants can achieve 1.5 mg/l

[94] Large scale steel coil coating (Sn or ECCS, electrochemical chromium plating) 0.02–0.2 mg/l

[95] Large scale steel coil coating (Zn or Zn-Ni) 0.2–2.2 mg/l

[96] Large scale steel coil coating (Sn or ECCS, electrochemical chromium plating) 0.03–1.0 mg/l

[97] 250 mg/l for wastewater from the manufacture of printed circuit boards

[98] Large scale steel coil coating (Sn or ECCS, electrochemical chromium plating) 120–200 mg/l

[99] 300 mg/l for wastewater from the manufacture of printed circuit boards

Parameter	Unit	State of the art Direct discharge	STM BREF 2006	National Ordinance
AOX	mg/l	0.04–1.0[100]		1[101]
Low **volatile lipophilic substances**	mg/l	2–15		20
Hydrocarbon index	mg/l	0.1–3.0	1–5	5
Total anionic and non-ionic surfactants	mg/l	1.0–5.0		
POX	mg/l		0.1–0.5	0.1[102]

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[100] When using sodium hypochlorite (CN treatment) or insoluble anodes with chloride in the process bath (drag-in or as auxiliary) the AOX emissions are in the upper range

[101] In the case of wastewater from electroplating or mechanical processing (Section 1(2)(1) or 13), the emission limit for AOX shall also be deemed to have been complied with if:
1. the hydraulic oils, grease agents, water displacers and cooling lubricants have been shown to contain no organohalogenic compounds, and
2. the hydrochloric acid used in production and wastewater treatment has been shown to have caused no higher contamination by organohalogenic compounds than is permitted by ÖNORM EN 939 “Products for the treatment of water intended for human consumption – Hydrochloric acid” (January 2000); and
3. the aluminium or iron salts used in wastewater treatment have been shown to have caused no higher loads of organic halogen compounds than 100 milligrams of AOX per kilogram of aluminium or iron in the respective treatment agent; and,
4. to the extent possible, due to the required product quality and the applied production process, cyanide-based technologies are replaced by cyanide-free technologies; and
5. in cases where the use of cyanide-based technology is unavoidable, the cyanides are destroyed by non-halogenated solvents or other chemicals or, if halogenated or dispersing chemicals are used, the increase in the AOX content in the wastewater stream from cyanide oxidation is not greater than 0.5 mg/l.

[102] The emission limit for POX shall be imposed only when highly volatile halogenated hydrocarbons (HFCs) are used; it shall be monitored in the partial wastewater flow from the application of these substances. Instead of the parameter POX, the sum of dichloromethane, 1-1-1-trichloroethane, 1-2-dichloroethane, trichloroethene, tetrachloroethene and an otherwise used volatile halogenated hydrocarbon (other than Cl) can be determined, provided that the water law authority is notified of the volatile halogenated compounds that are used and has issued an authorisation for the discharge of wastewater accordingly. The determination of the individual HFCs shall be carried out in accordance with the methodology laid down in Section II of Annex A to the Ordinance on Methodology for Water (MVW).

The lower ranges of values for emissions of metals and cyanide in the column ‘State of the art’ refer to installations where the respective substances are not used in the process, except where two separate ranges (with and without use) are indicated (see footnote).

Table 31: Wastewater emissions Indirect discharge – state of the art, STM BREF 2006, National Ordinance Surface treatment

Parameter	Unit	State of the art Indirect discharge	STM BREF 2006	National Ordinance
Temperature	°C	35		35
Bacteria toxicity G_L				
Fish toxicity G_F,Ei				
TSS	mg/l	10–50[103]		150
pH value		6.5–10.0		6.5–10.0
Aluminium	mg/l	0.3–1.5		limited by TSS
Arsenic	mg/l			0.1
Barium	mg/l			5
Lead	mg/l	0.02–0.1[104] 0.02–0.5[105]	0.05–0.5	0.5
Cadmium	mg/l	0.0005–0.01[104]	0.1–0.2	0.1
Cadmium – prod. Specific cargo	g/kg			0.2
Total chromium	mg/l	0.001–0.01[104] 0.01–0.5[105]	0.1–2.0[106]	0.5
Chromium VI	mg/l	0.01–0.1	0.1–0.2[107]	0.1
Cobalt	mg/l			1

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[103] The upper end of the range can be 100 mg/l given that no deposits will be formed in the sewer system which lead to disturbances of the sewer system or the communal wastewater treatment plant

[104] For wastewater from electroplating without the use of the respective metal

[105] For wastewater from electroplating with the use of the respective metal

[106] Large scale steel coil coating (Sn or ECCS, electrochemical chromium plating) 0.03–1.0 mg/l

[107] Large scale steel coil coating (Sn or ECCS, electrochemical chromium plating) 0.0001–0.01 mg/l

Parameter	**Unit**	**State of the art Indirect discharge**	**STM BREF 2006**	**National Ordinance**
Iron	mg/l	0.02–1.0	[108]	limited by TSS
Copper	mg/l	0.1–0.3[104] 0.2–0.5[105]	0.2-2.0	0.5
Nickel	mg/l	0.01[109]–0.5	0.2-2.0	0.5
Selenium	mg/l			0.5
Silver	mg/l	<0.001–-0.025[104] < 0.01–0.1[105]	0.1–0.5	0.1
Zinc	mg/l	0.01–2.0[110]	0.2–2.0[111] [112]	2
Tin	mg/l	0.03–1.0	0.2–2[113]	1
Free chlorine	mg/l			0.2
Ammonium (NH_4-N)	mg/l			200
Ammonia (NH_3-N)	mg/l			20
Cyanide – free	mg/l	0.01–0.06	0.01–0.2	0.1
Cyanide – total	mg/l			2
Fluoride	mg/l	3–20		20
Nitrite (NO_2-N)	mg/l	0.1–8.0		10
Sulphate	mg/l			–[114]
Sulphide	mg/l			1
AOX	mg/l	0.04–1.0[115]		1[116]

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[108] Large scale steel coil coating (Sn or ECCS, electrochemical chromium plating) 2–10 mg/l

[109] Values from 0.001 mg/l to 0.01 mg/l were reported from installations without Ni coating

[110] Large scale steel coil zinc coating plants 0.3–1.0 mg/l; in-house electroplating plants can achieve 1.5 mg/l

[111] Large scale steel coil coating (Sn or ECCS, electrochemical chromium plating) 0.02–0.2 mg/l

[112] Large scale steel coil coating (Zn or Zn-Ni) 0.2–2.2 mg/l

[113] Large scale steel coil coating (Sn or ECCS, electrochemical chromium plating) 0.03–1.0 mg/l

[114] The emission limit shall be determined on a case-by-case basis in the event of a risk of corrosion for cement-bound materials in the area of the public sewerage or wastewater treatment plant (technical standard on “execution of sewerage systems” in accordance with Section IV of Annex A to the Ordinance on Methodology for Water, MVW)

[115] When using sodium hypochlorite (CN treatment) or insoluble anodes with chloride in the process bath (drag-in or as auxiliary) the AOX emissions are in the upper range

[116] In the case of wastewater from electroplating or mechanical processing (Section 1(2)(1) or 13), the emission limit for AOX shall also be deemed to have been complied with if:

Parameter	**Unit**	**State of the art Indirect discharge**	**STM BREF 2006**	**National Ordinance**
Low **volatile lipophilic substances**	mg/l	2–50		100[117]
Hydrocarbon index	mg/l	0.1–5.0		15
POX	mg/l			0.1[118]

2.1.11 General BAT soil and groundwater protection

The following techniques (applied either individually or in an appropriate combination) are considered to be BAT for the prevention of soil and groundwater emissions:

- Loading of raw materials and auxiliary materials exclusively in designated areas. For raw and auxilliar materials with soil or water harmful properties the loading areas

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1. the hydraulic oils, grease agents, water displacers and cooling lubricants have been shown to contain no organohalogenic compounds, and
2. hydrochloric acid used in production and wastewater treatment has been shown to have caused no higher contamination by organohalogenic compounds than is permitted by ÖNORM EN 939 “Products for the treatment of water intended for human consumption – Hydrochloric acid” January 2000; and
3. the aluminium or iron salts used in wastewater treatment have been shown to have caused no higher loads of organic halogen compounds than 100 milligrams of AOX per kilogram of aluminium or iron in the respective treatment agent; and,
4. to the extent possible, due to the required product quality and the applied production process, cyanide-based technologies are replaced by cyanide-free technologies; and,
5. in cases where the use of cyanide-based technology is unavoidable, the cyanides are destroyed by non-halogenated or other chemicals or, if halogenated or dispersing chemicals are used, the increase in the AOX content in the wastewater stream from cyanide oxidation is not greater than 0.5 mg/l.

[117] In the case of wastewater from mechanical processing (Section 1(2)(13)), an emission limit of 250 mg/l applies.

[118] The emission limit for POX shall be imposed only when the use of highly volatile halogenated hydrocarbons (HFCs) is used; it shall be observed in the partial wastewater flow from the application of these substances. Instead of the parameter POX, the sum of dichloromethane, 1-1-1-trichloroethane, 1-2-dichloroethane, trichloroethene, tetrachloroethene and an otherwise used volatile halogenated hydrocarbon (other than Cl) can be determined, provided that the water law authority is notified of the volatile halogenated compounds that are used and has issued an authorisation for the discharge of wastewater accordingly. The determination of the individual HFCs shall be carried out in accordance with the methodology laid down in Section II of Annex A to the Ordinance on Methodology for Water (MVW).

have to be secured against unwanted leakages (soil sealing, sufficient cover and absorber material);

- Collection and interim storage of all materials in designated areas while awaiting their disposal. For materials with soil or water harmful properties the designated areas need to be secured against leakages;
- Equip all sump pumps or other intermediate storage tanks for environmental harmful liquids with an alarm system which is triggered when there is a high level of liquid;
- Creating and implementing a system for testing and inspecting tanks and pipelines carrying raw materials, additives and other substances;
- Carrying out leakage checks (optical checks) of all flanges and valves on pipes used for the transport of materials and maintaining an operations logbook of those inspections;
- Provide a catchment system to collect any outlets from flanges and valves of pipes used to transport materials, except where the flanges and valves are constructed technically dense;
- Provide an adequate amount of safety containers and appropriate absorbers;
- Prevention of underground pipelines for the transport of substances (except water);
- Safe collection and disposal of fire extinguishing water (in case of fire);
- Impermeable flooring in basins or other containers for surface water or other wastewater streams to prevent unwanted leakage.

2.2 Specific BAT

In addition to the techniques described in 2.1, the following techniques (applied either individually or in an appropriate combination) are considered to be BAT:

2.2.1 EDTA

Ethylenediaminetetraaceticacid (EDTA) forms strong complexes and is virtually non-biodegradable. Complexing agents can affect the precipitation of metals during wastewater treatment or release precipitated metals in aquatic environments. EDTA is widely used in the electroplating industry, for example in degreasing baths. EDTA is also used in the production of printed circuit boards, for example in etching baths.

It is BAT to:

- substitute the use of EDTA with biodegradable substitutes (e.g. glucolic acid or tartaric acid based);
- avoid the use of EDTA by using alternative manufacturing processes (e.g. direct metallisation in PCB manufacturing).

Where the use of EDTA cannot be avoided, it is BAT to

- reduce the release of EDTA to the environment by means of material and water saving measures (e.g. recycling of rinsing water in the process bath to compensate for losses of carry-over and evaporation, if necessary after pre-treatment);
- recover EDTA and its salts from chemical copper baths and their rinsing waters;
- destroy EDTA in wastewater by UV radiation and hydrogen peroxide (see 2.1.9).

2.2.2 Cyanide

Cyanides are toxic substances that form complexes with some metals (e.g. nickel) and thus make metal precipitation in wastewater treatment difficult. Cyanide forms hydrogen cyanide in an acidic environment.

It is BAT to:

- not use cyanide in degreasing;
- replace cyanide zinc with acid galvanising or alkaline cyanide-free galvanising;
- replace cyanide copper by acid copper or copper-pyrophosphate (except for strike plating on steel, zinc die cast, aluminium and aluminium alloys).

Where the use of cyanide cannot be avoided, it is BAT to

- extract exhaust air from cyanide-containing process baths and treat them with air scrubbers;
- avoid bath agitation by air injection, as this increases the formation of carbonate;
- reduce the release of cyanide to the environment by means of material and water saving measures;
- treat cyanide-containing wastewater by means of oxidation processes (see 2.1.9).

2.2.3 PFOS and PFAS

Perflurooctane sulphonic acid (PFOS) belongs to the group of poly- and perfluorinated alkyl substances (PFAS). PFAS include more than 4,700 artificial chemicals. PFAS are persistent, bioaccumulative, ubiquitous and partly toxic[119]. PFOS and related substances have been restricted under the Stockholm Convention since 2009.

Before the Stockholm Convention, PFOS was used as a wetting agent or mist suppressor in Cr(VI) coating, as well as in the field of plastic electroplating (etching) to reduce the formation of chromic acid aerosols and to reduce workers' risk of lung cancer associated with occupational exposure to Cr(VI) compounds. Chromic acid is highly oxidative, and a variety of wetting agents would oxidise quickly in Cr(VI) baths. PFOS salts, on the other hand, can withstand the loads in the chromium bath.

According to the Regulation on Persistent Organic Pollutants (POPs Regulation (EU) 2019/1021[120]), the use of PFOS in hard chromium (Cr(VI)) coating has only been allowed in closed loop systems (current deadline 07.09.2025).

The substitution of PFOS with 6:2 fluorotelomer sulphonic acid (6:2-FTS) has been completed according to current knowledge. 6:2-FTS is a polyfluorinated wetting agent that enters the environment via the sewage path. Polyfluorinated compounds with C-H bonds are less stable than perfluorinated compounds with exceptionally stable C-F bonds. Therefore, the dosing of 6:2-FTS needs to be 2-5 times higher than with PFOS. (Blepp, Willand, Weber, 2017; Blepp, Willand, Weber, 2020)

6:2 FTS degrades in the environment into persistent, highly mobile short-chain perfluorinated compounds (as detected in surface water, groundwater, drinking water, plant enrichment, human exposure via environmental pathways). It is currently being examined whether short-chain perfluorinated substances and their precursors (such as 6:2 FTS) should be regulated as 'Substances of Very High Concern' (SVHCs) under REACH. (Blepp, Willand, Weber, 2020; Brendel et al. 2018)

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[119] Due to the large number of PFAS, not all chemicals can be examined in detail for their toxic effects. Of those PFAS that were studied in more detail, most were found to be moderately to highly toxic (EEA, 2020)

[120] In 2021 PFOA, its salts and related compounds were included in the POP regulation. A limitation of PFHxA, its salts and related compounds in the course of the Stockholm Convention pending. From 2023 on limitations or bans under REACH for C9-C14-PFCA, its salts and C9-C14-PFCA-related substances will take action.

Where the use of PFOS-containing wetting agents cannot be avoided, it is BAT to close the material cycle. A material cycle is considered to be closed if the following points are met:

- Process trays/tanks with efficient suction/extraction to minimise contamination of to the environment with chromic acid aerosols;
- Exhaust air scrubber with recirculation of the wash solution into the process solution;
- Only PFOS dosage related to throughput or demand (usage needs to be documented);
- Recovery of the PFOS-containing chromium electrolyte by rinsing the parts directly above the process bath;
- Multi-stage cascade rinsing system for extensive recirculation of PFOS to achieve a high rinse criterion with a minimum amount of excess water;
- Use of an evaporator to concentrate rinsing water and recover the extracted process solution with simultaneous use of excess heat – due to the poor electricity yield of the chromium plating process;
- Recovery of rinse water concentrates to compensate for evaporation losses of the electrolytes;
- Extension of the working life of the PFOS-containing chromium electrolytes by using cation exchange technology for the separation of foreign metals and chromium(III) from rinsing water concentrates; regeneration of cation exchange resins with sulphuric acid and their reuse in the wastewater treatment process;
- Treatment of PFOS-containing effluent streams using PFOS-specific ion exchangers.

Where the use of 6:2-FTS-containing wetting agents cannot be avoided, BAT is to treat the total wastewater flow by means of 6:2-FTS-specific ion exchangers.

Treatment of 6:2-FTS-containing wastewater streams using 6:2-FTS-specific ion exchangers:

According to a case study described by Blepp, Willand, Weber (2020) on the fate of 6:2-FTS used in Cr(VI) coating plants, additional treatment of the total amount of wastewater regarding 6:2-FTS is recommended. “Due to the observed carry-over of the 6:2 FTS in the automatic electroplating machine by ad- and desorption operations, it must be assumed that only partial flow treatment of the chromium (VI)-containing wastewater stream regarding 6:2 FTS is not sufficient.” (Blepp, Willand, Weber, 2020)

For the removal of 6:2 FTS, weak basic anion exchange resins may have proved to be effective in combination with strongly basic anion exchange resins. In combination with an evaporator, the ion exchangers can be significantly smaller.

The use of PFAS can be avoided when modified wet chemical processes or technological alternatives to wet chemical chromium plating are used. Table 32 gives an overview of alternative methods. Decorative coating on Cr(III) basis, functional chromium plating on Cr(III) basis, nickel-composite layers are used in Austria. The other technologies are not yet used in Austria, but are used in other countries. The technologies are described in chapters 2.3.1 and 2.3.2. Contrary to Cr(VI) electrolytes, the listed techniques are not a one fits all solution. The limits of applicability are described in chapters 2.3.1 and 2.3.2.

Table 32: Alternative wet chemical processes and technological alternatives to wet chemical processes

Wet chemical processes	Technological alternatives to wet chemical process
Decorative chrome plating on Cr(III) basis	High Velocity Oxygen Fuel (HVOF)
Functional chromium plating on Cr(III) basis	Physical Vapour Deposition (PVD)
Replacement of functional chromium plating with nickel-composite layers	Plasma nitriding
Functional chromium plating in closed reactor under negative pressure	Laser metal deposition (LMD) and extreme high-speed laser application welding (EHLA)

Source: Blepp, Willand, Weber, 2020

2.2.4 Hexavalent chromium

It is BAT to replace Cr(VI) with Cr(III) if the requirements to the layer properties allow it.

Layer properties are:

- Corrosion protection;
- Abrasion resistance;
- Wear resistance;
- Significant hardness;

- Durability;
- Aesthetics;
- Metallic character;
- Non-porous;
- Temperature resistant;
- Non-adhesive;
- Low friction;
- Good adhesion (of layer);
- Constant colour quality;
- Shininess;
- Reflective;
- Applicability as medical tool.

If layer properties such as corrosion protection, abrasion resistance or significant hardness are not primarily required, Cr(VI) can be replaced by Cr(III).

For good coating of Cr(VI) and Cr(III) a base nickel layer or base copper layer is required.

It is BAT to replace chromium-containing pickling solutions (chromium sulphur pickling solutions) with permanganate-based oxidising agents in plastic metallisation.

When changing from Cr(VI) to Cr(III) processes, higher loads of total chromium in the wastewater can occur.

2.3 Phasing out PFAS-containing wetting agents – Alternative wet chemical processes and technological alternatives to wet chemical processes

In the following the techniques listed in Table 32 are described with focus on the fields of applicability and limits of applicability).

2.3.1 Wet chemical processes

2.3.1.1 Decorative chrome plating on Cr(III) basis

The use of per- or polyfluorinated wetting agents is not required in chromium(III) electrolytes because they do not have the same oxidative conditions as chromium (VI) electrolytes. Conventional surfactants, such as those used in nickel electrolytes, can usually be used (Blepp, Willand, Weber, 2020).

Cr(III) electrolytes are more sensitive to impurities, reflected in the appearance and quality of the coating. Therefore, more intensive bath monitoring measures are needed than for Cr(VI) electrolytes. In wastewater treatment, attention should be paid to complexing agents that are frequently present. Metal complexes have to be treated by appropriate procedures (see 2.1.9). Cr(III) coatings are not UV resistant.

2.3.1.2 Functional chromium plating on Cr(III) basis

A wide application of the Cr(III) method in functional coating does not exist yet, due to, inter alia, insufficient layer thicknesses.

The Finnish company Savroc Oy has developed a hard chrome process based on chromium (III), which according to company data has been successfully used for years in Spain and Finland for wear parts, ball valves and hydraulic cylinder rods. The achievable hardness is between 1500 HV and 1800 HV. According to the developer, the process has already been tested on 50 plants or has been used for several years (e.g. Tecnocrom Industrial S.A.). (Blepp, Willand, Weber, 2020)

The layers have different properties compared to conventional hard chromium layers, as Cr(III) electrolytes are not separated from pure elementary chromium, but coarse-grained chromium compounds. The process requires the heating of the parts to 400–700 °C, which limits the use of the technology (possible deformation of workpiece does not allow process for medical technology). (Blepp, Willand, Weber, 2020) For big workpieces (pipline technology, printing rolls, shafts) the process is not applicable.

2.3.1.3 Replacement of functional chromium plating with nickel-composite layers

2.3.1.3.1 Nickel-tungsten alloy deposition

“Duratec NiW” is a process for the deposition of nickel-tungsten alloy layers with an alloy composition 65/35 percent Ni/W, ± 5 percent. The deposited layers have a high abrasion and corrosion resistance. This simple-to-lead process can in many cases replace hard chromium plating. (ZVO 2018d)

“A special advantage is the ductility of the alloy with up to 10 % elongation. This makes such nickel-tungsten layers an alternative to functional chromium layers as well as to nickel-phosphorus layers. According to the supplier, these coatings perform significantly better than hard chromium coatings, especially at higher operating temperatures." (Meyer 2018)

The high costs of tungsten limit its economic application. In wastewater treatment, attention should be paid to complexing agents. Due to nickel emissions, the process is not suitable for the food industry or the pharmaceutical industry. Layer properties: not non-adhesive, bad polishing properties, layer thickness is limited, low corrosion protection.

2.3.1.3.2 Chemical nickel with dispersion layers

Diamond and boron nitride particles which are present as a suspension in the electrolyte are deposited in the chemical nickel process. This creates sealant and resistant layers that replace hard chrome layers already in the textile machinery industry and in mechanical engineering. (Blepp, Willand, Weber, 2020)

In wastewater treatment, attention should be paid to complexing agents. Due to nickel emissions, the process is not suitable for the food industry or the pharmaceutical industry. Low non-adhesive properties.

2.3.1.3.3 Nickel alloy deposition

This is an alternative to functional chrome plating that uses a layer of two alloys of the metals copper, tin and nickel, i.e. a nickel-tin layer and a bronze interlayer (Kölle 2018). The layers have a high corrosion resistance and are marine water resistant. The maximum hardness attainable (about 600 HV) is far below the hardness levels that can be achieved with hard chromium coatings (1000 HV). (Blepp, Willand, Weber, 2020) With nickel alloy depositions only thin layers can be coated, limited by 5 µ.

The layers are sea salt resistant. Therefore, the process is used in wind power off-shore systems or for hydraulic cylinders of harbour cranes. (Candel-Ruiz A. 2019)

In wastewater treatment, attention should be paid to complexing agents. Due to nickel emissions, the process is not suitable for the food industry or the pharmaceutical industry.

2.3.1.4 Functional chromium plating in a closed reactor under negative pressure

Coating and rinsing occurs in a sequentially separated closed reactor. The use of wetting agents is not necessary as no chromic acid aerosols are released into the ambient air. However, special attention must be paid to explosion protection, as hydrogen and oxygen are also released during chrome plating in closed reactors. (Blepp, Willand, Weber, 2020)

The process has been applied for industrial uses for years. Due to the high degree of automation, however, it is designed for high quantities.

Currently no plants known in Austria.

2.3.2 Technological alternatives to wet chemical processes

Technological alternatives to wet chemical processes require a considerable exhaust air treatment system (in contrary to wet chemical processes where a considerable wastewater treatment system is required).

2.3.2.1 High Velocity Oxygen Fuel (HVOF)

In the HVOF process, continuous gas combustion takes place under high pressure within a combustion chamber in which a powder-shaped injection additive is fed in at the central axis of the chamber.

With the HVOF process, extremely thin layers and layers of about 50 µm up to 0.5 mm thickness with a high corrosion resistance, wear resistance and high dimensional accuracy can be produced. Other advantages of the process are the possibility of on-site repairs with mobile devices and, unlike galvanic chromium plating, there are no limitations regarding the component size. Through this process, tungsten carbide layers (WC Co Cr) can be deposited (for example), which are even harder than hard chromium layers and also have a very good corrosion resistance due to the chromium content. (Blepp, Willand, Weiland, 2020) Chromium oxides are formed.

The process is already widely used (450 plants in Germany, 2000 plants across Europe) and has been tested for many industrial applications. HVOF is an alternative to hard chromium plating, e.g. for pressure rollers. Other applications include aircraft suspensions, pistons and rollers, hydraulic pistons and piston rods, sliding surfaces of steam iron rollers for the photo industry, parts for petrochemical and chemical machines, e.g. pumps, sliders, ball valves, mechanical seals, repairs and prolonging the life span of agricultural machinery, etc. (Blepp, Willand, Weiland, 2020)

Internal coatings are possible up to a diameter of 100 mm. The process is not suitable for complex geometries or for work pieces with undercuts. The process parameters for high-temperature flame spraying of chromium must be kept in the optimal range, otherwise the formation of chromium (VI) compounds is possible in combination with atmospheric oxygen. On site repares are not possible with this process.

2.3.2.2 Physical Vapour Deposition (PVD)

In physical vapour deposition (PVD) the starting material is transferred into the gas phase in a vacuum by means of physical processes by evaporation or from solids atomically, e.g. by laser bombardment. It then separates on the colder workpiece (substrate) by condensation.

Today, coatings are mainly based on titanium nitride (TiN), titanium carbonitride (TiCN), titanium aluminium nitride (TiAlN) or diamond (DLC). Chromium-based coating systems such as chromium nitride (CrN), chromium vanadium nitride (CrVN) and chromium aluminium nitride (CrAlN) are used for die cast parts made of aluminium and magnesium. (Blepp, Willand, Weber, 2020)

PVD coatings are used for cutting tools. Rolling bearings, chassis parts, weapon technology, actuators, balls in ball bearings, bearings and cylinders, flap systems and pumps are also manufactured using the PVD process. (Galvanotechnik 9/2019)

The procedures are only suitable for small components in non-corrosion-prone installation areas. Large components such as hydraulic rods in aircraft construction or rollers in the printing industry are less likely to be coated in a high vacuum.

2.3.2.3 Plasma nitriding

Plasma nitriding works with a nitrogen-hydrogen mixture which is ionised in a closed vacuum furnace under negative pressure by applying a voltage between the container wall and the batch. The process creates a recognisable glow discharge on the tool. The gas ions react with the iron from low and high alloy steels and form a hard nitrided zone.

Plasma nitriding is not a surface coating, but a diffusion process. The ionised gas atmosphere diffuses into the peripheral zone of the metal/steel components. The method is used to increase the hardness of functional surfaces (up to 1000 HV). It increases wear resistance and improves corrosion behaviour. The surface temperatures are 350-600 °C. At this temperatures the workpiece can get deformed.

Typical applications include gears, crankshafts, camshafts, valve components, extruder screws, casting tools, forging tools, cold forming tools, injection nozzles, plastic injection tools, long shafts, axles, couplings and engine parts.

The process is also suitable for very large steel or casting parts. Plasma nitriding can be applied to all major cast iron and steel castings used in the automotive sector. (Blepp, Willand, Weber, 2020)

2.3.2.4 Laser metal deposition (LMD) and extreme high-speed laser application welding (EHLA)

During laser application welding, metal powders are applied to the surface of a base material and melted by the laser. In the EHLA process, a powdered filler material already hits the laser light above the melting bath, which heats it up close to the melting point on its way to the component.

To increase component's service life, tungsten carbide, titanium and chromium carbide, but also iron, nickel and cobalt-based powders are used, depending on the requirements for the wear layer. The deposition rate is up to 1 000 cm²/min, the coating thicknesses are

10–250 µm and the feed speed is >100 m/min. Without vacuum this process is not feasible.

For brake discs, the process is more economical than hard chrome plating. The advantages of the process are the absence of environmentally harmful chemicals or additives, as well as a good material connection between layer and substrate. (Käszmann 2019a)

Possible fields of application: Brake discs, valves, piston rings, shafts in the automotive industry, dosing rollers, pressure, plate cylinders in the printing industry, hydraulic cylinders, pistons and rods in mechanical engineering.

The process can only be used for rotationally symmetrical workpieces. Complex geometries and workpieces with undercuts, blind holes etc. cannot be coated. (Blepp, Willand, Weber, 2020) The resulting surface is raw and difficult to polish mechanically.

2.4 Literature

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3 AT&S – Austria Technologie & Systemtechnik AG

AT&S is a globally leading manufacturer of high-end printed circuit boards and IC substrates. The company was founded in 1987 and operates worldwide. AT&S industrialises leading-edge technologies for its core business segments Mobile Devices & Substrates, Automotive, Industrial and Medical.

AT&S operates two PCB production sites in Austria – Leoben and Fehring. At the production site Leoben AT&S, manufactures high density interconnect (HDI) boards. At the production site Fehring multilayer boards (MLB) are produced. Both HDI and MLB consist of multiple conductive layers separated by insulating layers (and connected via holes). This allows high tracking density, which is a requirement for modern electronic equipment. HDI are a further development of MLB.

Environmental Management System
Both the production site Leoben and Fehring have an ISO 14001 certified environmental management system and an energy management system according to ISO 50001.

3.1 Technical description

At the production site Leoben high density interconnect (HDI) boards are produced. At the production site Fehring multilayer boards (MLB) are produced. The production process in both plants is in general the same, hence the following technical description accounts for both production sites.

In general the production process consists of the following operations:

- Photo process
- Lamination
- Drilling
- Plating
- Surface treatment

Processing is a set of several individual operation steps, which vary due to product requirements and can be repeated throughout the production process. In the following the production process is described starting from producing the HDI or MLB core and subsequently applying and manufacturing the outer layer of the HDI/MLB board.

The base materials are phenolic paper, epoxy paper or epoxy glass laminates, which are clad with copper (either on one or on both sides). Base materials are not produced on site.

In the photo process, the future track image of the PCB is put onto the base material.

- The photo process consists of the following steps:
- Mechanical and chemical pre-treatment
- Applying of photoresist
- Exposure
- Etching & stripping

Mechanical and chemical pre-treatment:

The base material is cut into shape, cleaned and etched. For cleaning (degreasing) NaOH or a mixture of tensides and acids (H_3PO_4) are used (STM BREF, 2006). For chemical roughening (or microetching) either copper chloride or a persulphate pickle consisting of sulphuric acid and sodium persulphate is used (STM BREF, 2006). For thin inner cores persulphate pickle is the preferred option (STM BREF, 2006). During microetching the copper value in the etching bath rises continuously. Once the copper concentration in the bath exceeds 30 g/l the pickling solution has to be renewed (STM BREF, 2006). The excess copper in the solution can be recycled electrolytically or has to be precipitated as copper hydroxide slurry in alkaline solution, pressed out and discarded as waste. On the premise Leoben efforts are undertaken to introduce economic viable recycling of the excess copper. Microetching stops the oxidation process and allows better adhesion of the photoresist.

Applying of photoresist:

The photoresist is a photosensitive layer, which is coated onto the pre-treated surface. Coating can be done in different ways, depending on the type of photoresist. There are two types of photoresist:

- Dry photoresist applied by lamination
- Liquid photoresist applied by roller coating

At the production sites Leoben and Fehring dry photoresists are applied by lamination. Applying of the photoresist is fully automatic.

Exposure:

For photo-printing a dia negative template of the PCB track image, is printed via a laser plotter onto glass or polyester. This will be subsequently referred to as the phototool. The phototool is covered with a silver-halide emulsion.

The phototool is put on top of the photoresist laminated base material and exposed to UV light. The UV light passes through the transparent areas of the phototool and polymerises the monomer components of the photoresist (STM BREF, 2006).

Alternatively to photo-printing the PCB track image can also be printed onto the photoresist by program-controlled lasers.

At the production site Leoben, both methods are in use. At the production site Fehring only photo-printing is applied.

Development:

The photoresist is typically developed by spraying with sodium carbonate solution in a continuous horizontal line (STM BREF, 2006). The photoresist areas which have not been exposed to UV radiation are therewith removed (STM BREF, 2006). The area that has been exposed to UV radiation remains adherent to the copper surface (STM BREF, 2006).

The remaining photoresist functions as etching protection.

Etching & stripping:

Copper, which is not protected by adherent photoresist, is etched off the PCB surface by the use of e.g. HCl. This leaves only the track image of the PCB behind. In order to uncover the remaining copper tracks from the photoresist the board needs to undergo stripping. This can be done by using NaOH (STM BREF, 2006). After stripping the core is finished and can undergo lamination.

Lamination

In the lamination process the core is laminated with its outer layers. Between the core and the outer layers an insulation layer called prepreg is needed.

Copper foil, prepregs and the core are laid up and pressed under vacuum. The prepregs are shaped sheets of pre-polymerised epoxy resin reinforced with glass fibre (STM BREF, 2006). They liquefy under the influence of pressure and temperature and bond with the inner cores (STM BREF, 2006). Pre-oxidising the cores of the multilayer enhances lamination.

Drilling

Drilling is the first step in connecting the layers of a multilayer board with each other. At the production site Leoben mechanical drills, laser drills and x-ray drills are in use.

Copper plating

After drilling the multilayer board enters copper plating where the drilled holes get plated with copper. This process, also referred to as plating through holes, provides electrically conductive connections between the individual layers.

Before copper plating the multilayer board has to undergo pre-treatment steps, i.e. desmearing, etching and activation.

Desmearing:

Drilling causes the drilled polymer residues to smear as films in the drilled holes. These impurities have to be removed prior to copper plating as they adversely affect the adhesion of the metal layer to be deposited. Desmearing is typically done in several steps. In a first step the work piece is degreased. Subsequently it passes swelling. Swellers are solvent based solutions that can swell and soften the substrate. This promotes the subsequent etching step. Etching can be done by using potassium or sodium permanganate (STM BREF, 2006).

Etching:

Etching is a prerequisite for good metal adhesion. Etching is carried out in an aqueous mixture of chromic acid, sulphuric acid and wetting agent (STM BREF, 2006). Etching oxidises and dissolves the butadiene component of the plastic surface creating a micro-rough surface with microscopic caverns.

Activation:

Activation is done by filling the microscopic caverns with palladium. The high standard electrode potential of palladium allows the autocatalytic deposition of copper on plastic.

Copper plating:

Copper plating is carried out in two steps. First copper is autocatalytically deposited onto the activated surface. Subsequently the copper coat gets strengthened by copper electroplating.

Autocatalytic plating: Copper deposition starts on metal nuclei of palladium and continues autocatalytically, thus providing an initial conductive layer. A typical process solution consists of copper, sodium hydroxide, chelating agents such as EDTA, and reducing agents such as formaldehyde (STM BREF, 2006).

After copper plating the multilayer board undergoes the photo process again to produce the track image of the outer layers. After passing the photo process, the multilayer board enters surface treatment.

At the production site Leoben autocatalytic and electrolytic plating of copper is carried out. At the production site Fehring only electrolytic plating of copper is carried out.

Surface treatment
Surface treatment consists of screen printing and applying the solder mask.

Screen printing:
Screen printing is used for labelling the board or certain parts. For screen printing a light sensitive emulsion has to be applied to a metal or plastic screen. The emulsion gets exposed to light and developed with water, resulting in a negative shape of the to be printed label. The varnish or resin is subsequently pressed through the empty parts of the screen onto the board.

After screen printing the screen needs to be washed with solvents and can then be used again.

Application of solder mask:

The solder mask protects the copper from corrosion and from solder bridging (unwanted connections between tracks from soldering). All copper sections which are not necessary for the assembly process are covered with an insulating resin mask. The solder mask is usually green.

Coating of the solder mask is done by curtain coating. The boards pass horizontally on a conveyer belt a curtain of solder mask.

The solder mask is photo sensitive. A phototool of the dia negative track image of required copper sections for assembly is put on the board. Subsequently it is exposed to UV radiation, where only the parts exposed to UV radiation polymerise. After exposure, the image is developed with organic solvents.

Tin plating

In order to protect the open copper tracks and keep them solderable a tin layer is deposited electrolitically onto the copper layer. Either pure tin or tin-lead plating is carried out at the production site Fehring. At the production site Leoben tin plating is not carried out. Work pieces which need to be tin plated are sent to Fehring.

Nickel gold plating

Alternatively to tin plating, nickel-gold plating can be applied for protecting and enhancing the connectivity of the remaining copper parts. For better adhesion nickel has to be applied before gold.

At the production site Leoben both, nickel and gold, are deposited electroless. At the production site Fehring nickel and gold are electrolytically deposited.

In a final step the multilayer or HDI board undergoes final high-pressure rinsing and quality control.

Process & cooling water

Process water is either softened (removal of calcium and magnesium) or deionised before entering the process. Water softening is done by ion exchange resin. Water deionisation by an additional reverse osmosis step.

Cooling water for the production site Leoben is taken from the river Mur and fed back into the river.

Rinsing

After each process step the work piece is rinsed. Multiple stage counterflow rinsing units consisting of two or three steps are used in order to minimise water use. Rinsing after gold plating is done in static rinsing units. The rinsing water is sent through ion exchangers in order to recuperate the gold.

Waste gas treatment

Waste gas is collected at several process steps. Process steps are usually fully encapsulated. Depending on the origin of the waste gas, it is either treated in sodium hydroxide scrubbers or in hydrogen chloride scrubbers. Exhaust air containing solvents (predominantly from surface treatment operations) is treated in bio-filters. After treatment, the exhaust air is emitted from stacks. Waste gas is collected separately, resulting in a vast number of emission points of release and air washers (approx. 40 per production site).

Emission limit values for air emission parameters are set by permit.

Bath life span

The process baths are regularly monitored and controlled in the in-house laboratory. This enables an accurate dosing of the needed chemicals and avoids excess use of chemicals. Additionally regular monitoring and maintenance (i.e. removing of sludge) increases the bath life spans.

Process wastewater

In the following, the treatment of process wastewater is described individually for each plant.

3.1.1 AT&S Leoben:

Treated wastewater is discharged directly and indirectly. Treated wastewater from rinsing and treated eluates from water purification are discharged directly. Other treated wastewater is discharged indirectly. Process wastewater is collected in separate streams and treated (or pre-treated) separately before being discharged or joining another wastewater treatment stream. In general wastewater treatment consists of:

- Neutralisation
- Precipitation
- Flocculation
- Settling
- Sludge dewatering
- Sand filtration
- Ion exchange
- Plating out (for gold)

Process wastewater is collected in the following streams:

- Rinsing water
- Acidic concentrates
- Alkaline concentrates
- Wastewater from swelling
- Potassium permanganate containing wastewater
- Rinsing water containing gold
- Concentrates containing gold
- Concentrates containing nickel
- Wastewater from stripping
- Wastewater from development
- Wastewater from solder mask application
- Eluates from water purification

Rinsing water

Wastewater form rinsing passes continuous flow neutralisation where the pH value is adjusted and precipitation of metals is triggered. Subsequently the precipitated metals are sediment in a settling tank. Adding flocculation agents helps settling. The clear water from sedimentation passes through sand filters, ion exchangers and final neutralisation before being directly discharged. Accruing sludge from sedimentation is dewatered in chamber filter presses. Thereof accruing wastewater re-enters the wastewater treatment.

Acidic concentrates

Acidic concentrates are discharged indirectly. Acidic concentrates are treated in batch neutralisation units where pH value adjusting, precipitation, flocculation and sedimentation takes place. After batch neutralisation the wastewater stream is combined with pre-treated wastewater from stripping and developing. The combined wastewater stream enters continuous flow neutralisation (consisting of pH value adjustment, precipitation, flocculation and sedimentation). Clear water from sedimentation passes through sand filters. Subsequently the stream is combined with wastewater from solder mask application. The combined streams pass ion exchangers and final neutralisation before being discharged into the public sewer. Accruing sludge from sedimentation is dewatered in chamber filter presses. Thereof accruing wastewater re-enters the wastewater treatment.

Alkaline concentrates

Alkaline concentrates are discharged indirectly. Their treatment is similar to the treatment of acidic concentrates, i.e. batch neutralization, combination with wastewater from stripping and developing, continuous flow neutralization, sludge dewatering, sand filtration, combination with wastewater from solder mask application, ion exchange, final neutralization, discharge into the public sewer.

Wastewater from swelling

Wastewater from swelling is discharged indirectly. The treatment is similar to the treatment of acidic concentrates.

Potassium permanganate containing wastewater

Wastewater containing potassium permanganate is discharged indirectly. The treatment is similar to the treatment of acidic concentrates.

Rinsing water containing gold

Rinsing water from gold plating is treated by adsorption of the gold content on ion exchange resins. Whilst precious metals in concentrated solutions are usually recovered electrolytically, more dilute solutions, e.g. rinsing water, are typically treated by adsorbtion on ion exchange resins. The adsorbed gold can be recovered from the resin and thus reused. Gold recovery from the resin does not take place on the site. The remaining wastewater after ion exchange is combined and treated together with the wastewater stream “acidic concentrates”.

Concentrates containing gold

Used concentrates containing gold pass firstly gold recovery. Gold is recovered electrolytically, so that the gold from the concentrate is plated onto the cathode. The gold plated cathodes are sold. The remaining cyanid containing concentrates are subsequently treated by an external disposal company.

Concentrates containing nickel

Used nickel concentrates are stored and treated by an external disposal company.

Wastewater from stripping

Wastewater from stripping is either treated in a batch neutralization plant consisting of pH value adjustment, precipitation, flocculation and sedimentation or via ultrafiltration. After pre-treatment the wastewater stream is combined with the wastewater stream “acidic concentrates”.

Wastewater from developing

Wastewater from developing is either treated in a batch neutralization plant consisting of pH value adjustment, precipitation, flocculation and sedimentation or via ultrafiltration. After pre-treatment the wastewater stream is combined with the wastewater stream “acidic concentrates”.

Eluates from water purification

The pH value is adjusted for eluates from water purification. The treated wastewater is directly discharged.

3.1.2 AT&S Fehring:

Treated wastewater is discharged directly and indirectly. Wastewater with a high organic load is treated on-site but discharged indirectly. Wastewater with high organic load stems from photo developing, photo resist stripping and process tanks due to their surfactant content. Remaining process wastewater is discharged directly after on-site treatment.

Process wastewater is collected in several separate streams and treated (or pre-treated) separately before being discharged or joining another wastewater treatment stream. In general wastewater treatment consists of:

- Neutralisation

- Precipitation
- Flocculation
- Settling
- Sludge dewatering
- Sand filtration
- Ion exchange
- Activated carbon filters
- Plating out (for gold)

Process wastewater for direct discharge is collected in the following streams:

- Complexing agent free concentrates
- Potassium permanganate containing concentrates
- Oxidizing agent containing concentrates
- Eluates from water purification
- Wastewater from exhaust air scrubbers
- Wastewater from pressurized air condensates
- Excess rinsing water

Complexing agent free concentrates
Complexing agent free concentrates are discharged directly after treatment. The concentrates are treated in a batch neutralisation unit where pH value adjusting, precipitation, flocculation and sedimentation takes place. Clear water from sedimentation passes through sand filters, ion exchangers and activated carbon filters. This can lead to a shift in the pH value wherefore final neutralisation before being discharged into the river Raab is carried out. Accruing sludge from sedimentation is dewatered in a chamber filter press. Thereof accruing wastewater re-enters wastewater treatment.

Potassium permanganate containing concentrates are treated likewise to complexing agent free concentrates.

Oxidizing agent containing concentrates
The reduction of oxidizing agents is done by sodium bisulfite. After the reduction of oxidising agents the wastewater stream is treated via batch neutralisation, sand filtration, ion exchange resins, activated carbon filters and final neutralisation before being discharged into the river Raab. Accruing sludge from sedimentation is dewatered in a chamber filter press. Thereof accruing wastewater re-enters wastewater treatment.

Less heavily polluted wastewater

Less heavily polluted wastewater streams are: eluates from water purification, wastewater from exhaust air scrubbers, wastewater from pressurized air condensates and excess rinsing water.

Less heavily polluted wastewater is discharged directly after treatment. Treatment consists of continuous flow neutralization where the pH value is adjusted and precipitation of metals is triggered. By adding flocculation agents settling is enhanced. The clear water from sedimentation passes through sand filters, ion exchangers, activated carbon filters and final neutralisation before being discharged into the river Raab. Accruing sludge from sedimentation is dewatered in chamber filter presses. Thereof accruing wastewater re-enters the wastewater treatment.

- Process wastewater for indirect discharge is collected in the following streams:
- Complexing agent containing concentrates
- Wastewater from photo development (photo-resist)
- Wastewater from tin plating

Complexing agent containing concentrates

Complexing agents used in certain processes make the precipitation of transition metals more difficult. Thus the complexes need to be reduced first before precipitation can take place. Sodium sulfide is used as reduction agent. After complex reduction the wastewater is treated in a batch neutralization unit where where pH value adjusting, precipitation, flocculation and sedimentation takes place. Clear water from sedimentation is combined with wastewater from photo development. Accruing sludge from sedimentation is dewatered in a chamber filter press together with sludge from photo-resist wastewater treatment. Thereof accruing wastewater re-enters wastewater treatment.

Wastewater from photo-development

Wastewater from photo-development is treated in a batch neutralisation unit where pH value adjusting, precipitation, flocculation and sedimentation takes place. In the batch neutralisation unit the wastewater stream is combined with the pre-treated wastewater containing complexing agents. Clear water from sedimentation passes sand filtration before being indirectly discharged via the public sewer system. Accruing sludge from sedimentation is dewatered in a chamber filter press. Thereof accruing wastewater re-enters wastewater treatment.

Wastewater from tin plating
Wastewater from tin plating needs to be treated separately due to its thiourea content. Thiourea is a nitrification inhibitor wherefore it needs to be treated before being sent to the communal WWTP. In a first step the pH value has to be increased (alkaline). Subsequently hydrogen peroxide is added over several hours triggering the disintegration of thiourea. Once pre-treatment is completed the wastewater enters batch neutralisation (pH value adjusting, precipitation, flocculation, sedimentation). Clear water from sedimentation passes sand filtration before being indirectly discharged via the public sewer system. Accruing sludge from sedimentation is dewatered in a chamber filter press. Thereof accruing wastewater re-enters wastewater treatment.

3.2 Current consumption & emission levels

3.2.1 Production site Leoben

Generated waste from PCB manufacturing is listed in Table 33. The quantities relate to the year 2017.

Table 33: Waste generation PCB manufacturing 2017, Production site Leoben

Waste generation PCB		
Non-hazardous waste	Origin	Quantity [t]
Used filter mediums (not containing hazardous admixtures)	Plating	14.12
Drilling chips	Drilling	55.64
Sludge from WWTP – containing copper	WWTP	1171.34
Plastic foil (PET)	Photo	27.27
Sludge (solvents free)	Photo	50.42
Hazardous waste	Origin	Quantity [t]
Used filter mediums containing hazardous admixtures	Electroplating	3.624
Sludge	WWTP	173.24

Waste generation PCB		
Copper(II)chloride	Photo	1697.66
Acid and acid mixtures	Electroplating (copper)	280.976
Acid and acid mixtures	Nickel plating	82.44
Concentrates containing cyanide (no gold)	Gold plating	4.13
Solvent-water mixtures	Photo process (solder mask)	0.37
Sludge from baths	Plating	93.56
Solvent mixtures (halogen free)	Surface treatment	0.894
Sludge containing solvents	Surface treatment	3.975
Acid and acid mixtures	Stripping	2.797
Other aqueous concentrates	PCB manufacturing	20.04

Source: AT&S, own recordings

Gold from used concentrates is plated out and sold. Rinsing water from gold plating is treated with ion exchange resins to capture the gold fraction of the rinsing water. The ion exchange resin is then sold.

Waste containing copper, gold or aluminum is collected separately and sold for further use. Copper, gold or aluminum waste stems from milling, drilling and finishing operations.

Copper from wastewater is recovered by centrifuges and sold. Silver waste from the photo process is collected separately and sold.

Excess copper in etching baths can be recycled electrolytically or has to be precipitated as copper hydroxide slurry in alkaline solution, pressed out and discarded as waste. On the premise Leoben efforts are undertaken to introduce economic viable recycling of the excess copper.

Emissions to air Leoben
Waste gas is collected at several process steps. Process steps are usually fully encapsulated. Depending on the origin of the waste gas it is either treated in sodium hydroxide scrubbers or in hydrogen chloride scrubbers. Exhaust air containing solvents (predominantly from surface treatment operations) is treated in bio-filters. After

treatment, the exhaust air is emitted from stacks. Waste gas is collected separately resulting in a vast number of emission points of release and air washers.

Emissions to air have to be monitored every five years by an accredited testing institute. The monitoring frequency and the ELVs for emissions to air are prescribed in permit (GZ.: 4.1-21-10/66, 2011).

Emissions to air have to be measured via 3 half-hour measurements. Measurements have to relate to 0°C, 1013 mbar and dry exhaust air.

Table 34 presents the prescribed parameters and ELVs for emissions to air. Table 35 and Table 36 present the monitoring results of emissions to air from PCB manufacturing. The monitoring was conducted in 2015. The presented values are average values over the 3 half-hour measurements.

Table 34: Parameters and emission limit values prescribed by permit (GZ.: 4.1-21-10/66, 2011) – 0°C, 1013 mbar, dry exhaust air

Parameter	Unit	ELV Permit
org. C	mg/Nm³	50
Aerosol	mg/Nm³	10
Dust	mg/Nm³	2
Cyanide, Fluoride	mg/Nm³	1
Ammonia	mg/Nm³	5
Nickel	mg/Nm³	0.5
Formaldehyde (HCOH)	mg/Nm³	1
HCl	mg/Nm³	10

Source: TÜV Austria, 2018

Table 35: Monitoring results of emissions to air PCB manufacturing; average of 3 half-hour measurements; 0 °C, 1013 mbar, dry exhaust air

Emissions to air 2015 – Production site Leoben (1/2)				
Process step	**Parameter**	**Concentration [mg/Nm³]**	**Load [g/h]**	**ELV [mg/Nm³]**
Bondfilm; copper plating	Aerosol	0,1	0,34	10
	HCOH	0,03	0,1	1
Etching	Aerosol	0,24	0,48	10
Etching	Aerosol	0,28	1,08	10
Etching; HCl storage	Aerosol	< 0,10	< 0,53	10
	HCl	1,22	6,39	10
Copper plating	Aerosol	0,11	0,82	10
Vacuum pump (lamination)	org. C	3	15,9	50
Vacuum pump (lamination)	org. C	< 3	< 6,3	50
Plasma etching (desmearing)	F·	0,23	0,2	1
	Aerosol	0,83	0,75	10
Intermediate layer cleaning (bondfilm)	Aerosol	0,1	0,09	10
Drilling	dust	< 1	< 0,90	2
Drilling	dust	< 1	< 3,24	2
Pumps (wastewater treatment)	Aerosol	0,43	0,61	10
Etching	Aerosol	2,99	9,57	10
Etching	Aerosol	8,98	33,2	10
	org. C	11	40,6	50
	HCl	8,05	29,7	10
Copper(II)chloride regeneration	HCl	3 ,27	2 ,61	1 0
	Aerosol	1,11	0,89	10
Nickel/gold plating	NH,	<0,1	< 0,41	5
	CN	<0, 04	< 0,16	1

Emissions to air 2015 – Production site Leoben (1/2)				
Process step	**Parameter**	**Concentration [mg/Nm^3]**	**Load [g/h]**	**ELV [mg/Nm^3]**
	Aerosol	< 0,10	< 0,41	10
	Ni	0,004	0,02	0,5
Copper plating	Aerosol	0,13	0,36	10
Degreaseing	Aerosol	3,03	8,16	10
Degreasing; annealing furnace	org. C	<3	< 28,0	50
Solder mask application	org.C	14	33,9	50
	Aerosol	0,37	0,9	10
Lamination; annealing furnace	org.C	<4	8,2	50
Developing (photo process)	org.C	<3	< 13 ,4	50
Wastewater treatment	NH_3	0,2	0,62	5
	Aerosol	< 0,10	< 0,31	10
Annealing oven	org. C	<3	< 4,7	50

Source: TÜV Austria, 2018

Table 36: Monitoring results of emissions to air PCB manufacturing; average of 3 half-hour measurements; 0 °C, 1013 mbar, dry exhaust air

Emissions to air 2015 – Production site Leoben (2/2)				
Process step	**Parameter**	**Concentration [mg/Nm^3]**	**Load [g/h]**	**ELV [mg/Nm^3]**
Developing (photo process)	Aerosol	< 0,10	< 0,21	10
	org.C	31	65 , 7	50
Copper plating; deburring	Aerosol	0,35	1,38	10
	HCOH	< 0 ,61	< 2,38	1

Emissions to air 2015 – Production site Leoben (2/2)

Process step	Parameter	Concentration	Load	ELV
		[mg/Nm³]	[g/h]	[mg/Nm³]
Copper plating; deburring	Aerosol	< 0,16	< 0,61	10
Nickel/gold plating; stripping	NH_3	0,7	4,76	5
	CN·	< 0,11	<0,75	1
	Aerosol	< 0,31	<2,11	10
Biofilter (surface treatment)	org.C	20	184	50
Laser drilling	dust	< 1	< 5,52	2
Mechanical drilling	dust	< 1	< 7,55	2
Mechanical drilling	dust	< 1	< 5,55	2
Cyanide storage tank	CN·	0,07	0,009	1
Etching	HCl	1,54	3,26	10
	Aerosol	0,33	0,69	10
Copper plating; deburring	Aerosol	0,17	0,37	10
Biofilter (surface treatment)	org. C	3	21	50
Copper plating	Aerosol	0,1	1,22	10
Drying	org. C	4	8,3	50
Room exhaust air – Copper(II)chloride regeneration	HCl	4,81	9,58	10

Source: TÜV Austria, 2018

Emissions to water Leoben

Treated process wastewater is discharged directly and indirectly. Monitoring has to be done using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit. Minimum monitoring frequencies for self-monitoring (performed by operator) and external-assessment are prescribed by permit. Emission limit values (ELV) are prescribed by permit.

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

Treated wastewater is discharged directly and indirectly. Treated wastewater from rinsing and treated eluates from water purification are discharged directly. Other treated wastewater is discharged indirectly. Process wastewater is collected in separate streams and treated (or pre-treated) separately before being discharged or joining another wastewater treatment stream. In general wastewater treatment consists of:

- Neutralisation
- Precipitation
- Flocculation
- Settling
- Sludge dewatering
- Sand filtration
- Ion exchange
- Plating out (for gold)

A detailed description of the on-site WWTP is presented in chapter 3.

Emissions to water (direct and indirect) are described in the following tables. In Table 37 – Table 39 the minimum monitoring frequencies and ELVs prescribed by permit are presented and compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. Table 40 – Table 60 present the monitoring recordings (self-monitoring and external-monitoring) of treated process wastewaters and wastewater from water purification from 2016, 2017 and 2018.

Table 37: Emission limit values for direct discharge – PCB manufacturing in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit – production site Leoben

Direct discharge				**PCB manufacturing – Production site Leoben**		
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)**	**Ordinance**	**Min. frequency self-monitoring**	**Min. frequency external-monitoring**
Arsenic – As	mg/l	0.1	–	0.1	–	6 months
Lead – Pb	mg/l	0.5	0.05–0.5	0.5	–	6 months
Cadmium – Cd	mg/l	0.1	0.1–0.2	0.1	–	6 months
Chromium total – Cr	mg/l	0.5	0.1–2.0	0.5	–	6 months
Cobalt – Co	mg/l	1	–	0.5	–	6 months
Iron – Fe	mg/l	2	0.1–5.0	2	–	6 months
Copper – Cu	mg/l	0.5	0.2–2.0	0.5	daily	6 months
Nickel – Ni	mg/l	0.5	0.2–2.0	0.5	daily	6 months
Silver – Ag	mg/l	0.1	0.1–0.5	0.1	–	6 months
Zinc – Zn	mg/l	1	0.2–2.0	1	daily	6 months
Tin – Sn	mg/l	1	0.2–2.0	1	–	6 months
Ammonium – NH_4-N	mg/l	20	–	50	–	6 months
Ammonia – NH_3-N	mg/l	0.5	–	0.5	–	6 months
Fluoride – F	mg/l	20	10–20	20	–	6 months
Nitrit – NO_2-N	mg/l	1.5	–	1.5	–	6 months
Phosphorus total – P	mg/l	2	0.5–10	2	–	6 months
Formaldehyde	mg/l	0.5	–	–	–	6 months
COD	mg/l	300	100–500	200	daily	6 months
AOX	mg/l	1	–	1	–	6 months

Direct discharge				PCB manufacturing – Production site Leoben		
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)**	**Ordinance**	**Min. frequency self-monitoring**	**Min. frequency external-monitoring**
Hydrogen Index	mg/l	5	1–5	0.1	–	6 months
Q	m³/d	1001	–	–	continuous	6 months
T	°C	30	–	30	continuous	6 months
TSS	–	30	5–30	30	–	6 months
pH	mS/cm	6.5-9.0	–	6.5–9.0	continuous	6 months
Conductivity	ml/l	–	–	–	continuous	6 months
Sulphide – S	mg/l	0.1	–	0.1	weekly	6 months

Source: Permit GZ.: 4.1-21-10/66; Permit GZ.: 4.1-21-10/79; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 38: Emission limit values for indirect discharge – PCB manufacturing in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit – production site Leoben

Indirect discharge				PCB manufacturing – Production site Leoben		
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)**	**Ordinance**	**Min. frequency self-monitoring**	**Min. frequency external-monitoring**
Arsenic – As	mg/l	0.1	–	0.1	–	6 months
Lead – Pb	mg/l	0.5	0.05–0.5	0.5	–	6 months
Cadmium – Cd	mg/l	0.1	0.1–0.2	0.1	–	6 months
Chromium total – Cr	mg/l	0.5	0.1–2.0	0.5	daily	6 months
Cobalt – Co	mg/l	1	–	0.5	–	6 months

Indirect discharge	PCB manufacturing – Production site Leoben					
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)**	**Ordinance**	**Min. frequency self-monitoring**	**Min. frequency external-monitoring**
Copper – Cu	mg/l	0.5	0.1–2.0	0.5	daily	6 months
Nickel – Ni	mg/l	0.5	0.2–2.0	0.5	daily	6 months
Mercury – Hg	mg/l	0.01	–	0.01	–	6 months
Silver – Ag	mg/l	0.1	0.1–0.5	0.1	–	6 months
Zinc – Zn	mg/l	1	0.2–2.0	1	daily	6 months
Tin – Sn	mg/l	1	0.2–2.0	1	–	6 months
Ammonium – NH_4-N	mg/l	–	–	200	–	6 months
Nitrogen total – TN	mg/l	–	–	–	–	6 months
Fluoride – F	mg/l	20	–	20	–	6 months
Nitrite – NO_2-N	mg/l	1.5	–	10	–	6 months
Phosphorus total – TP	mg/l	–	–	–	–	6 months
Formaldehyde	mg/l	1	–	–	–	6 months
Chloride – Cl	mg/l	–	–	–	–	6 months
COD	mg/l	2.800	–	–	daily	6 months
AOX	mg/l	1	–	1	–	6 months
Low volatile lipophilic substances	mg/l	100	–	100	–	6 months
Hydrocarbon Index	mg/l	15	–	0.1	–	6 months
TOC	mg/l	–	–	–	–	6 months
Q	m^3/d	400	–	–	continuous	6 months
T	°C	35	–	35	continuous	6 months
TSS	–	30	–	150	–	6 months
pH	mS/cm	6.5–9.0	–	6.5–10.0	continuous	6 months

Indirect discharge				PCB manufacturing – Production site Leoben		
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)**	**Ordinance**	**Min. frequency self-monitoring**	**Min. frequency external-monitoring**
Conductivity	ml/l	–	–	–	continuous	6 months
Sulphide – S	mg/l	0.1	–	1	–	6 months

Source: Permit GZ.: 4.1-21-10/66; Permit GZ.: 4.1-21-10/79; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 39: Emission limit values for indirect discharge – PCB manufacturing in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from water purification. Minimum monitoring frequencies for treated wastewater as prescribed by permit – production site Leoben

Direct discharge				Water purification – Production site Leoben		
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)**	**Ordinance**	**Min. frequency self-monitoring**	**Min. frequency external-monitoring**
Iron – Fe	mg/l	2	0.1–5.0	2	–	6 months
Copper – Cu	mg/l	0.5	0.2–2.0	0.5	weekly	6 months
Phosphorus total – P	mg/l	2	0.1–10	2	–	6 months
COD	mg/l	90	100–500	90	weekly	6 months
TOC	mg/l	30	–	–	weekly	6 months
AOX	mg/l	1	–	1	–	6 months
Q	m^3/d	404	–	–	continuous	6 months
T	°C	30	–	30	continuous	6 months
pH	–	6.5–8.5	–	6.5–8.5	continuous	6 months
Conductivity	mS/cm	–	–	–	continuous	6 months
TSS	mg/l	30	–	30	–	6 months

Direct discharge						Water purification – Production site Leoben
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)**	**Ordinance**	**Min. frequency self-monitoring**	**Min. frequency external-monitoring**
Chloride – Cl	mg/l	0.2	–	–	–	6 months

Source: Permit GZ.: 4.1-21-10/66; Permit GZ.: 4.1-21-10/79; STM BREF 2006; AEV Wasseraufbereitung BGBl. II Nr. 128/2019

Table 40: Self-monitoring of treated wastewater – production site Leoben

Self-monitoring 2016							Production site Leoben
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV**	**Number of samples**
Direct discharge							
Q	m³	35	915	774	595	1001	274
Cu	mg/l	0.05	0.50	0.46	0.27	0.50	273
Ni	mg/l	0.00	0.36	0.02	0.01	0.50	274
Zn	mg/l	0.00	0.24	0.01	0.00	1.00	274
CSB	mg/l	36.1	292	228	121	300	272
Indirect discharge							
Q	m³	86	360	304	233	400	274
Cu	mg/l	0.00	0.46	0.32	0.16	0.50	273
Ni	mg/l	0.00	0.08	0.02	0.01	0.50	274
Cr	mg/l	0.00	0.12	0.03	0.00	0.50	274
Zn	mg/l	0.00	0.07	0.01	0.00	1.00	274
CSB	mg/l	35	1291	654	362	2800	274

Source: Self-monitoring AT&S, 2016

Table 41: Self-monitoring of treated wastewater – production site Leoben

Self-monitoring 2017							**Production site Leoben**
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV**	**Number of samples**
Direct discharge							
Q	m³	30	830	759	565	1001	301
Cu	mg/l	0.01	0.50	0.43	0.24	0.50	301
Ni	mg/l	0.00	0.11	0.04	0.01	0.50	301
Zn	mg/l	0.00	0.18	0.01	0.01	1.0	301
CSB	mg/l	23	299	249	128	300	301
Indirect discharge							
Q	m³	22	400	316	224	400	300
Cu	mg/l	0.00	0.49	0.42	0.20	0.50	299
Ni	mg/l	0.00	0.30	0.04	0.02	0.50	300
Cr	mg/l	0.00	0.06	0.01	0.00	0.50	300
Zn	mg/l	0.00	0.25	0.01	0.00	1.00	300
CSB	mg/l	4	1515	754	345	2800	300

Source: Self-monitoring AT&S, 2017

Table 42: Self-monitoring of treated wastewater – production site Leoben

Self-monitoring 2018							**Production site Leoben**
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV**	**Number of samples**
Direct discharge							
Q	m³	91	861	770	532	1001	266
Cu	mg/l	0.02	0.56	0.43	0.25	0.50	266
Ni	mg/l	0.00	0.40	0.06	0.02	0.50	266
Zn	mg/l	0.00	0.09	0.01	0.00	1.00	266

Self-monitoring 2018							**Production site Leoben**
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV**	**Number of samples**
CSB	mg/l	0.00	299	252	122	300	266
Indirect discharge							
Q	m³	30	310	296	208.72	400	265
Cu	mg/l	0.01	0.46	0.35	0.17	0.50	265
Ni	mg/l	0.00	0.15	0.06	0.02	0.50	265
Cr	mg/l	0.00	0.28	0.03	0.01	0.50	265
Zn	mg/l	0.00	0.08	0.01	0.01	1.00	265
CSB	mg/l	15	2732	1174.80	484.75	2800	265

Source: Self-monitoring AT&S, 2018

Table 43: External-monitoring of process wastewater from PCB manufacturing – direct discharge, 24h flow proportional composite sample – production site Leoben

External-monitoring 2016					**Production site Leoben**
Direct discharge – PCB manufacturing					
Parameter	**Unit**	**24-hours flow proportional composite sample**		**ELV**	**Standard**
		15.06.2016	**22.11.2016**		
Arsenic – As	mg/l	<0.001	<0.001	0.1	DIN EN ISO 17294
Lead – Pb	mg/l	<0.001	<0.001	0.5	DIN EN ISO 17294
Cadmium – Cd	mg/l	<0.0005	<0.0005	0.1	DIN EN ISO 17294
Chromium total – Cr	mg/l	<0.001	0.0016	0.5	DIN EN ISO 17294
Cobalt – Co	mg/l	<0.001	<0.001	1	DIN EN ISO 17294
Iron – Fe	mg/l	0.01	0.01	2	DIN EN ISO 17294
Copper – Cu	mg/l	0.18	0.28	0.5	DIN EN ISO 17294
Nickel – Ni	mg/l	0.0027	0.0011	0.5	DIN EN ISO 17294

External-monitoring 2016					**Production site Leoben**
Direct discharge – PCB manufacturing					
Parameter	**Unit**	**24-hours flow proportional composite sample**		**ELV**	**Standard**
		15.06.2016	**22.11.2016**		
Silver – Ag	mg/l	<0.001	<0.001	0.1	DIN EN ISO 17294
Zinc – Zn	mg/l	0.0026	0.006	1	DIN EN ISO 17294
Tin – Sn	mg/l	<0.001	<0.001	1	DIN EN ISO 17294
NH_4-N	mg/l	1.31	0.83	20	DIN 38 406 - E 5
NH_3-N	mg/l	0.05	0.02	0.5	calculated
Fluoride – F	mg/l	1.21	1.01	20	DIN 38 405 - D 4
Nitrite – NO_2-N	mg/l	0.4	0.11	1.5	DIN EN 26777
Phosphorus total – TP	mg/l	<0.01	0.042	2	DIN EN 13346
Formaldehyde	mg/l	0.218	0.205	0.5	VDI 3484 Blatt 1
COD	mg/l	73	124	300	DIN 38 409 - H 44
AOX	mg/l	0.054	0.19	1	DIN EN ISO 9562
Hydrogen Index	mg/l	<0.08	<0.08	5	ÖNORM EN ISO 9377-2

Source: CLUG, 2016–2018

Table 44: External-monitoring of process wastewater from PCB manufacturing – direct discharge, spot samples – production site Leoben

External-monitoring 2016						**Production site Leoben**
Direct discharge – PCB manufacturing						
Parameter	**Unit**	**Spot samples – 15.06.2016**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		449		1001	
T	°C	27.8	27.1	27.4	30	DIN 38 404 - C 4

External-monitoring 2016						**Production site Leoben**
Direct discharge – PCB manufacturing						
Parameter	**Unit**	**Spot samples – 15.06.2016**			**ELV**	**Standard**
		A	**B**	**C**		
TSS	mg/l	4	6	8	30	DIN 38409 - H 2
pH	–	7.85	7.82	7.9	6.5–9.0	DIN 38 404 - C 5
Conductivity	mS/cm	15097	5.06	4.52	–	ÖNORM EN 27 888
Sulphide – S	mg/l	<0.025	<0.025	<0.025	0.1	DIN 38 405 - D 26
Parameter	**Unit**	**Spot samples – 22.11.2016**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		584		1001	
T	°C	27.1	27	25.5	30	DIN 38 404 - C 4
TSS	mg/l	14	11.2	22	30	DIN 38409 - H 2
pH	–	7.4	7.44	8.15	6.5–9.0	DIN 38 404 - C 5
Conductivity	mS/cm	4.16	4.21	4.05	–	ÖNORM EN 27 888
Sulphide – S	mg/l	<0.025	<0.025	<0.025	0.1	DIN 38 405 - D 26

Source: CLUG, 2016–2018

Table 45: External-monitoring of wastewater from water purification – direct discharge, 24-hours flow proportional composite sample – production site Leoben

External-monitoring 2016					**Production site Leoben**
Direct discharge – Water purification					
Parameter	**Unit**	**24-hours flow proportional composite sample**		**ELV**	**Standard**
		15.06.2016	**22.11.2016**		
Iron – Fe	mg/l	0.01	0.02	2	DIN EN ISO 17294
Copper – Cu	mg/l	0.028	0.023	0.5	DIN EN ISO 17294
Phosphorus total – P	mg/l	<0.01	0.01	2	DIN EN 13346
COD	mg/l	6.3	9	90	DIN 38 409 - H 44

External-monitoring 2016					Production site Leoben
Direct discharge – Water purification					
Parameter	**Unit**	**24-hours flow proportional composite sample**		**ELV**	**Standard**
		15.06.2016	**22.11.2016**		
TOC	mg/l	1.18	1.8	30	ÖNORM EN 1484
AOX	mg/l	0.198	0.26	1	DIN EN 1485

Source: CLUG, 2016–2018

Table 46: External-monitoring of wastewater from water purification – direct discharge, 24-hours flow proportional composite sample – production site Leoben

External-monitoring 2016						Production site Leoben
Direct discharge – Water purification						
Parameter	**Unit**	**Spot samples – 15.06.2016**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		232		404	
T	°C	18.9	18.4	19.5	30	DIN 38 404 - C4
pH	–	7.83	7.95	8.01	6.5–8.5	DIN 38 404 - C 5
Conductivity	mS/cm	8.18	5.75	4.24	–	ÖNORM EN 27 888
TSS	mg/l	<1.0	<1.0	<1.0	30	DIN 38409 - H 2
Chloride – Cl	mg/l	<0.05	<0.05	<0.05	0.2	DIN EN ISO 7393-1
Parameter	**Unit**	**Spot samples – 22.11.2016**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		225		404	
T	°C	18.2	18.3	17.8	30	DIN 38 404 - C4
pH	–	8.23	8	7.71	6.5–8.5	DIN 38 404 - C 5
Conductivity	mS/cm	1.55	1.42	11.3	–	ÖNORM EN 27 888
TSS	mg/l	3.2	6	10.4	30	DIN 38409 - H 2
Chloride – Cl	mg/l	<0.05	<0.05	<0.05	0.2	DIN EN ISO 7393-1

Source: CLUG, 2016–2018

Table 47: External-monitoring of wastewater PCB manufacturing – indirect discharge, 24-hours flow proportional composite sample – production site Leoben

External-monitoring 2016					**Production site Leoben**
Indirect discharge – PCB manufacturing					
Parameter	**Unit**	**24-hours flow proportional composite sample**		**ELV**	**Standard**
		15.06.2016	**22.11.2016**		
Arsenic – As	mg/l	<0.001	<0.001	0.1	DIN EN ISO 17294
Lead – Pb	mg/l	<0.001	<0.001	0.5	DIN EN ISO 17294
Cadmium – Cd	mg/l	<0.0005	<0.0005	0.1	DIN EN ISO 17294
Chromium total – Cr	mg/l	<0.001	<0.001	0.5	DIN EN ISO 17294
Cobalt – Co	mg/l	<0.001	0.0011	1	DIN EN ISO 17294
Copper – Cu	mg/l	0.071	0.044	0.5	DIN EN ISO 17294
Nickel – Ni	mg/l	0.008	<0.001	0.5	DIN EN ISO 17294
Mercury – Hg	mg/l	<0.0001	<0.0001	0.01	DIN EN ISO 17294
Silver – Ag	mg/l	<0.001	<0.001	0.1	DIN EN ISO 17294
Zinc – Zn	mg/l	0.005	<0.001	1	DIN EN ISO 17294
Tin – Sn	mg/l	<0.001	<0.001	1	DIN EN ISO 17294
NH_4-N	mg/l	2.39	1.31	–	DIN 38406- E 5
Nitrogen total – TN	mg/l	6.4	6.36	–	DIN EN ISO 11905-1
Fluoride – F	mg/l	0.56	0.81	20	DIN 38 405 - D 4
Phosphorus total – TP	mg/l	0.38	0.19	–	DIN EN ISO 6878
Formaldehyde	mg/l	0.247	0.086	1	VDI 3484 Blatt 1
Chloride – Cl	mg/l	2110	2470	–	DIN 38 405 – D 1
COD	mg/l	214	245	2800	DIN 38 409 - H 44

External-monitoring 2016					**Production site Leoben**
Indirect discharge – PCB manufacturing					
Parameter	**Unit**	**24-hours flow proportional composite sample**		**ELV**	**Standard**
		15.06.2016	**22.11.2016**		
Hydrogen Index	mg/l	<0.08	<0.08	15	ÖNORM EN ISO 9377-2
TOC	mg/l	79	77.9	–	DIN EN 1484

Source: CLUG, 2016–2018

Table 48: External-monitoring of wastewater from PCB manufacturing – indirect discharge, spot sample – production site Leoben

External-monitoring 2016						**Production site Leoben**
Indirect discharge – PCB manufacturing						
Parameter	**Unit**	**Spot samples – 15.06.2016**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		284		400	
T	°C	29	28.3	28.6	35	DIN 38 404 - C 4
pH	–	8.43	8.27	8.19	6.5-9.5	DIN 38 404 - C 5
Conductivity	mS/cm	23.2	22.1	21.4	–	ÖNORM EN 27 888
Settleable substances	ml/l	< 0.3	<0.3	<0.3	3	DIN 38 409 - H 9
Sulphide – S	mg/l	<0.025	<0.025	<0.025	1	DIN 38 405 - D 26
Parameter	**Unit**	**Spot samples – 22.11.2016**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		284		400	
T	°C	25.6	25.4	28.3	35	DIN 38 404 - C 4
pH	–	8.65	8.49	8.58	6.5–9.5	DIN 38 404 - C 5
Conductivity	mS/cm	18.2	17.8	24.8	–	ÖNORM EN 27 888

External-monitoring 2016						**Production site Leoben**
Indirect discharge – PCB manufacturing						
Parameter	**Unit**	**Spot samples – 15.06.2016**			**ELV**	**Standard**
		A	**B**	**C**		
Settleable substances	ml/l	< 0.3	<0.3	<0.3	3	DIN 38 409 - H 9
Sulphide – S	mg/l	<0.025	<0.025	<0.025	1	DIN 38 405 - D 26

Source: CLUG, 2016–2018

Table 49: External-monitoring of wastewater from PCB manufacturing – direct discharge, 24-hours flow proportional composite sample – production site Leoben

External-monitoring 2017					**Production site Leoben**
Direct discharge – PCB manufacturing					
Parameter	**Unit**	**24-hours flow proportional composite sample**		**ELV**	**Standard**
		20.06.2017	**28.11.2017**		
Arsenic – As	mg/l	<0.001	<0.001	0.1	DIN EN ISO 17294
Lead – Pb	mg/l	<0.001	<0.001	0.5	DIN EN ISO 17294
Cadmium – Cd	mg/l	<0.0005	<0.0005	0.1	DIN EN ISO 17294
Chromium total – Cr	mg/l	<0.001	0.0015	0.5	DIN EN ISO 17294
Cobalt – Co	mg/l	<0.001	<0.001	1	DIN EN ISO 17294
Iron – Fe	mg/l	0.01	0.01	2	DIN EN ISO 17294
Copper – Cu	mg/l	0.2	0.293	0.5	DIN EN ISO 17294
Nickel – Ni	mg/l	0.0013	0.016	0.5	DIN EN ISO 17294
Silver – Ag	mg/l	<0.001	<0.001	0.1	DIN EN ISO 17294
Zinc – Zn	mg/l	0.0012	<0.001	1	DIN EN ISO 17294
Tin – Sn	mg/l	<0.001	<0.001	1	DIN EN ISO 17294
NH_4-N	mg/l	0.52	2.03	20	DIN 38 406 - E 5
NH_3-N	mg/l	0.02	0.37	0.5	calculated

External-monitoring 2017					**Production site Leoben**
Direct discharge – PCB manufacturing					
Parameter	**Unit**	**24-hours flow proportional composite sample**		**ELV**	**Standard**
		20.06.2017	**28.11.2017**		
Fluoride – F	mg/l	0.81	0.567	20	DIN 38 405 - D 4
Nitrite – NO_2-N	mg/l	0.024	<0.01	1.5	DIN EN 26777
Phosphorus total – P	mg/l	0.018	0.63	2	DIN EN 13346
Formaldehyde	mg/l	0.046	0.219	0.5	VDI 3484 Blatt 1
COD	mg/l	39	119	300	DIN 38 409 - H 44
AOX	mg/l	0.091	0.075	1	DIN EN ISO 9562
Hydrogen Index	mg/l	<0.08	0.39	5	ÖNORM EN ISO 9377-2

Source: CLUG, 2016–2018

Table 50: External-monitoring of wastewater from PCB manufacturing – direct discharge, spot sample – production site Leoben

External-monitoring 2017						**Production site Leoben**
Direct discharge – PCB manufacturing						
Parameter	**Unit**	**Spot samples – 20.06.2017**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		488		1001	
T	°C	27.7	27.9	28.3	30	DIN 38 404 - C 4
TSS	mg/l	5.8	3	9.8	30	DIN 38409 - H 2
pH	–	8.01	8.13	7.28	6.5-9.0	DIN 38 404 - C 5
Conductivity	mS/cm	3.98	4.49	3.41	–	ÖNORM EN 27 888
Sulphide – S	mg/l	<0.025	<0.025	<0.025	0.1	DIN 38 405 - D 26
Parameter	**Unit**	**Spot samples – 28.11.2017**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		669		1001	

External-monitoring 2017						Production site Leoben
Direct discharge – PCB manufacturing						
Parameter	Unit	Spot samples – 20.06.2017			ELV	Standard
		A	B	C		
T	°C	26.2	26.4	26.2	30	DIN 38 404 - C 4
TSS	mg/l	6.3	5.3	24.7	30	DIN 38409 - H 2
pH	–	8.92	8.85	8.75	6.5-9.0	DIN 38 404 - C 5
Conductivity	mS/cm	6.53	6.09	7.31	–	ÖNORM EN 27 888
Sulphide – S	mg/l	<0.025	<0.025	<0.025	0.1	DIN 38 405 - D 26

Source: CLUG, 2016–2018

Table 51: External-monitoring of wastewater from water purification – direct discharge, 24-hours flow proportional composite sample – production site Leoben

External-monitoring 2017					Production site Leoben
Direct discharge – Water purification					
Parameter	Unit	24-hours flow proportional composite sample		ELV	Standard
		20.06.2017	28.11.2017		
Iron – Fe	mg/l	0.03	0.02	2	DIN EN ISO 17294
Copper – Cu	mg/l	0.0028	0.199	0.5	DIN EN ISO 17294
Phosphorus total – P	mg/l	0.055	<0.1	2	DIN EN 13346
COD	mg/l	6	<5	90	DIN 38 409 - H 44
TOC	mg/l	1.44	0.86	30	ÖNORM EN 1484
AOX	mg/l	0.24	0.22	1	DIN EN 1485

Source: CLUG, 2016–2018

Table 52: External-monitoring of wastewater from water purification – direct discharge, spot sample – production site Leoben

External-monitoring 2017						**Production site Leoben**
Direct discharge – Water purification						
Parameter	**Unit**	**Spot samples – 20.06.2017**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		263		404	
T	°C	18.8	18.9	19.4	30	DIN 38 404 - C4
pH	–	7.77	7.89	8.18	6.5-8.5	DIN 38 404 - C 5
Conductivity	mS/cm	15.5	9.39	1.2	–-	ÖNORM EN 27 888
TSS	mg/l	11.5	13.9	7	30	DIN 38409 - H 2
Chloride – Cl	mg/l	<0.05	<0.05	<0.05	0.2	DIN EN ISO 7393-1
Parameter	**Unit**	**Spot samples – 28.11.2017**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		194		404	
T	°C	18	18.2	18.3	30	DIN 38 404 - C4
pH	–	8.35	8.33	8.08	6.5–8.5	DIN 38 404 - C 5
Conductivity	mS/cm	1.26	1.2	2.89	–	ÖNORM EN 27 888
TSS	mg/l	<1.0	<1.0	2.8	30	DIN 38409 - H 2
Chloride – Cl	mg/l	<0.05	<0.05	<0.05	0.2	DIN EN ISO 7393-1

Source: CLUG, 2016–2018

Table 53: External-monitoring of wastewater from PCB manufacturing – indirect discharge, 24-hours flow proportional composite sample – production site Leoben

External-monitoring 2017					**Production site Leoben**
Indirect discharge – PCB manufacturing					
Parameter	**Unit**	**24-hours flow proportional composite sample**		**ELV**	**Standard**
		20.06.2017	**28.11.2017**		
Arsenic – As	mg/l	<0.001	<0.001	0.1	DIN EN ISO 17294
Lead – Pb	mg/l	<0.001	<0.001	0.5	DIN EN ISO 17294
Cadmium – Cd	mg/l	<0.0005	<0.0005	0.1	DIN EN ISO 17294
Chromium total – Cr	mg/l	<0.001	<0.001	0.5	DIN EN ISO 17294
Cobalt – Co	mg/l	0.001	<0.001	1	DIN EN ISO 17294
Copper – Cu	mg/l	0.06	0.063	0.5	DIN EN ISO 17294
Nickel – Ni	mg/l	0.002	0.0024	0.5	DIN EN ISO 17294
Mercury – Hg	mg/l	<0.0001	<0.0001	0.01	DIN EN ISO 17294
Silver – Ag	mg/l	<0.001	<0.001	0.1	DIN EN ISO 17294
Zinc – Zn	mg/l	<0.001	0.0048	1	DIN EN ISO 17294
Tin – Sn	mg/l	<0.001	<0.001	1	DIN EN ISO 17294
NH_4-N	mg/l	1.5	4.8	–	DIN 38406- E 5
Nitrogen total – TN	mg/l	3.54	11.8	–	DIN EN ISO 11905-1
Fluoride – F	mg/l	0.56	0.97	20	DIN 38 405 - D 4
Phosphorus total – TP	mg/l	0.33	2.52	–	DIN EN ISO 6878
Formaldehyde	mg/l	0.049	0.203	1	VDI 3484 Blatt 1
Chloride – Cl	mg/l	817	1850	–	DIN 38 405 – D 1
COD	mg/l	104	168	2800	DIN 38 409 - H 44
Hydrogen Index	mg/l	<0.08	<0.08	15	ÖNORM EN ISO 9377-2
TOC	mg/l	32	56.4	–	DIN EN 1484

Source: CLUG, 2016–2018

Table 54: External-monitoring of wastewater from PCB manufacturing – indirect discharge, spot sample – production site Leoben

External-monitoring 2017						**Production site Leoben**
Indirect discharge – PCB manufacturing						
Parameter	**Unit**	**Spot samples – 20.06.2017**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		218		400	
T	°C	28.3	28.2	27.3	35	DIN 38 404 - C 4
pH	–	8.43	8.42	8.25	6.5-9.5	DIN 38 404 - C 5
Conductivity	mS/cm	16.9	17.7	14.3	–	ÖNORM EN 27 888
Settleable substances	ml/l	< 0.3	<0.3	<0.3	3	DIN 38 409 – H 9
Sulphide – S	mg/l	<0.025	<0.025	<0.025	1	DIN 38 405 - D 26
Parameter	**Unit**	**Spot samples – 28.11.2017**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		206		400	
T	°C	26	25.6	24.9	35	DIN 38 404 - C 4
pH	–	6.89	7.1	7.15	6.5-9.5	DIN 38 404 - C 5
Conductivity	mS/cm	19.2	19.2	18.3	–	ÖNORM EN 27 888
Settleable substances	ml/l	< 0.3	<0.3	<0.3	3	DIN 38 409 – H 9
Sulphide – S	mg/l	<0.025	<0.025	<0.025	1	DIN 38 405 - D 26

Source: CLUG, 2016–2018

Table 55: External-monitoring of wastewater from PCB manufacturing – direct discharge, 24-hours flow proportional composite sample – production site Leoben

External-monitoring 2018					**Production site Leoben**
Direct discharge – PCB manufacturing					
Parameter	**Unit**	**24-hours flow proportional composite sample**		**ELV**	**Standard**
		25.06.2018	**21.11.2018**		
Arsenic – As	mg/l	<0.001	<0.001	0.1	DIN EN ISO 17294
Lead – Pb	mg/l	<0.001	<0.001	0.5	DIN EN ISO 17294
Cadmium – Cd	mg/l	<0.0005	<0.0005	0.1	DIN EN ISO 17294
Chromium total – Cr	mg/l	<0.001	<0.001	0.5	DIN EN ISO 17294
Cobalt – Co	mg/l	<0.001	<0.001	1	DIN EN ISO 17294
Iron – Fe	mg/l	<0.01	0.01	2	DIN EN ISO 17294
Copper – Cu	mg/l	0.18	0.15	0.5	DIN EN ISO 17294
Nickel – Ni	mg/l	0.0018	0.0024	0.5	DIN EN ISO 17294
Silver – Ag	mg/l	<0.001	<0.001	0.1	DIN EN ISO 17294
Zinc – Zn	mg/l	0.0074	<0.001	1	DIN EN ISO 17294
Tin – Sn	mg/l	<0.001	<0.001	1	DIN EN ISO 17294
NH_4-N	mg/l	2.13	2.16	20	DIN 38 406 - E 5
NH_3-N	mg/l	0.07	0.06	0.5	calculated
Fluoride – F	mg/l	1.78	1.82	20	DIN 38 405 - D 4
Nitrite – NO_2-N	mg/l	0.01	<0.01	1.5	DIN EN 26777
Phosphorus total – TP	mg/l	0.5	0.39	2	DIN EN 13346
Formaldehyde	mg/l	0.025	0.061	0.5	VDI 3484 Blatt 1
COD	mg/l	77	116	300	DIN 38 409 - H 44
AOX	mg/l	0.22	0.13	1	DIN EN ISO 9562
Hydrogen Index	mg/l	<0.08	<0.08	5	ÖNORM EN ISO 9377-2

Source: CLUG, 2016–2018

Table 56: External-monitoring of wastewater from PCB manufacturing – direct discharge, spot sample – production site Leoben

External-monitoring 2018						**Production site Leoben**
Direct discharge – PCB manufacturing						
Parameter	**Unit**	**Spot samples – 25.06.2018**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		595		1001	
T	°C	28	28	27.8	30	DIN 38 404 - C 4
TSS	mg/l	14.4	8.4	16.4	30	DIN 38409 - H 2
pH	–	7.95	8.01	7.74	6.5-9.0	DIN 38 404 - C 5
Conductivity	mS/cm	4.83	4.71	6.14	-	ÖNORM EN 27 888
Sulphide – S	mg/l	0.037	<0.025	<0.025	0.1	DIN 38 405 - D 26
Parameter	**Unit**	**Spot samples – 21.11.2018**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		580		1001	
T	°C	26.5	27	26.6	30	DIN 38 404 - C 4
TSS	mg/l	11.2	8.25	13.2	30	DIN 38409 - H 2
pH	–	7.72	7.65	7.52	6.5-9.0	DIN 38 404 - C 5
Conductivity	mS/cm	5.19	5.39	5.3	–	ÖNORM EN 27 888
Sulphide – S	mg/l	<0.025	<0.025	<0.025	0.1	DIN 38 405 - D 26

Source: CLUG, 2016–2018

Table 57: External-monitoring of wastewater from water purification – direct discharge, 24-hours flow proportional composite sample – production site Leoben

External-monitoring 2018					**Production site Leoben**
Direct discharge – Water purification					
Parameter	**Unit**	**24-hours flow proportional composite sample**		**ELV**	**Standard**
		25.06.2018	**21.11.2018**		
Iron – Fe	mg/l	0.012	0.016	2	DIN EN ISO 17294
Copper – Cu	mg/l	0.069	0.02	0.5	DIN EN ISO 17294
Phosphorus total – P	mg/l	0.02	<0.1	2	DIN EN 13346
COD	mg/l	6	6	90	DIN 38 409 - H 44
TOC	mg/l	1.66	1.04	30	ÖNORM EN 1484
AOX	mg/l	0.23	0.12	1	DIN EN 1485

Source: CLUG, 2016–2018

Table 58: External-monitoring of wastewater from water purification – direct discharge, spot sample – production site Leoben

External-monitoring 2018						**Production site Leoben**
Direct discharge – Water purification						
Parameter	**Unit**	**Spot samples – 25.06.2018**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		296		404	
T	°C	19	19.2	19.7	30	DIN 38 404 - C4
pH	–	8.14	8.09	8.25	6.5–8.5	DIN 38 404 - C 5
Conductivity	mS/cm	1.28	1.3	5.33	–	ÖNORM EN 27888
TSS	mg/l	4	2.8	9.2	30	DIN 38409 - H 2
Chloride – Cl	mg/l	<0.05	<0.05	<0.05	0.2	DIN EN ISO 7393-1
Parameter	**Unit**	**Spot samples – 21.11.2018**			**ELV**	**Standard**

External-monitoring 2018						Production site Leoben
Direct discharge – Water purification						
Parameter	Unit	Spot samples – 25.06.2018			ELV	Standard
		A	B	C		
Q	m³/d		359		404	
T	°C	18.6	18.5	18.5	30	DIN 38 404 - C4
pH	–	7.85	7.92	8.19	6.5–8.5	DIN 38 404 - C 5
Conductivity	mS/cm	12.4	7.79	1.45	–	ÖNORM EN 27888
TSS	mg/l	< 1.0	< 1.0	< 1.0	30	DIN 38409 - H 2
Chloride – Cl	mg/l	<0.05	<0.05	<0.05	0.2	DIN EN ISO 7393-1

Source: CLUG, 2016–2018

Table 59: External-monitoring of wastewater from PCB manufacturing – indirect discharge, 24-hours flow proportional composite sample – production site Leoben

External-monitoring 2018					Production site Leoben
Indirect discharge – PCB manufacturing					
Parameter	Unit	24-hours flow proportional composite sample		ELV	Standard
		25.06.2018	21.11.2018		
Arsenic – As	mg/l	<0.001	<0.001	0.1	DIN EN ISO 17294
Lead – Pb	mg/l	<0.001	<0.001	0.5	DIN EN ISO 17294
Cadmium – Cd	mg/l	<0.0005	<0.0005	0.1	DIN EN ISO 17294
Chromium total – Cr	mg/l	<0.001	<0.001	0.5	DIN EN ISO 17294
Cobalt – Co	mg/l	<0.001	<0.001	1	DIN EN ISO 17294
Copper – Cu	mg/l	0.11	0.15	0.5	DIN EN ISO 17294
Nickel – Ni	mg/l	0.0081	0.0085	0.5	DIN EN ISO 17294
Mercury – Hg	mg/l	<0.0001	<0.0001	0.01	DIN EN ISO 17294
Silver – Ag	mg/l	<0.001	<0.001	0.1	DIN EN ISO 17294
Zinc – Zn	mg/l	<0.001	<0.001	1	DIN EN ISO 17294

External-monitoring 2018					**Production site Leoben**
Indirect discharge – PCB manufacturing					
Parameter	**Unit**	**24-hours flow proportional composite sample**		**ELV**	**Standard**
		25.06.2018	**21.11.2018**		
Tin – Sn	mg/l	0.0033	<0.001	1	DIN EN ISO 17294
NH_4-N	mg/l	4.37	3.76	–	DIN 38406- E 5
Nitrogen total – TN	mg/l	14.3	11.5	–	DIN EN ISO 11905-1
Fluoride – F	mg/l	0.71	0.83	20	DIN 38 405 - D 4
Nitrite – NO_2-N	mg/l	–	<0.01	1.5	DIN EN 26777
Phosphorus total – TP	mg/l	1.54	0.13	–	DIN EN ISO 6878
Formaldehyde	mg/l	0.06	0.85	1	VDI 3484 Blatt 1
Chloride – Cl	mg/l	2240	4590	-	DIN 38 405 - D 1
COD	mg/l	310	538	2800	DIN 38 409 - H 44
AOX	mg/l	–	0.64	1	DIN EN 1485
Low volatile lipophilic substances	mg/l	–	23	100	DIN 38 409 - H 17
Hydrocarbon Index	mg/l	<0.08	<0.08	15	ÖNORM EN ISO 9377-2
TOC	mg/l	102	195	–	DIN EN 1484

Source: CLUG, 2016–2018

Table 60: External-monitoring of wastewater from water purification – direct discharge, spot sample – production site Leoben

External-monitoring 2018						**Production site Leoben**
Direct discharge – Water purification						
Parameter	**Unit**	**Spot samples – 25.06.2018**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		184		400	
T	°C	27	27.3	27.4	35	DIN 38 404 - C 4

External-monitoring 2018						**Production site Leoben**
Direct discharge – Water purification						
Parameter	**Unit**	**Spot samples – 25.06.2018**			**ELV**	**Standard**
		A	**B**	**C**		
pH	–	7.45	7.87	8.11	6.5–9.5	DIN 38 404 - C 5
Conductivity	mS/cm	13.8	12.4	9.83	–	ÖNORM EN 27 888
Settleable substances	ml/l	< 0.3	<0.3	<0.3	3	DIN 38 409 – H 9
Sulphide – S	mg/l	<0.025	0.1	0.15	1	DIN 38 405 - D 26
Parameter	**Unit**	**Spot samples – 21.11.2018**			**ELV**	**Standard**
		A	**B**	**C**		
Q	m³/d		191		400	
T	°C	25.2	25.4	23.8	35	DIN 38 404 - C 4
pH	–	8.04	8.2	8.51	6.5–9.5	DIN 38 404 - C 5
Conductivity	mS/cm	19	18.9	14.9	–	ÖNORM EN 27 888
Settleable substances	ml/l	< 0.3	<0.3	<0.3	3	DIN 38 409 - H 9
Sulphide – S	mg/l	<0.025	<0.025	<0.025	1	DIN 38 405 - D 26

Source: CLUG, 2016–2018

3.2.2 Production site Fehring

Specific consumption Fehring

Due to the increase in complexity of multilayer PCB manufacturing specific energy and water consumption expressed per m² of produced multilayer PCB can be misleading. Thus efforts are undertaken by AT&S to switch specific consumption value recording to kWh or m³ per kg manufactured multilayer PCB. Relating energy and water use to the weight of the produced multilayer PCB represents the complexity (amount of layers) of a multilayer PCB better. Lowering energy and water consumption, whilst maintaining the required product quality, is in the interest of the operator, wherefore consumption parameters are monitored at several process steps. In general approximately 90 kWh/m² and 0.4 m³/m² (water) are consumed (per m² manufactured multilayer PCB).

Generated waste from PCB manufacturing is listed in Table 61. The quantities relate to the years 2012, 2013 and 2018.

Table 61: Waste generation PCB manufacturing – production site Fehring

Waste generation 2012, 2013, 2018				**Production site Fehring**
Waste	**Quantity [t] 2012**	**Quantity [t] 2013**	**Quantity {t] 2018**	**Treatment**
Gold from electrolysis	0.0107	0.0094	0.01467	Precious metal recycling
Ferrous metal scrap (contaminated)	20.57	17.09	35.40	Authorised waste disposal company
PCB (without copper)	117.59	88.24	60.71	Metal and plastic recycling
PCB (containing gold)	41.30	38.94	42.33	Metal and plastic recycling
Aluminium	28.83	48.85	32.82	Metal and plastic recycling
Copper	79.37	112.66	49.31	Metal and plastic recycling
Non-ferrous metal scrap	0.34	0.69	0.49	Authorised waste disposal company
Sludge from WWTP (containing copper)	326.27	369.72	340.30	Authorised waste disposal company
Sludge from WWTP (containing copper)	1.89	1.13	1.43	Authorised waste disposal company
Celluloid waste	6.07	5.22	4.78	Authorised waste disposal company
Plastic sludge (solvent free)	32.44	39.96	65.46	Authorised waste disposal company
Used filter medium (contaminated)	25.00	8.46	20.49	Authorised waste disposal company
Metal sludge (containing tin)	1.88	5.93	1.23	Authorised waste disposal company
Copper chloride	680.72	402.08	5030.41	Chemical industry
Acids and acid mixtures (inorganic)	70.02	78.20	63.68	Authorised waste disposal company

Waste generation 2012, 2013, 2018				Production site Fehring
Waste	**Quantity [t] 2012**	**Quantity [t] 2013**	**Quantity {t] 2018**	**Treatment**
Alkaline solutions and mixtures	18.66	4.09	4.41	Authorised waste disposal company
Photo-developer	5.69	5.00	8.18	Authorised waste disposal company
Waste oil	0.47	2.39	0.20	Authorised waste disposal company
Oil-water mixtures	0.41	0.52	1.75	Authorised waste disposal company
Polyetheralcohols	6.99	5.90	3.67	Authorised waste disposal company
Solvents	1.09	1.07	2.22	Authorised waste disposal company
Varnish and paint sludge	17.29	16.43	0.00	Authorised waste disposal company
Tin bars	0.00	0.00	2.67	Metal and plastic recycling
Used filter medium (contaminated)	5.30	7.22	5.73	Authorised waste disposal company
Paint residues	9.84	5.86	7.64	Authorised waste disposal company

Source: AT&S, own recordings

Emissions to air

Waste gas is collected at several process steps. Process steps are usually fully encapsulated. Depending on the origin of the waste gas, it is either treated in sodium hydroxide scrubbers or in hydrogen chloride scrubbers. Exhaust air containing solvents (predominantly from surface treatment operations) is treated in bio-filters. After treatment, the exhaust air is emitted from stacks. Waste gas is collected separately, resulting in a vast number of emission points of release and air washers.

Emissions to air have to be monitored every five years by an accredited testing institute. The monitoring frequency and the ELVs for emissions to air are prescribed by permit.

Emissions to air have to be measured via 3 half-hour measurements. Measurements have to relate to 0°C, 1013 mbar and dry exhaust air.

Table 62, Table 63 and Table 64 present the most recent monitoring result for each emission to air point of release from PCB manufacturing. The monitorings were conducted between 2015 and 2019. The presented values are average values over the 3 half-hour measurements.

Table 62: Monitoring results of emissions to air PCB manufacturing; average of 3 half-hour measurements; 0 °C, 1013 mbar, dry exhaust air – production site Fehring

Emissions to air						**Production site Fehring (1/3)**
Parameter	**Measurement**	**Extraction capacity [Nm³/h]**	**Emission [Nm³/h]**	**ELV [Nm³/h]**	**Process step**	**Abatement technique**
Acid aerosol	2015	38	1,20	10	Chemical pre-treatment	–
H_2SO_4			0,60	10		
H_3PO_4			0,60	10		
Acid aerosol			1,20	10		
Alkaline aerosol (Na_2CO_3)	2016	1253	0,21	10	Photo-developing (alkaline)	–
Org.C	2017	212	5,00	75	UV dryer	–
Acid aerosol	2017	280	4,90	10	Pre-treatment surface treatment	–
Org.C	2019	968	0,60	75	Screen printing - screen preparation	–
Formic acid	2019	646	<0,01	10	Entek	Demister
H_2SO_4			0,93	10	Acidic cleaning	Demister
Org.C			1,20	75	Rinsing	Demister
Org.C	2017	4 537	3,00	75	Dryer	–
Org.C	2019	7 557	9,40	75	Biofilter left chamber	Biofilter

Emissions to air						**Production site Fehring (1/3)**
Parameter	**Measurement**	**Extraction capacity [Nm³/h]**	**Emission [Nm³/h]**	**ELV [Nm³/h]**	**Process step**	**Abatement technique**
Org.C	2019	7 557	7,40	75	Biofilter right chamber	Biofilter
Cl	2018	2 117	0,16	30	Etching	–
Org.C	2019	5 060	1,0	75	Sewer	–
Org. C	2019	451	5,9	75	Laminating	–
Dust	2019	5054	4,4	10	Central exhaust air extraction (east)	Cyclone
Dust	2019	655	2,2	10	Central exhaust air extraction (east)	Cyclone
Cl	2017	1113	0,15	30	Acidic etching	Wet scrubber

Source: Prüfbericht Kaufmann, 2015–2019

Table 63: Monitoring results of emissions to air PCB manufacturing; average of 3 half-hour measurements; 0 °C, 1013 mbar, dry exhaust air – production site Fehring

Emissions to air						**Production site Fehring (2/3)**
Parameter	**Measurement**	**Extraction capacity [Nm³/h]**	**Emission [Nm³/h]**	**ELV [Nm³/h]**	**Process step**	**Abatement technique**
Acid aerosol	2018	6614	0,38	10	Exhaust air surface treatment (STS)	–
Ni			0,001	0,5		
Cu			0,005	5		
Alkaline aerosol			0,11	10		
Cyanide	2018	704	<0,04	3	Gold plating	Wet scrubber

Emissions to air						**Production site Fehring (2/3)**
Parameter	**Measurement**	**Extraction capacity [Nm^3/h]**	**Emission [Nm^3/h]**	**ELV [Nm^3/h]**	**Process step**	**Abatement technique**
NH3	2019	1 312	4,10	5	Alkaline etching	Wet scrubber
Org.C	2019	735	6,7	75	Dryer (casting)	–
Acid aerosol	2017	202	0,88	10	Solder mask	–
KOH	2018	484	0,83	10	Stripping (alkaline etching)	–
NH_3			3,64	5		
Org.C	2017	3 498	1,70	75	Drying	–
Org.C	2017	3 031	1,60	75	Photo developing	–
Acid aerosols	2015	5 913	0,50	10	Copper plating	Wet scrubber
Cl			24,20	30		
Cu			0,02	5		
Pb			0,01	0,5		
SO_4	2018	290	0,067	10	Pre-treatment (copper plating)	–
Alkaline aerosol	2018	119	7,91	10	Na2CO3 mixer	–
NH_3	2017	467	0,36	5	Alkaline etching	Wet scrubber
Alkaline aerosol	2016	146	0,02	10	Photo developing - alkaline	–
HCl	2017	2 265	0,28	30	Tin stripping	Wet scrubber
HNO_3			0,45	10		
H_2SO_4			0,17	10		
SO_4	2015	536	0,90	10	Copper recovery (electrolytic)	Demister
Cu			0,01	5		
Acid aerosol	2015	293	0,4	10	Tin plating	–

Emissions to air						**Production site Fehring (2/3)**
Parameter	**Measurement**	**Extraction capacity [Nm^3/h]**	**Emission [Nm^3/h]**	**ELV [Nm^3/h]**	**Process step**	**Abatement technique**
Sn			0,01	5		
Cu			0,04	5		

Source: Prüfbericht Kaufmann, 2015–2019

Table 64: Monitoring results of emissions to air PCB manufacturing; average of 3 half-hour measurements; 0 °C, 1013 mbar, dry exhaust air

Emissions to air						**Production site Fehring (3/3)**
Parameter	**Measurement**	**Extraction capacity [Nm^3/h]**	**Emission [Nm^3/h]**	**ELV [Nm^3/h]**	**Process step**	**Abatement technique**
Cl	2015	3 340	22	30	Copper plating (vertical)	Wet scrubber
Cu			0,02	5		
H_2SO_4			0,4	10		
Cu	2017	4 569	0,01	5	Copper plating (horizontal) 1	Demister
H_2SO_4			0,20	10	Copper plating (horizontal) 2	
H_3PO_4			0,19	10	Copper plating (horizontal) 3	
Cl			0,94	30		
Org.C	2019	3 392	3,70	75		
Alkaline aerosol	2015	619	0,5	10	Photo-resist	–
Org.C	2018	619	2,4	75	Photoplotter	–
Alkaline aerosol	2018	776	0,71	10	Sewer (ground)	–
Acid aerosol			0,22	10		
Org.C	2019	1 269	4,9	75	Laminating	–

Emissions to air						**Production site Fehring (3/3)**
Parameter	**Measurement**	**Extraction capacity [Nm³/h]**	**Emission [Nm³/h]**	**ELV [Nm³/h]**	**Process step**	**Abatement technique**
Dust	2015	2 488	0,5	10	Central exhaust air extraction	Cyclone
Dust	2019	1 933	0,7	10	Central exhaust air extraction (nord)	–
Org.C	2019	326	1,1	75	Plasma etching (desmearing)	Wet scrubber
F	2019		<0,1	3		
Dust	2019	5 177	0,8	10	Drilling	Cyclone
Cu			<0,01	1		
Acid-alkaline aerosol (HCl, H_2SO4, NaOH)	2019	399	0,49	10	Bondfilm	Wet scrubber
Org. C	2019	837	1	75	Multilayerpress	–

Source: Prüfbericht Kaufmann, 2015 – 2019

Emissions to water

Treated process wastewater is discharged directly and indirectly. Monitoring has to be done using 24-hour flow-proportional composite samples (fpcs) unless prescribed different by permit. Minimum monitoring frequencies for self-monitoring (performed by operator) and external-assessment are prescribed by permit. Emission limit values (ELV) are prescribed by permit.

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

Treated wastewater is discharged directly and indirectly. Wastewater with a high organic load is treated on-site but discharged indirectly. Wastewater with high organic load stems from photo developing, photo resist stripping and process tanks due to their surfactant content. Remaining process wastewater is discharged directly after on-site treatment.

Process wastewater is collected in several separate streams and treated (or pre-treated) separately before being discharged or joining another wastewater treatment stream. In general wastewater treatment consists of:

- Neutralisation
- Precipitation
- Flocculation
- Settling
- Sludge dewatering
- Sand filtration
- Ion exchange
- Activated carbon filters
- Plating out (for gold)

Process wastewater for direct discharge is collected in the following streams:

- Complexing agent free concentrates
- Potassium permanganate containing concentrates
- Oxidizing agent containing concentrates
- Eluates from water purification
- Wastewater from exhaust air scrubbers
- Wastewater from pressurized air condensates
- Excess rinsing water

Process wastewater for indirect discharge is collected in the following streams:

- Complexing agent containing concentrates
- Wastewater from photo development (photo-resist)
- Wastewater from tin plating

A detailed description of the on-site WWTP is presented in chapter 3.1.

Emissions to water (direct and indirect) are described in the following tables. Table 65, Table 66 and Table 67 present the minimum monitoring frequencies and ELVs prescribed by permit compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. Table 68 – Table 80 present the monitoring recordings (self-monitoring and external-monitoring) of treated process wastewaters and wastewater from water purification from 2017, 2018 and 2019.

Table 65: Emission limit values for direct discharge – PCB manufacturing in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Direct discharge			**PCB manufacturing – Production site Fehring**			
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)**	**Ordinance**	**Min. frequency self-monitoring**	**Min. frequency external-monitoring**
Q	m^3/d	398	–	–	Cont.	6 months
Temperature	°C	30	–	30		6 months
pH-Wert		6.5–10.0	–	6.5–9.0	Cont.	6 months
Bacteria toxicity		8	–	8	–	6 months
Lead (Pb)	mg/l	0.5	0.05–0.5	0.5	–	6 months
Manganese (Mn)	mg/l	1	–	–	–	6 months
Copper (Cu)	mg/l	0.5	0.2–2.0	0.5	daily	6 months
Iron (Fe)	mg/l	2	0.1–5.0	2	daily	6 months
Nickel (Ni)	mg/l	0.5	–	0.5	–	6 months
Tin (Sn)	mg/l	1	0.2–2.0	1	–	6 months
Zinc (Zn)	mg/l	1	0.2–2.0	1	–	6 months
Sum of NH_3 and NH_4	mg/l	5	–	–	daily	6 months
Nitrite (NO_2)	mg/l	1.5	–	1.5	–	6 months
Sulphide (S)	mg/l	0.1	–	0.1	–	6 months

Direct discharge						PCB manufacturing – Production site Fehring
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)**	**Ordinance**	**Min. frequency self-monitoring**	**Min. frequency external-monitoring**
Total phosphorus (TP)	mg/l	2	0.5–10.0	2	–	6 months
COD	mg/l	300	100–500	300	daily	6 months
COD (monthly average)	mg/l	200	–	–	daily	6 months
COD load	kg/d	90	–	–	daily	6 months
Surfactants (anionic and non-ionic)	mg/l	1	–	–		6 months
Low volatile lipophilic substances	mg/l	20	–	20		6 months
Hydrocarbon index	mg/l	5	1–5	5		6 months

Source: Permit BHSO-64191/2015-12; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 66: Emission limit values for indirect discharge – PCB manufacturing in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Indirect discharge						PCB manufacturing – Production site Fehring
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)**	**Ordinance**	**Min. frequency self-monitoring**	**Min. frequency external-monitoring**
Q	m^3/d	200	–	–	Cont.	6 months
T	°C	35	–	35	–	6 months
pH		6.5–10.0	–	6.5–10.0	Cont.	6 months

Indirect discharge				PCB manufacturing – Production site Fehring		
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)**	**Ordinance**	**Min. frequency self-monitoring**	**Min. frequency external-monitoring**
Lead (Pb)	mg/l	0.5	0.05–0.5	0.5	–	6 months
Copper (Cu)	mg/l	0.5	0.2–2.0	0.5	daily	6 months
Nickel (Ni)	mg/l	0.5	0.2–2.0	0.5	–	6 months
Tin (Sn)	mg/l	1	0.2–2.0	1	–	6 months
Manganese (Mn)	mg/l	1	–	–	–	6 months
Ammonia (NH_3)	mg/l	20	–	20	–	6 months
Fluoride (F)	mg/l	20	–	20	–	6 months
Nitrite (NO_2)	mg/l	10	–	10	–	6 months
Sulphate (SO_4)	mg/l	2000	–	–	–	6 months
Sulphide (S)	mg/l	1	–	1	–	6 months
Sulphite (SO_3)	mg/l	10	–	–	–	6 months
Low volatile lipophilic substances	mg/l	100	–	100	–	6 months
Hydrocarbon index	mg/l	15	–	15	–	6 months
Phenol index	mg/l	10	–	–	–	6 months
Thiourea	mg/l	1	–	–	–	6 months
COD load	kg/d	320	–	–	–	6 months
Total N	kg/d	50	–	–	–	6 months
Total N – monthly average	kg/d	35	–	–	–	6 months
Sulphate (SO_4)	kg/d	300	–	–	–	6 months

Source: Permit BHSO-64191/2015-12; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 67: Emission limit values for direct discharge – water purification in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from water purification. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Direct discharge				**Water purification – Production site Fehring**		
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)**	**Ordinance**	**Min. frequency self-monitoring**	**Min. frequency external-monitoring**
Q	m³/d	122	–	–	Cont.	6 months
T	°C	30	–	30	–	6 months
TSS	mg/l	30	5–30	30	–	6 months
pH		6.5–8.5	–	6.5–8.5	Cont.	6 months
COD	mg/l	90	100–500	90	–	6 months
COD load	kg/d	10	–	–	–	6 months

Source: Permit BHSO-64191/2015-12; STM BREF 2006; AEV Wasseraufbereitung BGBl. II Nr. 128/2019

Table 68: Self-monitoring of treated wastewater – production site Fehring

Self-monitoring 2017 – PCB manufacturing						**Production site Fehring**	
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV**	**Number of samples**
Direct discharge							
pH		6.5	8.5	7.8	7.1	6.5–10.0	298
COD	mg/l	0.2	191.1	101.3	52.9	300.0	298
Cu	mg/l	0.01	0.40	0.23	0.09	0.5	197
Fe	mg/l	0.01	0.49	0.24	0.11	2	181
Mn	mg/l	0.02	1.00	0.49	0.15	1	259
NH_4-N	mg/l	0.0	5.0	2.7	1.1	5	295
Q	m³d	1.0	303.0	285.0	183.7	398	298

Self-monitoring 2017 – PCB manufacturing							**Production site Fehring**
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV**	**Number of samples**
COD load	kg/d	0.0	45.2	21.4	9.6	90	298
NH_4-N load	kg/d	0.0	1.1	0.5	0.2	–	298
Indirect discharge							
pH		6.9	9.5	8.4	7.9	6.5–10.0	298
COD	mg/l	32.0	3170.0	1874.3	1300.7	–	298
Cu	mg/l	0.00	0.35	0.14	0.07	0.5	193
NH_4-N	mg/l	2.0	352.0	285.5	185.6	–	298
Q	m^3/d	0.0	183.0	165.3	125.3	200.0	298
COD load	kg/d	0.2	319.7	233.7	160.9	320.0	298
NH_4-N load	kg/d	0.1	45.3	39.5	23.2	–	298

Source: Self-monitoring AT&S, 2017

Table 69: Self-monitoring of treated wastewater – production site Fehring

Self-monitoring 2018 – PCB manufacturing							**Production site Fehring**
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV**	**Number of samples**
Direct discharge							
pH		6.5	8.8	7.6	7.1	6.5–10.0	297
COD	mg/l	3.1	290.0	106.1	53.2	300.0	295
Cu	mg/l	0.01	0.48	0.20	0.09	0.5	265
Fe	mg/l	0.02	0.65	0.38	0.12	2	143
Mn	mg/l	0.02	0.99	0.78	0.21	1	268
NH_4-N	mg/l	0.0	4.9	2.5	0.8	5	289
Q	m^3d	0.0	320.0	252.4	172.7	398	297
COD load	kg/d	0.0	69.3	20.6	9.2	90	297
NH_4-N load	kg/d	0.0	1.2	0.3	0.1	–	297

Self-monitoring 2018 – PCB manufacturing							**Production site Fehring**
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV**	**Number of samples**
CN	mg/L	0.00	0.10	0.03	0.01	–	246
Indirect discharge							
pH		6.8	9.5	8.1	7.6	6.5–10.0	297
COD	mg/l	10.0	2769.0	1705.6	1108.1	–	297
Cu	mg/l	0.01	0.43	0.25	0.08	0.5	129
NH_4-N	mg/l	0.0	675.0	245.0	140.5	–	297
Q	m^3/d	8.0	198.0	168.0	126.1	200.0	297
COD load	kg/d	1.6	299.0	209.8	137.0	320.0	297
NH_4-N load	kg/d	0.0	48.6	36.2	17.6	–	297

Source: Self-monitoring AT&S, 2018

Table 70: Self-monitoring of treated wastewater – production site Fehring

Self-monitoring 2019 – PCB manufacturing							**Production site Fehring**
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV**	**Number of samples**
Direct discharge							
pH		6.5	8.9	7.7	7.2	6.5–10.0	277
COD	mg/l	17.2	235.7	138.0	67.4	300.0	277
Cu	mg/l	0.02	0.50	0.32	0.12	0.5	260
Fe	mg/l	0.01	1.31	0.17	0.10	2	78
Mn	mg/l	0.02	1.00	0.76	0.22	1	259
NH_4-N	mg/l	0.0	5.0	2.9	1.1	5	272
Q	m^3d	1.0	338.0	231.8	165.5	398	277
COD load	kg/d	0.03	45.0	24.2	11.2	90	277
NH_4-N load	kg/d	0.0	1.0	0.5	0.2	–	277
CN	mg/L	0.00	0.08	0.02	0.01	–	230

Self-monitoring 2019 – PCB manufacturing							**Production site Fehring**
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV**	**Number of samples**
Indirect discharge							
pH		6.5	8.9	8.0	7.5	6.5–10.0	277
COD	mg/l	13.0	3302.0	1763.8	1115.1	–	277
Cu	mg/l	0.02	0.49	0.22	0.08	0.5	136
NH_4-N	mg/l	25.0	628.0	312.2	180.4	–	277
Q	m^3/d	15.0	199.0	171.0	130.7	200.0	277
COD load	kg/d	2.3	315.0	213.2	141.8	320.0	277
NH_4-N load	kg/d	1.4	49.6	35.2	22.9	–	277

Source: Self-monitoring AT&S, 2019

Table 71: External-monitoring of wastewater from PCB manufacturing – direct discharge, production site Fehring

External-monitoring 2017					**Production site Fehring**
PCB manufacturing					
Parameter	**Unit**	**Direct discharge**		**ELV**	**Standard**
		09.05.2017	**19.09.2017**		
Q	m^3/d	199	311	398	IDM
T	°C	24.4	24.8	30	AAW 4.07.
pH		7.63	7.3	6.5–9.0	DIN 38404 - C 5
NO_2-N	mg/l	0.003	0.04	1.5	AAW 11.11.
Sum of NH_3/NH_4	mg/l	0.14	1.16	5	DIN 38405 - E5 - 1
COD	mg/l	37.8	57.9	300	AAW 7.01.
S	mg/l	<0.1	<0.1	1	ÖNORM M6615
Total P	mg/l	1.18	0.23	2	AAW 11.04.
Pb	mg/l	<0.010	<0.010	0.5	EN ISO 11885(MH)
Fe	mg/l	0.024	0.025	2	ÖNORM ISO 8288

External-monitoring 2017 PCB manufacturing					Production site Fehring
Parameter	**Unit**	**Direct discharge**		**ELV**	**Standard**
		09.05.2017	**19.09.2017**		
Cu	mg/l	0.033	0.095	0.5	EN ISO 11885(MH)
Mn	mg/l	0.117	0.039	1	ÖNORM ISO 8288
Ni	mg/l	<0.01	0.013	0.5	EN ISO 11885(MH)
Zn	mg/l	<0.01	<0.010	1	EN ISO 11885(MH)
Sn	mg/l	<0.010	<0.010	1	EN ISO 11885(MH)
Surfactants (anionic and non-ionic)	mg/l	<0.2	<0.2	1	DIN 38405-D23
Low volatile lipophilic substances	mg/l	<5	<5	20	DIN 38 409 - H17
Hydrocarbon index	mg/l	0.38	<0.03	5	ÖNORM M6608(MH)

Source: TB Chemie – Hutter, 2017–2019

Table 72: External-monitoring of wastewater from PCB manufacturing – indirect discharge, production site Fehring

External-monitoring 2017 PCB manufacturing					Production site Fehring
Parameter	**Unit**	**Indirect discharge**		**ELV**	**Standard**
		09.05.2017	**19.09.2017**		
Q	m^3/d	139	133	–	IDM
T	°C	25.4	25.9	35	AAW 4.07.
pH	–	7.52	7.96	6.5–10.0	DIN 38404 - C 5
NO_2-N	mg/l	0.72	2.9	10	AAW 11.11.
COD	mg/l	1248	1124	–	AAW 7.01.

External-monitoring 2017					**Production site Fehring**
PCB manufacturing					
Parameter	**Unit**	**Indirect discharge**		**ELV**	**Standard**
		09.05.2017	**19.09.2017**		
S	mg/l	<0.10	<0.10	1	ÖNORM M6615
SO_3	mg/l	4.9	3.5	10	EN ISO 10304-3(MH)
SO_4	mg/l	960	768	2000	DIN 38405-D19
F	mg/l	0.18	<0.05	20	EN ISO 10304-1(MH)
Pb	mg/l	<0.010	<0.01	0.5	EN ISO 11885(MH)
Cu	mg/l	0.049	0.065	0.5	EN ISO 11885(MH)
Ni	mg/l	0.025	0.021	0.5	EN ISO 11885(MH)
Sn	mg/l	0.036	0.033	1	EN ISO 11885(MH)
Mn	mg/l	0.09	0.2	1	ÖNORM ISO 8288
Phenol index	mg/l	0.014	0.014	10	EN ISO 14402(DEV-H37)(MH)
Low volatile lipophilic substances	mg/l	<5	<5	100	DIN 38 409 - H17
Hydrocarbon index	mg/l	<0.1	<0.1	15	ÖNORM M6608(MH)
Thiourea	mg/l	<0.3	0.43	1	HPLC-UV

Source: TB Chemie – Hutter, 2017–2019

Table 73: External-monitoring of wastewater from PCB manufacturing – direct discharge, production site Fehring

External-monitoring 2018					**Production site Fehring**
PCB manufacturing					
Parameter	**Unit**	**Direct discharge**		**ELV**	**Standard**
		04.04.2018	**25.09.2018**		
Q	m^3/d	195	220	398	IDM
T	°C	23.5	24.9	30	AAW 4.07.
pH		7.18	7.33	6.5–9.0	DIN 38404 - C 5
NO_2-N	mg/l	<0.01	0.049	1.5	AAW 11.11.
Sum of NH_3/NH_4	mg/l	0.36	0.26	5	DIN 38405 - E5 - 1
COD	mg/l	84.25	47.07	300	AAW 7.01.
S	mg/l	<0.1	<0.1	1	ÖNORM M6615
Total P	mg/l	0.06	0.07	2	AAW 11.04.
Pb	mg/l	<0.010	<0.010	0.5	EN ISO 11885(MH)
Fe	mg/l	0.065	0.07	2	ÖNORM ISO 8288
Cu	mg/l	0.069	0.17	0.5	EN ISO 11885(MH)
Mn	mg/l	0.301	0.163	1	ÖNORM ISO 8288
Ni	mg/l	0.033	0.019	0.5	EN ISO 11885(MH)
Zn	mg/l	0.012	0.012	1	EN ISO 11885(MH)
Sn	mg/l	<0.010	<0.010	1	EN ISO 11885(MH)
Surfactants (anionic and non-ionic)	mg/l	0.73	0.98	1	DIN 38405-D23
Low volatile lipophilic substances	mg/l	<5	<5	20	DIN 38 409 - H17
Hydrocarbon index	mg/l	0.2	<0.05	5	ÖNORM M6608(MH)

Source: TB Chemie – Hutter, 2017–2019

Table 74: External-monitoring of wastewater from PCB manufacturing – indirect discharge, production site Fehring

External-monitoring 2018					**Production site Fehring**
PCB manufacturing					
Parameter	**Unit**	**Indirect discharge**		**ELV**	**Standard**
		04.04.2018	**25.09.2018**		
Q	m^3/d	144	159	–	IDM
T	°C	24.5	26.3	35	AAW 4.07.
pH	–	6.52	6.74	6.5–10.0	DIN 38404 - C 5
NO_2-N	mg/l	3.89	0.45	10	AAW 11.11.
COD	mg/l	837.55	876.92	–	AAW 7.01.
S	mg/l	<0.10	<0.10	1	ÖNORM M6615
SO_3	mg/l	3.4	4.6	10	EN ISO 10304-3(MH)
SO_4	mg/l	624	816	2000	DIN 38405-D19
F	mg/l	0.16	<0.05	20	EN ISO 10304-1(MH)
Pb	mg/l	<0.010	<0.010	0.5	EN ISO 11885(MH)
Cu	mg/l	0.11	0.035	0.5	EN ISO 11885(MH)
Ni	mg/l	0.031	0.027	0.5	EN ISO 11885(MH)
Sn	mg/l	0.12	0.029	1	EN ISO 11885(MH)
Mn	mg/l	0.89	0.325	1	ÖNORM ISO 8288
Phenol index	mg/l	0.15	0.036	10	EN ISO 14402(DEV-H37)(MH)
Low volatile lipophilic substances	mg/l	<5	<5	100	DIN 38 409 - H17
Hydrocarbon index	mg/l	0.96	<0.05	15	ÖNORM M6608(MH)
Thiourea	mg/l	<0.3	<0.3	1	HPLC-UV

Source: TB Chemie – Hutter, 2017–2019

Table 75: External-monitoring of wastewater from PCB manufacturing – direct discharge, production site Fehring

External-monitoring 2019					**Production site Fehring**
PCB manufacturing					
Parameter	**Unit**	**Direct discharge**		**ELV**	**Standard**
		27.03.2019	**25.09.2019**		
Q	m^3/d	183	220	398	IDM
T	°C	23.9	26.8	30	AAW 4.07.
pH		7.33	7.33	6.5–9.0	DIN 38404 - C 5
NO_2-N	mg/l	0.56	<0.2	1.5	AAW 11.11.
Sum of NH_3/NH_4	mg/l	0.08	0.49	5	DIN 38405 - E5 - 1
COD	mg/l	38.05	52.4	300	AAW 7.01.
S	mg/l	<0.1	<0.1	1	ÖNORM M6615
Total P	mg/l	0.07	0.95	2	AAW 11.04.
Pb	mg/l	<0.010	<0.001	0.5	EN ISO 11885(MH)
Fe	mg/l	0.019	0.066	2	ÖNORM ISO 8288
Cu	mg/l	0.39	0.033	0.5	EN ISO 11885(MH)
Mn	mg/l	0.304	0.047	1	ÖNORM ISO 8288
Ni	mg/l	0.013	0.017	0.5	EN ISO 11885(MH)
Zn	mg/l	<0.010	0.014	1	EN ISO 11885(MH)
Sn	mg/l	<0.010	<0.01	1	EN ISO 11885(MH)
Surfactants (anionic and non-ionic)	mg/l	1	0.98	1	DIN 38405-D23
Low volatile lipophilic substances	mg/l	<5	<5	20	DIN 38 409 - H17
Hydrocarbon index	mg/l	<0.05	<0.05	5	ÖNORM M6608(MH)

Source: TB Chemie – Hutter, 2017–2019

Table 76: External-monitoring of wastewater from PCB manufacturing – indirect discharge, production site Fehring

External-monitoring 2019					Production site Fehring
PCB manufacturing					
Parameter	**Unit**	**Indirect discharge**		**ELV**	**Standard**
		27.03.2019	**25.09.2019**		
Q	m^3/d	144	159	–	IDM
T	°C	26.9	26.9	35	AAW 4.07.
pH	–	6.74	6.74	6.5–10	DIN 38404 - C 5
NO_2-N	mg/l	0.12	0.12	10	AAW 11.11.
COD	mg/l	746.2	746.2	–	AAW 7.01.
S	mg/l	<0.10	<0.10	1	ÖNORM M6615
SO_3	mg/l	5.1	5.1	10	EN ISO 10304-3(MH)
SO4	mg/l	832	832	2000	DIN 38405-D19
F	mg/l	0.6	0.6	20	EN ISO 10304-1(MH)
Pb	mg/l	<0.010	<0.010	0.5	EN ISO 11885(MH)
Cu	mg/l	0.02	0.02	0.5	EN ISO 11885(MH)
Ni	mg/l	0.025	0.025	0.5	EN ISO 11885(MH)
Sn	mg/l	0.012	0.012	1	EN ISO 11885(MH)
Mn	mg/l	0.264	0.264	1	ÖNORM ISO 8288
Phenol index	mg/l	0.012	0.012	10	EN ISO 14402(DEV-H37)(MH)
Low volatile lipophilic substances	mg/l	<5	<5	100	DIN 38 409 - H17
Hydrocarbon index	mg/l	0.12	0.12	15	ÖNORM M6608(MH)
Thiourea	mg/l	<0.3	<0.3	1	HPLC-UV

Source: TB Chemie – Hutter, 2017–2019

Table 77: External-monitoring of wastewater from water purification – direct discharge, production site Fehring

External-monitoring 2017–2019					**Production site Fehring**
Water purification					
Parameter	**Unit**	**Direct discharge**		**ELV**	**Standard**
		09.05.2017	**19.09.2017**		
Q	m³/d	69	48	122	IDM
T	°C	25	25	30	AAW 4.07.
pH	–	8.07	8.4	6.5–8.5	DIN 38404 - C 5
TSS	mg/l	<0.1	<0.1	30	AAW 09.04.
COD	mg/l	10	15.21	90	AAW 7.01.
		04.04.2018	**25.09.2018**		
Q	m³/d	60	82	122	IDM
T	°C	25	25	30	AAW 4.07.
pH	–	8.76	7.96	6.5–8.5	DIN 38404 - C 5
TSS	mg/l	<0.1	<0.1	30	AAW 09.04.
COD	mg/l	76.41	<0.1	90	AAW 7.01.
		27.03.2019	**25.09.2019**		
Q	m³/d	79	50	122	IDM
T	°C	25	25	30	AAW 4.07.
pH	–	7.96	7.96	6.5–8.5	DIN 38404 - C 5
TSS	mg/l	<0.1	<0.1	30	AAW 09.04.
COD	mg/l	<0.1	<0.1	90	AAW 7.01.

Source: TB Chemie – Hutter, 2017–2019

Table 78: External-monitoring of wastewater from PCB manufacturing – direct discharge, loads, production site Fehring

External-monitoring 2017–2019								**Production site Fehring**
PCB manufacturing								
				Direct discharge Loads				
Parameter	**Unit**	**09.05.17**	**19.09.17**	**04.04.18**	**25.09.18**	**27.03.19**	**25.09.19**	**ELV**
Q	m^3/d	199	311	195	220	183	183	398
Qmax	m^3/h	20	20	20	20	20	20	20
Qmax	l/s	10	10	10	10	10	10	10
COD	kg/d	7.5	18	16.4	10.4	7	9.6	90
COD monthly average	mg/l	37.3	61	49.5	41	50	64	200

Source: TB Chemie – Hutter, 2017–2019

Table 79: External-monitoring of wastewater from PCB manufacturing – indirect discharge, loads, production site Fehring

External-monitoring 2017–2019								**Production site Fehring**
PCB manufacturing								
				Indirect discharge Loads				
Parameter	**Unit**	**09.05.17**	**19.09.17**	**04.04.18**	**25.09.18**	**27.03.19**	**25.09.19**	**ELV**
Q	m^3/d	139	133	144	159	145	167	200
Qmax	m^3/h	15	15	15	15	15	15	15
COD	kg/d	173.5	149.5	120.6	139.4	108.2	129.6	320
Sum of NH_3/NH_4	kg/d	34.1	13.9	16.3	23.2	25.5	27.2	50
NH_4/NH_3 monthly average	kg/d	22.7	18	15.9	16	22.1	13.5	35

External-monitoring 2017–2019								**Production site Fehring**
PCB manufacturing								
				Indirect discharge Loads				
Para-meter	**Unit**	**09.05.17**	**19.09.17**	**04.04.18**	**25.09.18**	**27.03.19**	**25.09.19**	**ELV**
SO_4	kg/d	133.4	102.1	89.9	129.7	120.6	128.3	300

Source: TB Chemie – Hutter, 2017–2019

Table 80: External-monitoring of wastewater from water purification – direct discharge, loads, production site Fehring

External-monitoring 2017–2019								**Production site Fehring**
Water purification								
				Direct discharge Loads				
Para-meter	**Unit**	**09.05.17**	**19.09.17**	**04.04.18**	**25.09.18**	**27.03.19**	**25.09.19**	**ELV**
Q	m^3/d	69	48	60	82	79	50	122
Qmax	m^3/h	2.9	2	2.5	3.4	3.3	2.1	7
COD	kg/d	0.7	0.7	4.6	0.008	0.008	0.005	10

Source: TB Chemie – Hutter, 2017–2019

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4 Collini GmbH – Hohenems

Collini GmbH is a specialist sub-contractor (jobbing shop) operating several surface treatment installations worldwide. In Austria Collini operates batch galvanizing (zinc), powder coating, cathodic dip coating (CDC) and two electroplating installations located in Hohenems and Vienna. In the following the installation Hohenems is discussed.

On the premise Hohenems, different types of electroplating and coatings are carried out in either rack, drum or continuous motion lines. Processes carried out are:

- Alkaline copper electroplating (cyanide copper)
- Acid copper electroplating
- Nickel electroplating
- Cr(III) electroplating
- Cr(VI) electroplating
- Acid zinc electroplating
- Anodising of aluminium

Environmental Management System

The electroplating plant has an according to EMAS certified environmental management system implemented.

4.1 Technical description

In the following, the different types of electroplating and coating taking place on site are described below.

Continuous Motion Line (CML)

A continuous motion line (CML) is a mixture of a rack electroplating plant and a continuous coil electroplating plant. Small work pieces, usually zinc die casts, are automatically assembled on (and off) a rack and pass the individual treatment steps automatically. The CML plant is fully encapsulated.

Process steps consist of:

- Aqueous cleaning
- Electrolytically assisted degreasing
- Alkaline copper electroplating (cyanide copper)
- Acid copper electroplating
- Nickel electroplating
- Cr(III) electroplating

Aqueous cleaning

For aqueous cleaning the work piece is either placed in or sprayed with an alkaline solution for several minutes. The solution work temperature is usually between 40 °C–90 °C (STM BREF, 2006). Main components of the aqueous cleaning system are alkalis, silicates, phosphates and complexing and wetting agents (STM BREF, 2006). Aqueous cleaning systems work either by forming unstable emulsions (known as weak emulsion systems) or stable emulsions (STM BREF, 2006). The Process solution life span depends on throughput and the amount of oil or grease on the work pieces, but is usually considered to be short.

Electrolytically assisted degreasing

Electrolytically assisted degreasing removes the remains of unwanted residues from the surface, such as oil and dirt, which remain trapped in the micro-roughness of the work piece surface. By the formation of H_2 at the surface of the cathode and O_2 at the surface of the anode, electrolytically assisted degreasing takes place. Wetting agents are omitted to prevent foaming (STM BREF, 2006). The solution lifetime is mainly determined by dilution through drag-in of rinse-water and drag-out of process solution.

Alkaline copper electroplating

Cyanide copper plating is necessary for strike plating the work piece (zinc die cast) to prevent spontaneous cementation of copper and poor adhesion of subsequent metal deposit (STM BREF, 2006). Cyanide copper electrolytes are usually based on copper cyanide and sodium cyanide. Potassium cyanide and potassium hydroxide based alternatives exist for forming a thicker layer on the work piece. Potassium based electrolytes have to be discarded, however, once the content of potassium carbonate exceeds 90 g/l whilst sodium based solutions can be regenerated by precipitation of sodium carbonate (STM BREF, 2006).

Acid copper electroplating

Acid copper electrolytes are based on copper sulphate and sulphuric acid (STM BREF, 2006). They make polishing prior to decorative bright nickel plating redundant. The solution is cyanide free.

Nickel electroplating

Bright nickel plating is carried out in Watt's-type nickel solutions consisting of nickel sulphate, nickel chloride and boric acid (STM BREF, 2006). The electrolyte is operated above room temperature (50–60 °C) (STM BREF, 2006). To achieve a bright nickel layer and to reduce gas bubble retention on the nickel surface, wetting agents (< 10 ml/l) and organic brighteners (10–20 ml/l) are added (STM BREF, 2006).

Watts-type solutions can have an almost indefinite working life, as nickel metal deposited at the cathode is rather more than fully replenished by that dissolved at the anode (STM BREF, 2006). Working life can be shortened by the introduction of contamination, which can be inorganic or organic. Some inorganic contaminants (e.g. Fe) can be removed by high pH precipitation and others (e.g. Cu, Zn) by plating out. Organic contaminants can be removed by filtration over active carbon or using adsorber polymers.

Wastewaters containing nickel must be separated from cyanide containing wastewaters, as nickel forms stable complexes with cyanide. Nickel and its salts have adverse health effects (STM BREF, 2006). Aerosols and airborne particles can arise from electroplating as well as from plant and solution maintenance operations. Due to a high electricity yield of the process bath and the use of wetting agents, the discharge of aerosols and airborne particles from electroplating is relatively low. Furthermore, the CML unit of Collini Hohenems is fully encapsulated.

Cr(III) plating

Bright trivalent chromium electrolytes are based on Cr(III) compounds, such as sulphate or chloride, together with proprietary chemicals. The electrolyte contains only about 20 g/l of the trivalent chromium, compared with about 200 g/l of chromic acid in the hexavalent chromium process. (STM BREF, 2006)

The lower electrolyte concentration has a lower viscosity than the hexavalent electrolyte. This results in better draining of plated parts, and subsequently less drag-out, less loss of electrolyte, less effluent treatment required and less chromium-containing waste being produced.

The use of trivalent chromium eliminates the carcinogenic and other hazards associated with hexavalent chromium in the workplace. PFOS-based fume suppressants to reduce the formation of Cr(VI) aerosols are not needed in Cr(III) plating. However, additives are required to prevent the formation of free chlorine and AOX (STM BREF, 2006).

Rinsing

Rinsing is done after each process bath by spray rinsing over the rinsing water tank. In order to minimize drag-in of process solutions into others, air knives are applied after spray rinsing.

Waste gas

The CML unit is fully encapsulated. Exhaust air from the process baths is extracted in two streams, i.e. acidic and cyanide-alkaline. The extracted waste gas is subsequently treated in wet scrubbers.

Nickel-Copper electroplating

Nickel copper plating is done in several lines in barrel or rack systems. Process steps consist of:

- Aqueous cleaning
- Degreasing
- Pickling
- Alkaline copper electroplating
- Pickling
- Nickel electroplating
- Post-treatment (optional)

Aqueous cleaning

For aqueous cleaning the work piece is either placed in or sprayed with an alkaline solution for several minutes. The solution work temperature is usually between 40 °C–90 °C (STM BREF, 2006). Main components of the aqueous cleaning system are alkalis, silicates, phosphates and complexing and wetting agents (STM BREF, 2006). Aqueous cleaning systems work either by forming unstable emulsions (known as weak emulsion systems) or stable emulsions (STM BREF, 2006). Process solutions life span depend on throughput and the amount of oil or grease on the work pieces, but is usually considered to be short.

Degreasing & pickling

Subsequently alkaline degreasing and pickling with HCl is carried out. Pickling removes remaining oil films from the substrate surface and activates the surface layer for the electrolytic deposition.

Alkaline copper electroplating

Cyanide copper plating is necessary for strike plating the work piece (zinc die cast) to prevent spontaneous cementation of copper and poor adhesion of subsequent metal deposit (STM BREF, 2006). Cyanide copper electrolytes are usually based on copper cyanide and sodium cyanide. Potassium cyanide and potassium hydroxide based alternatives exist for forming a thicker layer on the work piece. Potassium based electrolytes have to be discarded, however, once the content of potassium carbonate exceeds 90 g/l whilst sodium based solutions can be regenerated by precipitation of sodium carbonate (STM BREF, 2006).

Nickel electroplating

Nickel plating is carried out in Watt's-type nickel solutions consisting of nickel sulphate, nickel chloride and boric acid (STM BREF, 2006). The electrolyte is operated above room temperature (50–60 °C) (STM BREF, 2006). Wetting agents and organic brighteners to achieve a bright nickel layer and to reduce gas bubble retention are present in the electrolyte.

Watts-type solutions can have an almost indefinite working life, as nickel metal deposited at the cathode is rather more than fully replenished by that dissolved at the anode (STM BREF, 2006). Working life can be shortened by the introduction of contamination, which can be inorganic or organic. Some inorganic contaminants (e.g. Fe) can be removed by high pH precipitation and others (e.g. Cu, Zn) by plating out. Organic contaminants can be removed by filtration over active carbon or using adsorber polymers.

Wastewaters containing nickel must be separated from cyanide containing wastewaters, as nickel forms stable complexes with cyanide. Nickel and its salts have adverse health effects (STM BREF, 2006). Aerosols and airborne particles can arise from electroplating as well as from plant and solution maintenance operations. Due to a high electricity yield of the process bath and the use of wetting agents, the discharge of aerosols and airborne particles from electroplating is relatively low.

Post-treatment

For enhancing corrosion resistance, a solvent-based immersion coating can be applied to the electroplated work pieces. The solvents used are aromatic compound free. After immersion, the work pieces are dried through centrifuging in the barrel. Air extraction is applied which collects solvent gases. The gases are condensed and collected in a tank for re-use or for waste disposal.

Rinsing

Rinsing is done after each process bath. The degreasing unit as well as the pickling unit are equipped with three stage counter-current cascade rinsing units. The copper plating unit as well as the nickel plating unit are equipped with individual eco-rinses. In the eco-rinse unit diluted process solution is used. The work piece is dipped into the diluted process solution before and after entering the electrolyte, so that dilution of the electrolyte through drag-in and the drag-out of process solution is reduced. During normal operation no water has to be added into the eco-rinse unit, as drag-in is equivalent to drag-out. Subsequently the work piece passes two stage counter-current cascade rinsing units. The barrels are equipped with rinse water and compressed air inlets to allow rinsing and blowing out of excess rinse water from the barrels inside. This takes places above the respective process tank.

Waste gas

Waste gas is extracted at the edges of the process baths. Waste gas streams are separated into acidic and cyanide-alkaline waste gas. Waste gas is treated with droplet-separators and wet scrubbers.

Cyanide-alkaline waste gas is treated via wet scrubbers. Acidic waste gas is treated via droplet separators. The treated waste gas is subsequently emitted via stacks.

Bath life span

Bath life span of the nickel and copper solution is extended by filtration. Two activated carbon filters are installed for each the nickel and the copper units. The filter capacity for nickel is 45 m^3/h and for copper 30 m^3/h. To prolong the lifespan of the aqueous cleaning solution an oil-separator is used.

Wastewater streams

Wastewater from nickel-copper plating is collected in separate streams, i.e.:

- Alkaline wastewater
- Alkaline cyanide containing rinsing water
- Alkaline cyanide containing concentrates
- Nickel containing wastewater

Acid zinc electroplating

Acid zinc electroplating is carried out in a rack system.

The production process of zinc electroplating consists in general of the following:

- Pre-treatment:
    - Degreasing
    - Etching
    - Electrolytically assisted degreasing
    - Descaling
- Acid zinc electroplating
- Chromium conversion coating

Pre-treatment

Pre-treatment consists of alkaline degreasing above room temperature, etching with HCl, electrolytically assisted degreasing and descaling.

Electrolytically assisted degreasing removes the remains of unwanted residues from the surface, such as oil and dirt, which remain trapped in the micro-roughness of the work piece's surface. These residues are removed by the electrolytic formation of H_2 gas at the surface of the cathode and of O_2 gas at the surface of the anode. (STM BREF, 2006)

Before entering zinc electroplating the work piece passes descaling in order to enhance metal adhesion.

Electroplating

After pre-treatment the work piece is zinc electroplated. Zinc electroplating is carried out in acid zinc electrolytes, which give bright decorative layers. For providing corrosion resistance comparable with alkaline zinc electrolytes, post-treatment is required. Metal distribution is enhanced with warm electrolytes.

Acid zinc electrolytes contain typically zinc chloride, potassium and/or sodium chloride, boric acid and wetting agents (STM BREF, 2006). The solution has a good conductivity and high cathode efficiency leading to a lower energy demand than alkaline zinc electrolytes (STM BREF, 2006).

Chromium conversion coating

After zinc electroplating the work pieces pass only trivalent chromium conversion (passivation). Chromium conversion coatings enhance corrosion protection, preventing the zinc surface to form white rust.

Rinsing

After each process step rinsing is applied. Multiple stage counterflow rinsing units, consisting of two steps, or static rinsing units followed by final flow rinse with recirculated water are used. The latter are applied after descaling, zinc electroplating and chromium conversion coating.

Waste gas

Edge exhausts are installed at the edges of the pickling baths, degreasing and the zinc electrolyte tanks. The extracted air separated into acidic and alkaline streams. Waste gas is treated with wet scrubbers (one per line).

Bath life span

The process baths are regularly monitored and controlled. This enables an accurate dosing of the needed chemicals and avoids excess use of chemicals.

Anodising of aluminium

Anodising of metals is an electrolytic surface oxidation process resulting in an oxide layer, which is firmly attached to the work piece, providing corrosion protection. In anodising, the work piece is (as the name indicates) connected as the anode. During the anodising process the negatively charged anion migrates to the anode where it is discharged with a loss of one or more electrons. The metal reacts with the oxygen of the anion and a layer of oxide forms on the surface. (STM BREF, 2006)

Aluminium is predominantly anodised, with alumina ($Al2O3$) formed at the surface. (STM BREF, 2006). Magnesium, titanium, tantalum and niobium can be also anodised. At Collini Hohenems only aluminium is anodised.

Aluminium is typically anodised in sulphuric acid electrolytes (STM BREF, 2006).

To increase corrosion resistance and to retain surface colouring, sealing is applied to the anodised work piece. Sealing can be carried out in hot or cold processes. At Collini Hohenems hot water sealing is applied.

With hot sealing, the pores in the oxide layer are closed by hydrating the aluminium oxide to boehmite (AlO(OH)): the pores are closed by the increased volume of the bohemite structure. The sealing process is carried out by dipping the anodised parts in hot or boiling (minimum 96°C) deionised water. (STM BREF, 2006)

Work pieces are moved by a crane system. The anodising unit is fully automatized. The production steps consist of:

- Degreasing
- Pickling
- Anodising
- Sealing

Degreasing & pickling
For degreasing sodium hydroxide together with wetting agents is used. For pickling nitric acid is used. Both treatment steps are carried out at temperatures around 60 °C.

Anodising
Anodising of aluminium is done in sulphuric acid electrolytes, which is the most common technique for anodising of aluminium. The temperature of the electrolyte is typically between 15 and 30 °C.

In the Anodising process are no PFAS-containing wetting agents in use (based on Information of safety data sheets).

Colouring
At Collini Hohenems no colouring is in use.

Sealing
After dip dyeing hot sealing is applied to increase corrosion resistance. The sealing process

is carried out by dipping the anodised parts in hot or boiling (minimum 95- 96 °C) deionised water (STM BREF, 2006).

Waste gas

Waste gas is extracted at the edge of each process bath and collected in separate streams, i.e. alkaline and acidic. The collected waste gas is subsequently treated with wet scrubbers (one per line).

Chromium VI containing baths

Bright chromium and black chromium plating based on chromium VI processes are partly substituted by Chromium III processes due to an internal substitution plan. But the substitution of black chromium is not in sight yet. At Collini Hohenems no hard chromium plating is carried out.

Hexavalent chromium has adverse health effects, causing skin and mucus membrane irritation and certain cancers (STM BREF, 2006). Aerosols are generated from Cr(VI) process solutions by a significant hydrogen evolution at the cathode. Thus workplace health and safety regulations require measures to meet maximum allowable concentrations. For meeting these regulations, fume suppressants are used to reduce the amount of aerosol. Fume suppressants were usually based on PFOS which is toxic and persistent (STM RBEF, 2006).

Today the use of PFOS-free fume suppressants is state of the art. Alternatives are, however, based on per- and polyfluoroalkyl substances (PFAS). PFAS are as well persistent, bio accumulative and ubiquitous. Around 4700 man-made chemicals belong to the group of PFAS. Of the relatively few well-studied PFAS, most are considered moderately to highly toxic, particularly for children's development.

At Collini Hohenems a PFOS-free fume suppressant is in use (but not PFAS-free suppressants).

Cr (VI) is also soluble at a wide range of pH-values, contributing to high aquatic toxicity (STM BREF, 2006). Therefore, it must be reduced to trivalent chromium first before precipitating in wastewater treatment plants. Solid sodium disulphite (($Na2S2O5$) forming with water into sodium hydrogen sulphite) is typically used for the reduction of Cr (VI) to Cr (III).

Process wastewaters

Electroplating wastewaters

Treated wastewater is discharged directly into the Emsbach. Process wastewater from electroplating is collected in separate streams and pre-treated individually before entering the on-site biological treatment step. Wastewater streams from electroplating are:

- Alkaline cyanide containing rinsing water
- Alkaline cyanide containing concentrates
- Cr(VI) containing wastewaters
- Alkaline wastewater for batch treatment
- Nickel containing wastewater for batch treatment

Pre-treatment consist of:

- Cr(VI) reduction
- Cyanide oxidation
- Neutralisation
- Settling
- Sludge dewatering
- Ion-exchange resin & sand filtration

Cr(VI) reduction

Cr(VI) has to be reduced to Cr(III) as Cr(VI) is difficult to precipitate.

At Collini Hohenems Cr(VI) reduction is done by using sodium hydrogen sulphite (bisulphite). The reduction is made at pH values under 2,5.

Cyanide oxidation

Cyanide oxidation is done by using sodium hypochlorite. The use of sodium hypochlorite is associated with the formation of organic chlorine compounds, measured as AOX (STM BREF, 2006).

Cyanides are well-known hazardous substances which can also form complexes with certain metals such as nickel which complicates precipitation in wastewater treatment.

Therefore, cyanide containing wastewater streams are collected separately at Collini Hohenems. In acid conditions cyanide gives off cyanide gas.

Neutralisation

Neutralisation is done separately for nickel containing wastewater. The other metals are neutralized together.

For the precipitation of metals the pH value is increased to 9.0 – 10.5 by adding NaOH.

If the targeted pH value is exceeded diluted H2SO4 is added. Dosing of NaOH and H2SO4 is automatic, depending on the monitored pH value. It is important that the pH value is stable for an appropriate time frame of ca. 20 minutes to ensure that the precipitation of metals is completed. Flocculation agents can be added.

Settling

By using a two stage settling tank, suspended solids can be removed efficiently. In stage one, the bigger flocs are separated from the wastewater which flows over into stage two, where smaller flocs are settling. Clear wastewater is removed from the top of the tank.

Sludge dewatering

Hydroxide sludge from metal precipitation is dewatered in chamber filter presses. Due to the separate neutralisation of alkaline wastewater and nickel containing wastewater, nickel mono sludge can be gained which can be reused materially. Accruing wastewater from sludge dewatering re-enters the wastewater treatment.

Sand filtration & ion-exchange resin

Before entering the biological treatment step the pre-treated wastewater is sent through sand filters and ion exchange resins (selective complexing cation-exchanger resins for heavy metals (Cu, Ni).

Anodizing wastewater

Process wastewater from anodizing is collected in a separate stream and is pre-treated in a dedicated WWTP before entering the on-site biological treatment step. Pre-treatment consists of:

- Pre-Neutralisation
- Neutralisation
- Settling
- Pre-treatment control
- Sludge dewatering

Pre-neutralisation

The pH value of the wastewater is adjusted to a range of 5 – 6 by adding used acid solutions.

Neutralisation

By adding spent acid or alkaline solutions the pH value of the wastewater gets adjusted to 7.5. It is important that the pH value is stable for an appropriate time frame of ca. 20 minutes to ensure that the precipitation of metals is completed. Flocculation agents are added to improve settling.

Settling

By using a two stage settling tank, suspended solids can be removed efficiently. In stage one, the bigger flocs are separated from the wastewater which flows over into stage two, where smaller flocs are settling. Clear wastewater is removed from the top of the tank.

Pre-treatment control

The clear wastewater passes a turbidity test and pH control. Only if the requirements are met will the clear wastewater be sent to the on-site biological WWTP.

Sludge dewatering

The settled solids from the settling tank are sent to a chamber filter press for sludge dewatering. The dewater sludge is disposed and the accruing water sent back to wastewater treatment.

Biological treatment step

After pre-treatment, the wastewater streams are sent to the on-site biological treatment step. On-site biological treatment consists of aerobic treatment, nitrogen removal (nitrification), but only partly denitrification due to malnutrition of BOD-5 in the inflow. Clear wastewater is achieved by membrane filtration.

Subsequently the treated wastewater is discharged into the Emsbach.

Excess biological sludge which contains heavy metals is going to an external dewatering process and waste disposal by combustion.

4.2 Current consumption and emission levels

Specific consumption values from 2018 are presented in Table 81. Specific consumption values relate to the tonne of produced product.

Table 81: Specific consumption values

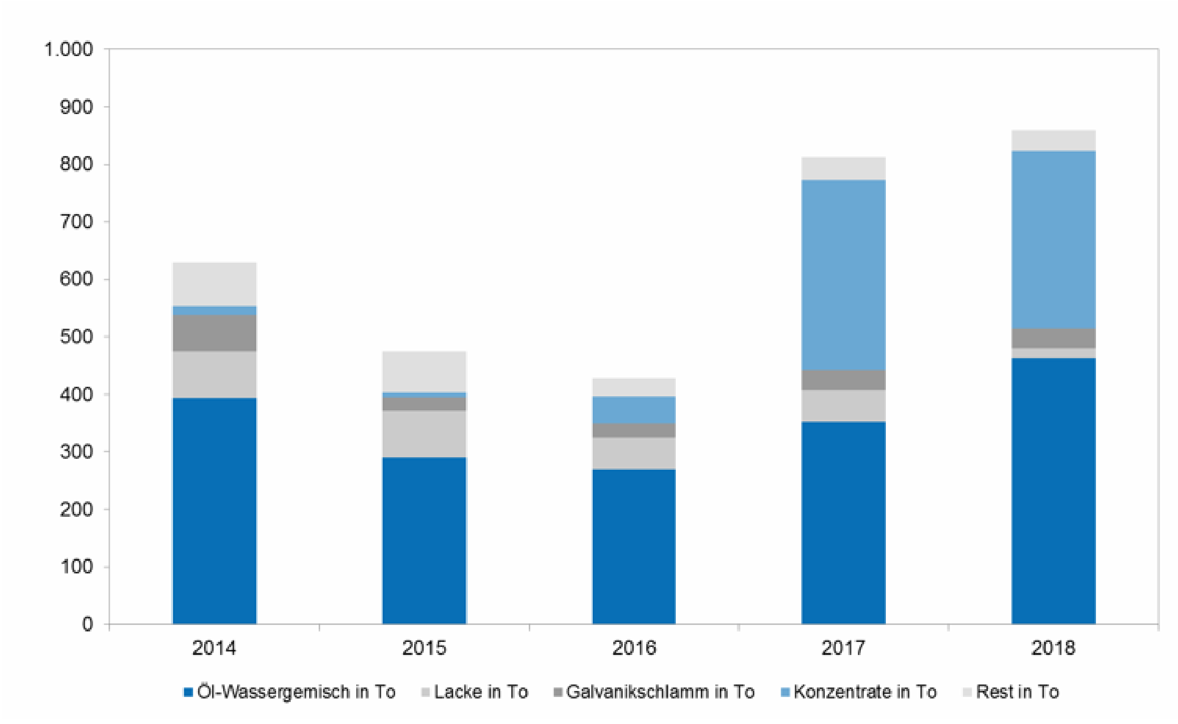
	Unit	specific consumption (per t produced product)
Energy	kWh/t	1000
electricity	kWh/t	600
heat	kWh/t	400
Water	m^3/t	5
Waste	kg/t	102
Chemicals	kg/t	128

	Unit	specific consumption (per t produced product)
Anodes, metals	kg/t	22

Source: EMAS environmental report Collini GmbH, 2019

Waste generation from 2018 is listed in Table 82. At Collini Hohenems efforts are undertaken to minimize the fraction of not reusable waste by e.g. separate pre-treatment of individual wastewater streams to regain metal hydroxides in economically reusable form. Figure 1 presents total amounts of hazardous wastes generated from 2014–2018.

Figure 1: Total amount of hazardous waste in tonnes 2014 – 2018; Öl-Wassergemisch = Oil-water mixtures, Lacke = Varnish, Galvanikschlamm = Galvano sludge, Konzentrate = Concentrates, Rest = Other



Source: EMAS environmental report Collini GmbH, 2019

Table 82: Waste generation 2018

	Waste generation 2018 in t
Waste total	6397
Waste – reusable	5241
Metals	268
Wood	127
Packaging	122
Heavy metals hydroxide	746
Aluminium hydroxide	1370
Nickel hydroxide	333
Sludge from biological wastewater treatment	296
Acids	13
Alkaline solutions	1962
Aluminium hydroxide sludge	6
Other waste	54
Waste – not reusable	1156
Industrial waste	54
Oil-water mixtures	465
Galvano sludge	35
Varnish	18
Spent concentrates	308
Other waste	36
Waste – not reusable	1156
Industrial waste	54
Oil-water mixtures	465
Galvano sludge	35
Varnish	18
Spent concentrates	308
Other waste	36

Source: EMAS environmental report Collini GmbH, 2019

Continuous Motion Line (CML)

Emissions to air

The CML unit is fully encapsulated. Exhaust air from the process baths is extracted in two streams, i.e. acidic and cyanide-alkaline. The extracted waste gas is subsequently treated in individual wet scrubbers before being emitted via stacks.

Table 83 and Table 84 present the monitoring results from 2019. The waste gas volume flow was 4,400 Nm³/h for alkaline waste gas and 8,300 Nm³/h for acidic waste gas.

Table 83: Monitoring results of emissions to air from CML, 0 °C, 1013 mbar, dry exhaust air

	Cyanide-alkaline waste gas stream		
Parameter	**Half-hour measurements [mg/Nm³, no correction of O_2 content]**		
Cu	0.011	0.015	0.023
CN	1.05	1.14	1.16
HCN	1.09	1.18	1.2
Dust	< 0.50	< 0.50	< 0.50
Zn	< 0.010	< 0.010	< 0.010

Source: Kalb Analytik, 2019

Table 84: Monitoring results of emissions to air from CML, 0 °C, 1013 mbar, dry exhaust air

	Acidic waste gas stream		
Parameter	**Half-hour measurements [mg/Nm³, no correction of O_2 content]**		
Cr	< 0.010	< 0.010	< 0.010
Cu	< 0.010	< 0.010	< 0.010
Ni	< 0.010	< 0.010	< 0.010
Dust	< 0.50	< 0.50	< 0.50

Source: Kalb Analytik, 2019

Nickel-Copper plating

Nickel copper plating is done in several lines in barrel or rack systems.

Waste gas is extracted at the edges of the process baths. Waste gas streams are separated into acidic and cyanide-alkaline waste gas. Cyanide-alkaline waste gas is treated with wet scrubbers. Acidic waste gas is treated with droplet separators. The treated waste gas is subsequently emitted via stacks.

Line 1

Monitoring requirements and ELVs for Cu, CN, HCN and Ni are prescribed by permit (11-1301-98/2016-28, ll -3101-2005/0061). Monitoring has to be done by an authorized institute all 3 years. Table 85, Table 86, Table 87 & Table 88 present the results of the air emission monitoring from Line 1 from 2018.

Measurements expressed as concentrations were below the prescribed ELVs. The ELVs regarding load limit values for CN and HCN were not met.

Table 85: Monitoring results of emissions to air from nickel-copper electroplating, 0 °C, 1013 mbar, dry exhaust air

Parameter	**Cyanide-alkaline waste gas stream – Concentrations** **Half-hour measurements [mg/Nm³, no correction of O_2 content]**						**ELV permit [mg/Nm³]**
Cu	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	1
CN	0.36	0.55	0.59	0.57	0.57	0.76	1
HCN	0.37	0.57	0.61	0.59	0.6	0.79	1

Source: Kalb Analytik, 2018

Table 86: Monitoring results of emissions to air from nickel-copper electroplating, 0 °C, 1013 mbar, dry exhaust air

Parameter	**Cyanide-alkaline – Loads** **[g/h]**						**ELV permit [g/h]**
Cu	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	< 0.30	5
CN	10	16	17	17	17	22	5
HCN	11	17	18	17	17	23	5

Source: Kalb Analytik, 2018

Table 87: Monitoring results of emissions to air from nickel-copper electroplating, 0 °C, 1013 mbar, dry exhaust air

Parameter	**Acidic waste gas stream – Concentrations** **Concentrations**						**ELV permit [mg/Nm³]**
Ni	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	0.5

Source: Kalb Analytik, 2018

Table 88: Monitoring results of emissions to air from nickel-copper electroplating, 0 °C, 1013 mbar, dry exhaust air

Parameter	**Acidic waste gas stream – Loads** **Concentrations**						**ELV permit [g/h]**
Ni	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	< 0.35	2.5

Source: Kalb Analytik, 2018

Line 2

Table 89 and Table 90 present the monitoring results from 2019. The waste gas volume flow was 17,700 Nm³/h for alkaline waste gas and 19,900 Nm³/h for acidic waste gas of Line 2.

Table 89: Monitoring results of emissions to air from nickel-copper electroplating, 0 °C, 1013 mbar, dry exhaust air

Parameter	**Cyanide-alkaline waste gas stream** **Half-hour measurements [mg/Nm³, no correction of O_2 content]**					
Cu	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
CN	0.11	0.17	0.1	0.08	0.13	0.16
HCN	0.12	0.17	0.1	0.08	0.13	0.17
Dust	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Zn	< 0.010	0.014	< 0.010	0.012	0.01	0.014

Source: Kalb Analytik, 2019

Table 90: Monitoring results of emissions to air from nickel-copper electroplating, 0 °C, 1013 mbar, dry exhaust air

Parameter	**Acidic waste gas stream** **Half-hour measurements [mg/Nm³, no correction of O_2 content]**					
Ni	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010
B	< 0.010	< 0.010	0.01	0.017	0.012	< 0.010
Dust	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50
Hydrocarbons	16	15	13	15	14	16
Dust	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50	< 0.50

Source: Kalb Analytik, 2019

Line 3

Table 91 and Table 92 present the monitoring results from 2019. The waste gas volume flow was 27,400 Nm³/h for alkaline waste gas and 14,400 Nm³/h for acidic waste gas of Line 3.

Table 91: Monitoring results of emissions to air from nickel-copper electroplating, 0 °C, 1013 mbar, dry exhaust air

Parameter	**Cyanide-alkaline waste gas stream**		
	Half-hour measurements [mg/Nm^3, no correction of O_2 content]		
Cu	< 0.010	< 0.010	< 0.010
CN	0.22	0.26	0.24
HCN	0.23	0.27	0.25
Dust	< 0.50	< 0.50	< 0.50

Source: Kalb Analytik, 2019

Table 92: Monitoring results of emissions to air from nickel-copper electroplating, 0 °C, 1013 mbar, dry exhaust air

Parameter	**Acidic waste gas stream**		
	Half-hour measurements [mg/Nm^3, no correction of O_2 content]		
Ni	< 0.010	< 0.010	< 0.010
B	< 0.010	< 0.010	< 0.010
Dust	< 0.50	< 0.50	< 0.50

Source: Kalb Analytik, 2019

Line 4

Monitoring requirements and ELVs for Cu, CN, HCN and Ni are prescribed by permit (II-1301-2011/0017). Monitoring has to be conducted by an authorized institute all 3 years. Table 93–Table 96 present the results of the air emission monitoring from Line 4 from 2019.

Table 93: Monitoring results of emissions to air from nickel-copper electroplating, 0 °C, 1013 mbar, dry exhaust air

Parameter	Cyanide-alkaline waste gas stream – Concentrations			
	Half-hour measurements [mg/Nm³, no correction of O_2 content]			ELV permit
Cu	< 0.010	< 0.010	< 0.010	1
CN	0.071	0.042	0.027	1
HCN	0.074	0.043	0.028	1
Dust	< 0.50	< 0.50	< 0.50	–

Source: Kalb Analytik, 2019

Table 94: Monitoring results of emissions to air from nickel-copper electroplating, 0 °C, 1013 mbar, dry exhaust air

Parameter	Acidic waste gas stream – Concentrations			
	Half-hour measurements [mg/Nm³, no correction of O_2 content]			ELV permit
Ni	< 0.010	< 0.010	< 0.010	1
B	0.021	0.023	0.022	–
Dust	< 0.50	< 0.50	< 0.50	–

Source: Kalb Analytik, 2019

Table 95: Monitoring results of emissions to air from nickel-copper electroplating, 0 °C, 1013 mbar, dry exhaust air

Parameter	**Cyanide-alkaline waste gas stream – Loads**			
	Half-hour measurements [g/h, no correction of O_2 content]			**ELV permit**
Cu	0.154	0.154	0.154	5
CN	1.0934	0.6468	0.4158	5
HCN	1.1396	0.6622	0.4312	5

Source: Kalb Analytik, 2019

Table 96: Monitoring results of emissions to air from nickel-copper electroplating, 0 °C, 1013 mbar, dry exhaust air

Parameter	**Acidic waste gas stream – Loads**			
	Half-hour measurements [g/h, no correction of O_2 content]			**ELV permit**
Ni	0.159	0.159	0.159	2.5

Source: Kalb Analytik, 2019

Emissions to Water

Treated process wastewater is discharged directly. Monitoring has to be conducted using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit. Minimum monitoring frequencies for self-monitoring (performed by operator) and external-monitoring are prescribed by permit. Emission limit values (ELV) are prescribed by permit.

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

The on-site WWTP consists of:

- Cr(VI) reduction
- Cyanide oxidation
- Neutralisation

- Settling
- Sludge dewatering
- Ion-exchange resin & sand filtration
- Biological treatment (aerobic treatment, nitrogen removal)

A detailed description of the on-site WWTP is presented in chapter 3.1.

Emissions to water are described in the following tables. In Table 97 the minimum monitoring frequencies and ELVs prescribed by permit are presented and compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. In Table 98, Table 99 & Table 100 the self-monitoring recordings of treated process wastewater are presented. Table 101–Table 107 present the results from external-monitoring of treated process wastewater for the years 2017, 2018 & 2019. Table 108 presents the monitoring standards from external-monitoring.

Table 97: Emission limit values for the process wastewater in comparison to BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Parameter	Unit	ELV	BAT-AEL (BREF 2006)	Ordinance (direct discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Temperature	°C	30	–	30	cont.	–
pH		6.5–8.5	–	6.5–9.0	cont.	6x per year
TSS	mg/l	30	5–30	30	–	6x per year
BOD_5	mg/l	20	–	–	–	6x per year
COD	mg/l	150	100–500	200	260	6x per year
Ammonium – NH_4-N	mg/l	10	–	50	260	6x per year

Parameter	Unit	ELV	BAT-AEL (BREF 2006)	Ordinance (direct discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Phosphorus total – TP	mg/l	1[121]	–	2	260	6x per year
Chlorine free	mg/l	< 0.05	–	0.2	260	6x per year
Aluminium – Al	mg/l	3	1–10	3	260	6x per year
Copper – Cu	mg/l	0.5	0.2–2.0	0.5	260	6x per year
Zinc – Zn	mg/l	1	0.2–2.0	2	260	6x per year
Chromium total – Cr total	mg/l	0.5	0.1–2.0	0.5	260	6x per year
Hexavalent Chromium – Cr(VI)	mg/l	0.1	0.1–0.2	0.1	260	6x per year
Nickel – Ni	mg/l	0.5	0.2–2.0	0.5	260	6x per year
Tin – Sn	mg/l	1	0.2–2.0	1	260	6x per year
Cyanide free – CN free	mg/l	0.1	0.01–0.2	0.1	260	6x per year
Cyanide total – CN total	mg/l	2	–	2	52	6x per year
Fluoride – F	mg/l	20	10–20	20	52	6x per year
Nitrite – NO_2-N	mg/l	1.5	–	1.5	260	6x per year
Low volatile lipophilic substances	mg/l	20	–	20	–	6x per year
Hydrocarbon index – HC index	mg/l	3	1–5	5	–	6x per year
Adsorbable organic halides – AOX	mg/l	1.0	–	1.0	–	6x per year

Source: Permit II-3101-2005/0061; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

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[121] Exceedance up to 2 mg/l allowed; annual average has to be < 1mg/l TP

Table 98: Self-monitoring of treated process wastewater 2017

		Self-monitoring 2017					
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
pH	–	6.60[122]	8.50	8.30	7.61	6.5–8.5	370
F	mg/l	0.09	19.00	7.00	4.55	20	256
COD	mg/l	30.00	150.00[123]	105.15	66.68	150	358
NH_4-N	mg/l	0.00	10[124]	4.75	8.86	10	364
NO_2-N	mg/l	0.00	0.84[125]	0.31	0.10	1.5	260
NO_3-N	mg/l	0.00	340.00	116.80	76.00	–	351
TN	mg/l	54.60	206.00	145.00	114.44	–	349
OrgN	mg/l	0.44	97.56	62.82	28.39	–	247
PO_4-P	mg/l	0.00	4.23	1.91	0.75	–	253
TP	mg/l	0.07	2.00[126]	1.75	0.92	1[127]	357
CN free	mg/l	0.00	0.09[128]	0.06	0.03	0.1	259
CN total	mg/l	0.00	1.10	0.23	0.07	2	253
Cl free	mg/l	0.00	0.04[129]	0.02	0.01	< 0.05	264
Cr(VI)	mg/l	0.00	0.10[130]	0.08	0.03	0.1	262
Al	mg/l	0.00	0.78	0.19	0.04	3	262
Cr total	mg/l	0.00	0.49[131]	0.31	0.14	0.5	356
Cu	mg/l	0.01	0.50[132]	0.45	0.29	0.5	360

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[122] 3 exceedances (max. 6.2 mg/l)

[123] 5 exceedances, during start-up after company vacation (max. 288 mg/l)

[124] 52 exceedances (max. 90.6 mg/l)

[125] 3 exceedances, during start-up after company vacation (max. 5 mg/l)

[126] 40 exceedances (max. 5.55 mg/l)

[127] Exceedance up to 2 mg/l allowed; annual average has to be < 1mg/l TP

[128] 11 exceedances (max. 0.49 mg/l)

[129] 5 exceedances (max. 0.2 mg/l)

[130] 7 exceedances (max. 0.4 mg/l)

[131] 4 measurements above ELV but no exceedance due to „4 out of 5“ rule (0.57 mg/l – 0.71 mg/l)

[132] 18 exceedances (max. 1.56 mg/l)

Parameter	Unit	Self-monitoring 2017 Daily min	Daily max	95 Percentile	Annual average	ELV permit	Number of samples
Fe	mg/l	0.00	0.84	0.09	0.03	–	357
Ni	mg/l	0.00	0.50[133]	0.44	0.28	0.5	356
Zn	mg/l	0.00	0.78	0.25	0.07	1	357
Sn	mg/l	0.00	0.23	0.02	0.01	1	48
Mg	mg/l	1.80	27.81	12.62	6.93	–	49
BOD_5	mg/l	1.00	3.00	2.70	1.71	–	7
DOC (Dissolved Organic Carbon)	mg/l	12.00	26.00	23.50	15.83	–	6
Low volatile lipophilic substances	mg/l	1.00	12.00	11.40	8.86	20	7
HC index	mg/l	0.00	1.00	1.00	0.88	3	8
TSS	mg/l	4.00	9.00	9.00	6.25	30	8
AOX	mg/l	0.00	1.00	1.00	0.57	1.0	7

Source: Self-monitoring Collini GmbH, 2017

Table 99: Self-monitoring of treated process wastewater 2018

Parameter	Unit	Self-monitoring 2018 Daily min	Daily max	95 Percentile	Annual average	ELV permit	Number of samples
pH	–	6.50[134]	8.40[135]	8.10	7.47	6.5–8.5	371
F	mg/l	1.07	13.46	5.25	3.48	20	256
COD	mg/l	24.00	150.00[136]	133.60	79.23	150	358

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[133] 75 exceedances (max. 1.81 mg/l)

[134] 6 exceedances of min. pH value (4.5 – 6.4)

[135] 2 exceedances of max. pH value (8.8; 8.9)

[136] 23 exceedances (max. 289 mg/l)

		Self-monitoring 2018					
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
NH_4-N	mg/l	0.00	9.20[137]	5.99	1.65	10	361
NO_2-N	mg/l	0.00	0.54	0.28	0.06	1.5	262
NO_3-N	mg/l	15.00	182.10	114.70	81.51	–	351
TN	mg/l	42.20	206.00	140.00	104.97	–	349
OrgN	mg/l	0.01	115.66	57.79	22.28	–	244
PO_4-P	mg/l	0.00	2.97	2.04	0.51	–	255
TP	mg/l	0.00	1.98[138]	1.48	0.72	1[139]	355
CN free	mg/l	0.00	0.07[140]	0.03	0.01	0.1	269
CN total	mg/l	0.00	0.79	0.10	0.04	2	258
Cl free	mg/l	0.00	0.04	0.02	0.01	< 0.05	271
Cr(VI)	mg/l	0.00	0.10[141]	0.08	0.02	0.1	272
Al	mg/l	0.00	0.96	0.28	0.09	3	263
Cr total	mg/l	0.00	0.50[142]	0.38	0.19	0.5	362
Cu	mg/l	0.00	0.50[143]	0.47	0.31	0.5	362
Fe	mg/l	0.00	0.66	0.12	0.04	–	356
Ni	mg/l	0.00	0.50[144]	0.39	0.16	0.5	356
Zn	mg/l	0.00	1.00	0.17	0.06	1	357
Sn	mg/l	0.00	0.18	0.10	0.01	1	50
Mg	mg/l	0.33	16.40	12.36	7.18	–	50
BOD_5	mg/l	2.00	7.00	7.00	3.75	–	8

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[137] 7 exceedances (max. 49.07 mg/l)

[138] 31 exceedances (max. 3.54 mg/l)

[139] Exceedance up to 2 mg/l allowed; annual average has to be < 1mg/l TP

[140] 3 exceedances (max 0.43 mg/l)

[141] 1 exceedance (0.16 mg/l), 5 measurements above the ELV (0.11 mg/l – 0.15 mg/l)

[142] 22 exceedances (max. 3.0 mg/l)

[143] 41 exceedances (max. 1.26 mg/l)

[144] 7 exceedances (max. 1.82 mg/l)

			Self-monitoring 2018				
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
DOC (Dissolved Organic Carbon)	mg/l	7.00	26.00	26.00	16.25	–	8
Low volatile lipophilic substances	mg/l	10.00	12.00[145]	12.00	12.38	20	8
HC index	mg/l	1.00	1.00	1.00	1.00	3	8
TSS	mg/l	6.00	26.00	21.10	10.38	30	8
AOX	mg/l	0.12	1.00[146]	0.94	0.64	1.0	7

Source: Self-monitoring Collini GmbH, 2018

Table 100: Self-monitoring of treated process wastewater 2019

			Self-monitoring 2019				
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
pH	–	6.70	8.50[147]	8.40	7.80	6.5–8.5	394
F	mg/l	1.19	16.00	5.50	3.35	20	261
COD	mg/l	0.00	149.00[148]	130.00	66.66	150	362
NH_4-N	mg/l	0.00	9.92[149]	5.44	3.86	10	375
NO_2-N	mg/l	0.00	1.37[150]	0.74	0.51	1.5	274
NO_3-N	mg/l	0.00	330.00	123.58	92.11	–	359
TN	mg/l	51.20	300.00	162.00	127.11	–	346
OrgN	mg/l	0.36	104.67	75.80	31.08	–	240

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[145] 1 measurement above ELV, no exceedance due to „4 out of 5“ rule

[146] 1 exceedance (1.5 mg/l)

[147] 1 exceedance of max. pH value (8.8)

[148] 2 measurements above ELV, no exceedance due to „4 out of 5“ rule

[149] 24 exceedances (max. 41.96 mg/l)

[150] 7 exceedances (max. 18.83 mg/l)

Parameter	Unit	Self-monitoring 2019 Daily min	Daily max	95 Percentile	Annual average	ELV permit	Number of samples
PO_4-P	mg/l	0.03	1.99	0.53	0.22	–	242
TP	mg/l	0.00	1.46[151]	0.76	0.36	1	361
CN free	mg/l	0.00	0.06[152]	0.03	0.01	0.1	282
CN total	mg/l	0.00	1.36[153]	0.12	0.05	2	259
Cl free	mg/l	0.00	0.04[154]	0.02	0.00	< 0.05	281
Cr(VI)	mg/l	0.00	0.10[155]	0.09	0.03	0.1	278
Al	mg/l	0.00	1.60	0.31	0.10	3	266
Cr total	mg/l	0.00	0.50[156]	0.38	0.19	0.5	366
Cu	mg/l	0.00	0.49[157]	0.44	0.30	0.5	369
Fe	mg/l	0.00	0.47	0.08	0.03	–	353
Ni	mg/l	0.00	0.45[158]	0.32	0.14	0.5	369
Zn	mg/l	0.00	0.32	0.08	0.02	1	369
Sn	mg/l	0.00	0.75	0.27	0.07	1	63
Mg	mg/l	0.34	10.20	9.44	5.05	–	49
BOD_5	mg/l	0.00	11.00	11.00	4.56	–	16
DOC (Dissolved Organic Carbon)	mg/l	14.00	26.00	24.70	21.07	–	14
Low volatile lipophilic substances	mg/l	0.00	20.00	14.40	1.94	20	17
HC index	mg/l	0.00	1.00	0.20	0.06	3	17

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[151] 3 exceedances (max. 5.2 mg/l)

[152] 1 exceedance (0.66 mg/l)

[153] 1 measurement above ELV (2.16 mg/l)

[154] 1 measurement above the ELV (0.06 mg/l)

[155] 4 exceedances (max. 0.4 mg/l); 10 measurements above ELV, no exceedance due to „4 out of 5 rule“

[156] 13 exceedances (max. 1.24 mg/l)

[157] 12 exceedances (max. 1.35 mg/l)

[158] 1 exceedance (max. 0.83 mg/l)

Self-monitoring 2019							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
TSS	mg/l	0.00	28.00	24.00	12.59	30	17
AOX	mg/l	0.12	0.68	0.62	0.36	1.0	16

Source: Self-monitoring Collini GmbH, 2019

Table 101: External-monitoring of process wastewater 2017 – Part A

External-monitoring 2018					
Parameter	**Unit**	**12.04.2017**	**10.05.2017**	**07.06.2017**	**ELV permit**
24h flow proportional composite sample					
Q	m^3/d	880	875	800	
pH		7.67	8.11	7.99	6.5–8.5
COD	mg/l	91	69	80	150
BOD$_5$	mg/l	2.4	2	< 1.0	20
DOC	mg/l	12	13	26	
low volatile lipophilic substances	mg/l	< 12	< 9.0	< 10	20
Hydrocarbon index	mg/l	< 1.0	< 1.0	< 1.0	3
F	mg/l	6.3	4.2	4.6	20
TP	mg/l	0.57	0.84	1	1
NH$_4$-N	mg/l	0.23	0.077	0.036	10
Al	mg/l	0.14	0.19	0.24	3
Cr total	mg/l	0.16	0.18	0.088	0.5
Cu	mg/l	0.18	0.18	0.36	0.5
Ni	mg/l	0.23	0.16	0.15	0.5
Zn	mg/l	0.052	0.048	0.042	1
SN	mg/l	< 0.010	< 0.010	< 0.010	1

		External-monitoring 2018			
Parameter	**Unit**	**12.04.2017**	**10.05.2017**	**07.06.2017**	**ELV permit**
		Spot sample			
pH		7.1	7.31	7.63	6.5–8.5
TSS	mg/l	4	6.8	8.8	30
AOX	mg/l	0.48	0.27	0.78	1
CN free	mg/l	< 0.030	< 0.030	0.031	0.1
CN total	mg/l				2
Cl total	mg/l	< 0.20	< 0.20	< 0.20	
Cl free	mg/l	< 0.20	< 0.20	< 0.20	< 0.05
Cr(VI)	mg/l	< 0.020	< 0.020	< 0.020	0.1
NO_2-N	mg/l	0.003	0.0065	0.011	1.5

Source: Kalb Analytic, 2017

Table 102: External-monitoring of process wastewater 2017 – Part B

		External-monitoring 2018			
Parameter	**Unit**	**28.06.2017**	**13.07.2017**	**04.10.2017**	**ELV permit**
		24h flow proportional composite sample			
Q	m^3/d	824	829	856	
pH		8.2	7.81	8.06	6.5–8.5
COD	mg/l	57	61	56	150
BOD_5	mg/l	2.7	2.3	1.4	20
DOC	mg/l	13	15	16	
low volatile lipophilic substances	mg/l	< 10	< 10	< 10	20
Hydrocarbon index	mg/l	< 1.0	< 1.0	< 1.0	3
F	mg/l	4.5	2.3	< 0.20	20
TP	mg/l	1.7	0.37	0.86	1

		External-monitoring 2018			
Parameter	**Unit**	**28.06.2017**	**13.07.2017**	**04.10.2017**	**ELV permit**
NH_4-N	mg/l	0.081	0.31	0.032	10
Al	mg/l	0.12	0.13	0.17	3
Cr total	mg/l	0.16	0.096	0.17	0.5
Cu	mg/l	0.026	0.21	0.31	0.5
Ni	mg/l	< 0.010	0.89	0.28	0.5
Zn	mg/l		0.31	0.051	1
SN	mg/l				1
		Spot sample			
pH		7.52	6.88	7.69	6.5–8.5
TSS	mg/l	6.8	5.6	8.8	30
AOX	mg/l	0.89	0.64	1.4	1
CN free	mg/l	< 0.030	< 0.030	< 0.030	0.1
CN total	mg/l		0.017	0.01	2
Cl total	mg/l	< 0.20	< 0.020	< 0.020	
Cl free	mg/l	< 0.20	< 0.020	< 0.020	< 0.05
Cr(VI)	mg/l	< 0.020	< 0.020	< 0.020	0.1
NO_2-N	mg/l	0.0061	0.038	0.012	1.5

Source: Kalb Analytic, 2017

Table 103: External-monitoring of process wastewater 2018 – Part A

		External-monitoring 2018			
Parameter	**Unit**	**20.03.2018**	**17.04.2018**	**27.06.2018**	**ELV permit**
		24h flow proportional composite sample			
Q	m^3/d	873	892	836	
pH		7.62	7.53	8.07	6.5–8.5
COD	mg/l	65	85	85	150

			External-monitoring 2018		
Parameter	**Unit**	**20.03.2018**	**17.04.2018**	**27.06.2018**	**ELV permit**
BOD_5	mg/l	2	6.9	5	20
DOC	mg/l	19	26	16	
low volatile lipophilic substances	mg/l	< 10	< 10	< 10	20
Hydrocarbon index	mg/l	< 1.0	< 1.0	< 1.0	3
F	mg/l	4.7	2.5	3.9	20
TP	mg/l	0.34	0.45	0.37	1
NH_4-N	mg/l	0.076	< 0.010	0.57	10
Al	mg/l	0.13	0.24	0.3	3
Cr total	mg/l	0.21	0.14	0.1	0.5
Cu	mg/l	0.48	0.51	0.39	0.5
Ni	mg/l	0.25	0.34	0.12	0.5
Zn	mg/l	0.16	0.2	0.27	1
			Spot sample		
pH		7.27	6.94	7.47	6.5–8.5
TSS	mg/l	6.4	12	7.6	30
AOX	mg/l	1	1	0.77	1
CN free	mg/l	< 0.030	< 0.030	< 0.010	0.1
CN total	mg/l	0.013	0.012	0.022	2
Cl total	mg/l	< 0.020	< 0.020	< 0.020	
Cl free	mg/l	< 0.020	< 0.020	< 0.020	< 0.05
Cr(VI)	mg/l	< 0.020	< 0.020	0.035	0.1
NO_2-N	mg/l	0.024	0.22	0.51	1.5

Source: Kalb Analytic, 2018

Table 104: External-monitoring of process wastewater 2018 – Part B

		External-monitoring 2018			
Parameter	**Unit**	**18.07.2018**	**09.08.2018**	**04.09.2018**	**ELV permit**
		24h flow proportional composite sample			
Q	m³/d	846	819	908	
pH		8.09	8.14	7.84	6.5–8.5
COD	mg/l	82	74	84	150
BOD_5	mg/l	1.9	2.2	2.4	20
DOC	mg/l	13	11	6.6	
low volatile lipophilic substances	mg/l	< 12	< 25	< 10	20
Hydrocarbon index	mg/l	< 1.0	< 1.0	< 1.0	3
F	mg/l	3.3	2.6	3.5	20
TP	mg/l	0.34	0.31	0.57	1
NH_4-N	mg/l	1	0.28	0.42	10
Al	mg/l	0.12	0.19	0.36	3
Cr total	mg/l	0.068	0.078	0.14	0.5
Cu	mg/l	0.26	0.23	0.3	0.5
Ni	mg/l	0.12	0.12	0.23	0.5
Zn	mg/l	0.047	0.04	1	1
		Spot sample			
pH		7.38	7.31	7.9	6.5–8.5
TSS	mg/l	6.6	7.6	8	30
AOX	mg/l	0.44	2.1	0.16	1
CN free	mg/l	0.0026	< 0.0020	< 0.010	0.1
CN total	mg/l	0.014	0.013	< 0.010	2
Cl total	mg/l	< 0.020	< 0.020	< 0.02	
Cl free	mg/l	< 0.020	< 0.020	< 0.02	< 0.05
Cr(VI)	mg/l	< 0.020	< 0.020	< 0.020	0.1

External-monitoring 2018					
Parameter	**Unit**	**18.07.2018**	**09.08.2018**	**04.09.2018**	**ELV permit**
NO_2-N	mg/l	0.032	0.02	0.011	1.5

Source: Kalb Analytic, 2018

Table 105: External-monitoring of process wastewater 2019 – Part A

External-monitoring 2019						
Parameter	**Unit**	**10.04.**	**30.04.**	**15.05.**	**12.06.**	**ELV permit**
24h flow proportional composite sample						
Q	m^2/d	844	822	790	822	
pH		8.08	8.11	8.13	8.1	6.5–8.5
COD	mg/l	68	90	67	90	150
BOD_5	mg/l	2	2	3.5	6	20
DOC	mg/l	16	18	14	22	
low volatile lipophilic substances	mg/l	<20	<20	<16	<10	20
Hydrocarbon index	mg/l	<1.0	<1.0	<1.0	<1.0	3
F	mg/l	2.9	3.6	4.2	1.8	20
TP	mg/l	0.44	0.63	0.37	0.35	1
NH_4-N	mg/l	1.6	14	3	1.7	10
Al	mg/l	0.17	0.31	0.49	0.21	3
Cr total	mg/l	0.088	0.13	0.32	0.41	0.5
Cu	mg/l	0.27	0.54	0.56	0.67	0.5
Ni	mg/l	0.31	0.33	0.22	0.14	0.5
Zn	mg/l	0.022	0.058	0.074	0.039	1
Sn	mg/l	<0.010	<0.010	<0.010	<0.010	1
Spot sample						
pH		7.19	7.17	7.45	7.35	6.5–8.5

		External-monitoring 2019				
Parameter	**Unit**	**10.04.**	**30.04.**	**15.05.**	**12.06.**	**ELV permit**
TSS	mg/l	6	12	11	10	30
AOX	mg/l	0.24	0.14	0.18	0.43	1
CN free	mg/l	<0.010	<0.010	<0.010	<0.010	0.1
CN total	mg/l	<0.010	<0.010	<0.010	0.014	2
Cl total	mg/l	<0.02	<0.02	<0.02	<0.02	
Cl free	mg/l	<0.02	<0.02	<0.02	<0.02	< 0.05
Cr(VI)	mg/l	<0.020	<0.020	<0.020	<0.020	0.1
NO_2-N	mg/l	0.14	0.12	0.45	0.075	1.5

Source: Kalb Analytic, 2019

Table 106: External-monitoring of process wastewater 2019 – Part B

		External-monitoring 2019				
Parameter	**Unit**	**26.06.**	**31.07.**	**05.08.**	**03.09.**	**ELV permit**
		24h flow proportional composite sample				
Q	m²/d	832	492	235	818	
pH		8.12	8.07	8.06	8.26	6.5–8.5
COD	mg/l	82	72	77	77	150
BOD_5	mg/l	7.4	4.5	11	3.2	20
DOC	mg/l	22	23	21	18	
low volatile lipophilic substances	mg/l	<10	13	<10	<10	20
Hydrocarbon index	mg/l	<1.0	<1.0	<1.0	<1.0	3
F	mg/l	4.5	8.4	6.7	8.1	20
TP	mg/l	0.37	0.23	0.21	0.33	1
NH_4-N	mg/l	0.9	1.3	0.75	0.3	10
Al	mg/l	0.34	0.34	0.31	0.71	3

External-monitoring 2019						
Parameter	**Unit**	**26.06.**	**31.07.**	**05.08.**	**03.09.**	**ELV permit**
Cr total	mg/l	0.064	0.042	0.21	0.29	0.5
Cu	mg/l	0.51	0.44	0.43	0.49	0.5
Ni	mg/l	0.092	0.11	0.11	0.06	0.5
Zn	mg/l	0.039	0.026	0.029	0.051	1
Sn	mg/l	<0.010			<0.010	1
Spot sample						
pH		7.58	7.88	7.4	7.61	6.5–8.5
TSS	mg/l	4	9	28	14	30
AOX	mg/l	0.32	0.68	0.41	0.25	1
CN free	mg/l	<0.010	<0.010	<0.010	<0.010	0.1
CN total	mg/l	0.018	<0.010	<0.010	0.034	2
Cl total	mg/l	<0.02	<0.02	<0.02	<0.02	
Cl free	mg/l	<0.02	<0.02	<0.02	<0.02	< 0.05
Cr(VI)	mg/l	<0.020	<0.020	0.025	<0.020	0.1
NO_2-N	mg/l	0.027	<0.030	<0.030	0.01	1.5

Source: Kalb Analytic, 2019

Table 107: External-monitoring of process wastewater 2019 – Part C

External-monitoring 2019					
Parameter	**Unit**	**01.10.**	**06.11.**	**03.12.**	**ELV permit**
24h flow proportional composite sample					
Q	m^3/d	931	822	855	
pH		8.24	8.15	8.11	6.5–8.5
COD	mg/l	71	77	52	150
BOD_5	mg/l	3.7	2.9	7.2	20
DOC	mg/l	12	17	11	

		External-monitoring 2019			
Parameter	**Unit**	**01.10.**	**06.11.**	**03.12.**	**ELV permit**
low volatile lipophilic substances	mg/l	<10	<10	<10	20
Hydrocarbon index	mg/l	<1.0	<1.0	<1.0	3
F	mg/l	6.2	3.7	3.7	20
TP	mg/l	0.2	0.46	0.49	1
NH_4-N	mg/l	0.023	0.72	0.38	10
Al	mg/l	0.47	0.98	0.22	3
Cr total	mg/l	0.098	0.17	0.2	0.5
Cu	mg/l	0.39	0.37	0.3	0.5
Ni	mg/l	0.13	0.1	0.089	0.5
Zn	mg/l	0.025	0.033	0.017	1
Sn	mg/l	<0.010	<0.010	<0.010	1
		Spot sample			
pH		7.48	7.48	7.81	6.5–8.5
TSS	mg/l	6	9	< 4.0	30
AOX	mg/l	0.15	< 0.43	0.21	1
CN free	mg/l	<0.0020	<0.0020	<0.010	0.1
CN total	mg/l	0.017	0.011	<0.010	2
Cl total	mg/l	<0.02	<0.02	<0.20	
Cl free	mg/l	<0.02	<0.02	<0.20	< 0.05
Cr(VI)	mg/l	<0.020	<0.020	<0.020	0.1
NO_2-N	mg/l	0.077	0.046	0.003	1.5

Source: Kalb Analytic, 2019

Table 108: Monitoring standards external-monitoring

Parameter	Standard
24h flow proportional composite sample	
Q	
pH	DIN EN ISO 10523
COD	DIN 38409-41
BOD_5	DIN EN 1899-1
DOC	DIN EN 1484
low volatile lipophilic substances	DIN ISO 11349 (DEV H56)
Hydrocarbon index	ÖNORM EN ISO 9377-2
F	DIN 38405 - D4-1
TP	DIN EN ISO 11885
NH_4-N	ÖNORM EN ISO 11732
Al	DIN EN ISO 11885
Cr total	DIN EN ISO 11885
Cu	DIN EN ISO 11885
Ni	DIN EN ISO 11885
Zn	DIN EN ISO 11885
Sn	EN ISO 17294-2
Spot sample	
pH	DIN EN ISO 10523
TSS	DIN 38409-2
AOX	DIN 38409-22
CN free	ÖNORM EN ISO 14403-2
CN total	ÖNORM EN ISO 14403-2
Cl total	EN ISO 7393-2
Cl free	EN ISO 7393-2
Cr(VI)	ISO 11083
NO_2-N	ÖNORM EN ISO 13395

Source: Kalb Analytic, 2019

4.3 References

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Permit II-3101-2005/0061: Bescheid, II-3101-2005/0061, BH Dornbirn, 2011

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5 Collini GmbH – Vienna

Collini GmbH is a specialist sub-contractor (jobbing shop) operating several surface treatment installations worldwide. In Austria Collini operates batch galvanizing (zinc), powder coating, cathodic dip coating (CDC) and two electroplating installations located in Hohenems and Vienna. In the following the installation Vienna is discussed.

On the premise Vienna the following processes are carried out:

- Nickel plating (autocatalytic; nickel composite)
- Anodizing
- Cr(VI) electroplating
- Copper electroplating
- Silver electroplating
- Tin electroplating

Work pieces used in plating are out of steel, brass, copper or aluminium. Plating is carried out in rack or drum systems.

Environmental Management System
Collini Vienna has an according to ISO 14001 certified environmental management system implemented.

5.1 Technical description

At Collini Vienna several (electro) plating lines are in operation. Plating is carried out in either rack or drum systems. The lines are:

- Anodizing of aluminium
- Autocatalytic nickel
  - Autocatalytic nickel, autocatalytic nickel-polytetrafluoroethylene (PTFE aka Teflon), tin electroplating
  - Autocatalytic nickel, autocatalytic nickel-PTFE
- Cr(VI) electroplating

- Silver, copper, tin, autocatalytic nickel

In the following, the different processes taking place on site are described.

Anodising of aluminium

Anodising of metals is an electrolytic surface oxidation process resulting in an oxide layer, which is firmly attached to the work piece, providing corrosion protection. In anodising, the work piece is (as the name indicates) connected as the anode. During the anodising process the negatively charged anion migrates to the anode where it is discharged with a loss of one or more electrons. The metal reacts with the oxygen of the anion and a layer of oxide forms on the surface. (STM BREF, 2006)

Aluminium is predominantly anodised, with alumina (Al2O3) formed at the surface. (STM BREF, 2006). Magnesium, titanium, tantalum and niobium can be also anodised. At Collini Vienna only aluminium is anodised.

Aluminium is typically anodised in sulphuric acid electrolytes (STM BREF, 2006).

To increase corrosion resistance and to retain surface colouring, sealing is applied to the anodised work piece. Sealing can be carried out in hot or cold processes. At Collini Vienna hot water sealing is applied.

With hot sealing, the pores in the oxide layer are closed by hydrating the aluminium oxide to bohemite (AlO(OH)): the pores are closed by the increased volume of the bohemite structure. The sealing process is carried out by dipping the anodised parts in hot or boiling (minimum 96°C) deionised water. (STM BREF, 2006)

Work pieces are moved by a crane system. The anodising unit is fully automatized. The production steps consist of:

- Degreasing
- Pickling
- Anodising
- Sealing

Degreasing & pickling

For degreasing sodium hydroxide together with wetting agents is used. For pickling nitric acid is used. Both treatment steps are carried out at temperatures around 60 °C.

Anodising

Anodising of aluminium is done in sulphuric acid electrolytes, which is the most common technique for anodising of aluminium. The temperature of the electrolyte is typically between 15 and 30 °C. Also hard anodising is carried out at Collini Vienna. Hard anodising results in thicker oxide layers for better corrosion resistance. For hard anodising, the electrolyte has to be operated below 5 °C. Even though with special electrolytes, hard anodising at 10 °C is possible. Hard anodised layers are normally not sealed.

Electrolytes for anodising used to contain PFOS based wetting agents. The use of PFOS based wetting agents is not BAT according to the STM BREF 2006, as alternatives to PFOS exist and are successfully used (STM BREF, 2006). At Collini Vienna PFOS free electrolytes for anodising are in use.

Colouring

Colouring of the anodised work piece can be done by dip dyeing. Paint particles will settle in the pores of the oxide layer. Colouring is optional and if done then before sealing.

Sealing

After dip dyeing hot sealing is applied to increase corrosion resistance. The sealing process is carried out by dipping the anodised parts in hot or boiling (minimum 95- 96 °C) deionised water (STM BREF, 2006).

Autocatalytic nickel; autocatalytic nickel-polytetrafluoroethylene, tin

Autocatalytic plating is also known as electroless plating. The fundamental reaction requires the presence of a catalytic metal – the metal being deposited – that allows the reaction to proceed.

Autocatalytic nickel provides uniform thickness of deposit regardless of the size and shape of the to be plated work piece. Furthermore, it results in high resistance against wear and abrasion and it is easily soldered to. Application of autocatalytic nickel plated products include data storage devices, electronics industry, automotive industry, etc.

Autocatalytic nickel

Autocatalytic nickel electrolytes are based on nickel sulphate and nickel chloride. Sodium hypophosphite is the most often used reducing agent. Solutions also contain chelating agents (organic carboxylic acids) and buffers as sodium hydroxide and sodium carbonate (STM BREF, 2006).

Process steps include degreasing, pickling, activation, autocatalytic nickel, drying and annealing.

Autocatalytic nickel-polytetrafluoroethylene

Almost uniquely, nickel matrixes can be formed in which inert, non-metallic particles, such as silicon carbide, diamond or polytetrafluoroethylene (PTFE) are incorporated by co-deposition to improve engineering properties such as hardness, abrasion resistance and coefficient of friction (STM BREF, 2006). At Collini Vienna PTFE (commonly known as Teflon) is added.

Tin electroplating

Plated tin coatings are ductile, resistant to corrosion, easy to coat, and have high throwing and good distribution properties. Tin finishes are also subsequently easier to solder components onto Apart from coating steel coil for packaging of food, beverages or aerosols, it is also widely used in printed circuit boards, electronic components, appliance chassis, as well as for kitchen utensils. (STM BREF, 2006)

There are several different electrolytes available for tin electroplating. Stannous sulphate baths containing stannous sulphate, sulphuric acid and addition agents (antioxidants for stannous tin, plus grain refiner) are the most popular tin electrolytes in both rack and barrel applications because of their high current efficiency. (STM BREF, 2006)

Waste gas

Fume extraction may be required at process tanks including mist elimination to remove nickel and tin containing aerosols (STM BREF, 2006).

Bath life span

The solution working life is short due to the formation of reaction by-products, which lower process performance significantly requiring frequent discarding. Bath life span can be prolonged by the use of electrodialysis to continuously remove by-products from the plating solution (STM BREF, 2006).

Wastewater

Wastewaters from autocatalytic nickel need pre-treatment. Ammonia can complex with other metals and can be oxidised before. Hypophosphite ions and phosphite ions can be oxidised to phosphates. The phosphate ion can be precipitate by adding calcium ions during the neutralisation. Metals can be separated from effluents by precipitation, plate-out or ion-exchange. (STM BREF, 2006)

Hard chromium plating

Hard chromium plating is a functional coating that consists of heavy deposits (thick layer) to ensure high resistance to mechanical and wear damage. Hard chromium electrolytes are based on Cr(VI) and different catalysts i.e. sulphuric acid, hexafluorosilicates, methanesulfonic acid. For significant improving of the corrosion protection the work piece can be (electro)plated with e.g. nickel before hard chromium plating or hard chromium plating can be varied resulting in duplex or triplex hard chromium layers.

Hexavalent chromium has adverse health effects, causing skin and mucus membrane irritation and certain cancers (STM BREF, 2006). Aerosols are generated from Cr(VI) process solutions by a significant hydrogen evolution at the cathode. Thus, workplace health and safety regulations require measures to meet maximum allowable concentrations. For meeting these regulations, fume suppressants are used to reduce the amount of aerosol. Fume suppressants were usually based on PFOS which is toxic and persistent (STM RBEF, 2006).

Today the use of PFOS-free fume suppressants is state of the art. Alternatives are, however, based on per- and polyfluoroalkyl substances (PFAS). PFAS are as well persistent, bio accumulative and ubiquitous. Around 4700 man-made chemicals belong to the group of PFAS. Of the relatively few well-studied PFAS, most are considered moderately to highly toxic, particularly for children’s development.

At Collini Vienna a PFOS-free fume suppressant is in use.

Cr (VI) is also soluble at a wide range of pH-values, contributing to high aquatic toxicity (STM BREF, 2006). Therefore, it must be reduced to trivalent chromium first before precipitating in wastewater treatment plants. Solid sodium disulphite ((Na2S2O5) forming with water into sodium hydrogen sulphite) is typically used for the reduction of Cr (VI) to Cr (III).

Silver, copper, tin, autocatalytic nickel

Silver electroplating

The majority of silver electrolytes are based on potassium-silver cyanide. A silver content of 30 – 65 g/l with free potassium cyanide of 100 – 160 g/l and potassium carbonate (15 – 20 g/l) is necessary for good plating performance. However, a potassium carbonate concentration of over 200 g/l makes it necessary to discard the electrolytes. (STM BREF, 2006)

Alkaline copper electroplating

Cyanide copper plating is necessary for strike plating the work piece (steel) to prevent spontaneous cementation of copper and poor adhesion of subsequent metal deposit (STM BREF, 2006). Cyanide copper electrolytes are usually based on copper cyanide and sodium cyanide. Potassium cyanide and potassium hydroxide based alternatives exist for forming a thicker layer on the work piece. Potassium based electrolytes have to be discarded, however, once the content of potassium carbonate exceeds 90 g/l whilst sodium based solutions can be regenerated by precipitation of sodium carbonate (STM BREF, 2006).

Tin electroplating

Stannous sulphate baths containing stannous sulphate, sulphuric acid and addition agents (antioxidants for stannous tin, plus grain refiner) are the most popular tin electrolytes in both rack and barrel applications because of their high current efficiency. (STM BREF, 2006)

Autocatalytic nickel

Autocatalytic nickel electrolytes are based on nickel sulphate and nickel chloride. Sodium hypophosphite is the most often used reducing agent. Solutions also contain chelating agents (organic carboxylic acids) and buffers as sodium hydroxide and sodium carbonate (STM BREF, 2006).

Resource efficiency

The cost of silver makes recovery economic. Residues of silver may be recovered from rinse water through electrolysis or ion exchange. Recovery of silver from spent electrolytes may be achieved through precipitation with zinc powder. (STM BREF, 2006)

Bath life span

The autocatalytic nickel solution working life is short due to the formation of reaction by-products, which lower process performance significantly requiring frequent discarding. Bath life span can be prolonged by the use of electrodialysis to continuously remove by-products from the plating solution (STM BREF, 2006).

Wastewater

Cyanide containing wastewaters need pre-treatment (oxidation) before merging with other wastewater streams, to avoid formation of complexes with other metals (e.g. nickel).

Wastewaters from autocatalytic nickel need pre-treatment. Ammonia can complex with other metals and can be oxidised before. Hypophosphite ions and phosphite ions can be oxidised to phosphates. The phosphate ion can be precipitate by adding calcium ions during the neutralisation. Metals can be separated from effluents by precipitation, plate-out or ion-exchange. (STM BREF, 2006)

The autocatalytic nickel solution working life is short due to the formation of reaction by-products, which lower process performance significantly requiring frequent discarding. Bath life span can be prolonged by the use of electrodialysis to continuously remove by-products from the plating solution (STM BREF, 2006).

Rinsing water

In order to reduce the amount of fresh water consumed for rinsing, spray rinsing and multiple-stage counter flow rinse units are in use.

Resource efficiency

In order to prolong the life span of the degreasing baths and the autocatalytic nickel baths, filters with active carbon have been installed.

Silver is recuperated from rinsing water or spent concentrates.

Waste gas treatment

Wet scrubbers and dust filters are installed to treat the extracted waste gas from process baths before being emitted over stack.

Two alkaline scrubbers are installed to treat the waste gas from wastewater treatment (i.e. cyanide and acidic wastewaters).

Process wastewaters

Treated wastewater is discharged indirectly. Process wastewater is collected in separate streams and pre-treated individually if necessary. Process wastewater streams are:

- Acidic wastewater
- Alkaline wastewater
- Cyanide containing wastewater
- Cr(VI) containing wastewaters
- Alkaline wastewater for batch treatment
- Nickel containing wastewater for batch treatment
- Rinsing water containing nickel

Treatment consists of:

- Cr(VI) reduction
- Cyanide oxidation
- Neutralisation
- Settling
- Sludge dewatering
- Ion-exchange resin
- Final neutralisation

Cr(VI) reduction

Cr(VI) has to be reduced to Cr(III) as Cr(VI) is difficult to precipitate.

At Collini Vienna Cr(VI) reduction is done by using sodium hydrogen sulphite (bisulphite). The reduction is made at pH values under 2.5.

Cyanide oxidation

Cyanide oxidation is done by using sodium hypochlorite. The use of sodium hypochlorite is associated with the formation of organic chlorine compounds, measured as AOX (STM BREF, 2006).

Cyanides are well-known hazardous substances which can also form complexes with certain metals such as nickel which complicates precipitation in wastewater treatment. Therefore, cyanide containing wastewater streams are collected separately at Collini Vienna. In acid conditions cyanide gives off cyanide gas.

Neutralisation

Batch neutralisation is done separately for nickel containing wastewaters and alkaline, acidic, pre-treated cyanide and pre-treated Cr(VI) containing wastewater. For the precipitation of metals the pH value is increased to 8.5–9.0 by adding lime milk or NaOH.

If the targeted pH value is exceeded HCl is added. Dosing of NaOH and HCl is automatic, depending on the monitored pH value. It is important that the pH value is stable for an appropriate time frame of ca. 20 minutes to ensure that the precipitation of metals is completed. Flocculation agents can be added.

Settling

In settling tanks the flocs are separated from the clear water. There are dedicated settling tanks for nickel wastewater and for other wastewaters.

Sludge dewatering

Hydroxide sludge from metal precipitation is dewatered in chamber filter presses. Separte chamber filter presses for nickel wastewater and non-nickel wastewater are operated.

Ion-exchange resin

Before entering the final neutralisation step the pre-treated wastewater is sent through ion exchange resins (cation and anion resins). Again, separate ion exchangers are installed for either nickel wastewater or other wastewater. Nickel containing rinsing water is directly sent to the nickel ion exchanger.

Final neutralisation

In the final neutralization step the wastewater streams are combined and the pH value can be adjusted if necessary before discharging into the public sewer.

5.2 Current consumption and emission levels

Specific consumption values from 2018 are presented in Table 109. Specific consumption values relate to the tonne of produced product.

Table 109: Specific consumption values 2018

	Unit	specific consumption (per t produced product)
Energy		
Electricity	kWh/m²	11.844
District heat	kWh/m²	17.855
Water consumption	m³/m²	0.207
Waste	kg/m²	1.96
Chemicals	kg/m²	3.925

Source: Specific consumption values 2018

Waste generation

Waste generation from 2018 is listed in Table 110.

Table 110: Waste generation 2018

Waste type	Quantities 2018 [t]	hazardous	non-hazardous
Concentrates (nickel, pickling)	379.22	X	
Metal hydroxide sludge	159.64	X	
Liquid concentrates from air scrubber	126.04	X	

Waste type	Quantities 2018 [t]	hazardous	non-hazardous
Acids, acid mixtures (anodizing)	109.965	X	
Concentrates containing Cr(VI)	17.085	X	
Metal scrap	7.471		X
Organic acids	4.662	X	
Spent filters	4.516	X	
Inorganic acids and acid mixtures	3.78	X	
Spent ion exchange resins	3.043		X
Oil-water mixtures	1.12	X	
Concentrates containing cyanide	1.04	X	
Cyanide containing wastewater	0.941	X	
Alkaline solutions and mixtures	0.92	X	
Copper	0.322		X
Aluminium	0.162		X

Source: EMAS environmental report Collini GmbH, 2019

Emissions to air

Wet scrubbers and dust filters are installed to treat the extracted waste gas from process baths before being emitted over stack.

Table 111 presents the monitoring results from 2017.

Table 111: Monitoring results of emissions to air, 0 °C, 1013 mbar, dry exhaust air

Parameter	Half-hourly measurements [mg/Nm³, no correction of O_2 content]		
Cr	0.002	0.001	0.002
Cr (VI)	< 0.001	< 0.001	< 0.001
Ni	0.003	0.002	0.002
Dust	0.3	0.3	0.3

Source: Laboratorium Umweltanalytik GmbH, 2017

Two alkaline scrubbers are installed to treat the waste gas from wastewater treatment (i.e. cyanide and acidic wastewaters). Table 112 presents the monitoring results from 2018.

Table 112: Monitoring results of emissions to air from wastewater treatment – alkaline waste gas, 0 °C, 1013 mbar, dry exhaust air

Parameter	Waste gas from wastewater treatment Half-hour measurements [mg/Nm³, no correction of O_2 content]		
HCN	< 0.5	< 0.5	< 0.5
HCl	< 2	< 2	< 2
Cr	< 0.01	< 0.01	< 0.01
Cu	< 0.01	< 0.01	< 0.01
Ni	< 0.01	< 0.01	< 0.01

Source: Laboratorium Umweltanalytik GmbH, 2018

Emissions to water

Treated process wastewater is discharged indirectly. Monitoring has to be conducted using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit. Emission limit values (ELV) are prescribed by permit.

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

The on-site WWTP consists of:

- Cr(VI) reduction
- Cyanide oxidation
- Neutralisation
- Settling
- Sludge dewatering
- Ion-exchange resin
- Final neutralisation

A detailed description of the on-site WWTP is presented in chapter 3.1.

Emissions to water are described in the following tables. In Table 113 the minimum monitoring frequencies and ELVs prescribed by permit are presented and compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. Table 114–Table 116 present the self-monitoring recordings of treated process wastewater. Table 117–Table 120 present the results from external-monitoring of treated process wastewater for the years 2017, 2018 & 2019.

Table 113: Emission limit values for the process wastewater in comparison to BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)	Ordinance (indirect discharge)	Min. frequency self-monitoring	Min. frequency external-monitoring
pH		6,5–9,5	–	6,5–9,5	every working day	1
Copper – Cu	mg/l	0,5	0,2–2,0	0,5	every working day	1
Zinc – Zn	mg/l	1	0,2–2,0	2	every working day	–
Chromium total – Cr total	mg/l	0,5	0,1–2,0	0,5	every working day	1
Nickel – Ni	mg/l	0,5	0,2–2,0	0,5	every working day	1
Tin – Sn	mg/l	1	0,2–2,0	1	every working day	1
Cyanide free – CN free	mg/l	0,1	0,01–0,2	0,1	every working day	1
Hydrocarbon index – HC index	mg/l	20	–	15	every working day	6
Sulphate – SO_4	mg/l	1200	–	–	once per week	1
Silver – Ag	mg/l	0,1	0,1–0,5	0,1	every working day	1

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)	Ordinance (indirect discharge)	Min. frequency self-monitoring	Min. frequency external-monitoring
Total Organic Carbon – TOC	mg/l	–	–	–	–	6
Total Nitrogen – TN	mg/l	–	–	–	–	6
Total Phosphorus – TP	mg/l	–	–	–	–	6
Chloride – Cl	mg/l	–	–	–	–	6

Source: STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 114: Self-monitoring of treated process wastewater 2017

				Self-monitoring 2017			
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
pH		6,60[159]	9,1[160]	8,58	7,57	6,5–9,5	245
CN – free	mg/l	0,00	0,1[161]	0,05	0,01	0,1	242
Cr(VI)	mg/l	0,00	3,36	0,07	0,03	–	234
Ni	mg/l	0,00	0,50[162]	–	0,90	0,5	245
Cu	mg/l	0,00	0,50[163]	–	0,18	0,5	245
Cr – total	mg/l	0,00	0,50[164]	0,38	0,15	0,5	245
Ag	mg/l	0,00	0,10[165]	0,07	0,02	0,1	245
Zn	mg/l	0,00	1,00	0,23	0,04	1	245

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[159] pH: 2 values below the ELV (min. 6.3)

[160] pH: 3 values above the ELV (max. 10)

[161] CN free: 1 exceedance (max. 0.43 mg/l)

[162] Ni: 64 exceedances (max. 20.6 mg/l)

[163] Cu: 10 exceedances (max. 3.3 mg/l)

[164] Cr – total: 5 exceedances (max. 4.9 mg/l)

[165] Ag: 3 measurements above the ELV, no exceedance due to „4 out of 5“ rule

Self-monitoring 2017							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Sn	mg/l	0,00	1,0[166]	0,44	0,14	1	245
SO_4	mg/l	1000,60	2357,00	1410,38	1151,06	–	45
Conductivity	µS/cm	1047,00	24300,00	11459,50	6644,20	–	242
Q	m^3/d	1,70	348,00	310,00	193,15	–	184

Source: Self-monitoring Collini GmbH, 2017

Table 115: Self-monitoring of treated process wastewater 2018

Self-monitoring 2018							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
pH		2,40[167]	9,5[168]	8,58	7,44	6,5–9,5	246
CN – free	mg/l	0,00	0,1[169]	–	0,03	0,1	240
Cr(VI)	mg/l	0,00	4,86	0,16	0,12	–	138
Ni	mg/l	0,00	0,5[170]	–	2,26	0,5	246
Cu	mg/l	0,00	0,5[171]	–	0,27	0,5	246
Cr – total	mg/l	0,00	0,5[172]	–	0,19	0,5	246
Ag	mg/l	0,00	0,1[173]	0,08	0,02	0,1	244
Zn	mg/l	0,00	1[174]	0,33	0,08	1	243

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[166] Sn: 1 exceedance (max. 2.2 mg/l)

[167] pH: 6 measurements below the ELV (min. 2.4)

[168] pH: 5 values above the ELV (max. 11.6)

[169] CN: 9 exceedances (max. 0.49 mg/l)

[170] Ni: 129 exceedances (max. 163.7 mg/l)

[171] Cu: 21 exceedances (max. 5.8 mg/l)

[172] Cr – total: 12 exceedances (max. 8.5 mg/l)

[173] Ag: 10 measurements above the ELV, no exceedance due to „4 out of 5“ rule (max. 0.36 mg/l)

[174] Zn: 2 measurements above the ELV, no exceedance due to „4 out of 5“ rule (max. 1.18 mg/l)

Self-monitoring 2018							
Parameter	Unit	Daily min	Daily max	95 Percentile	Annual average	ELV permit	Number of samples
Sn	mg/l	0,00	1[175]	0,87	0,26	1	244
SO_4	mg/l	1021,60	4208,00	3201,83	1644,36	–	24
Conductivity	µS/cm	1041,00	55800,00	9132,50	4254,08	–	244
Q	m^3/d	2,00	384,00	329,00	218,60	–	343

Source: Self-monitoring Collini GmbH, 2018

Table 116: Self-monitoring of treated process wastewater 2019

Self-monitoring 2019							
Parameter	Unit	Daily min	Daily max	95 Percentile	Annual average	ELV permit	Number of samples
pH		6,50[176]	9.5[177]	9,00	8,05	6,5–9,5	225
CN – free	mg/l	0,00	0,1[178]	0,04	0,04	0,1	225
Cr(VI)	mg/l	0,00	0,29	0,00	0,01	–	160
Ni	mg/l	0,00	0,5[179]	–	1,80	0,5	225
Cu	mg/l	0,00	0,5[180]	–	0,25	0,5	225
Cr – total	mg/l	0,00	0,5[181]	0,24	0,07	0,5	225
Ag	mg/l	0,00	0,1[182]	0,05	0,02	0,1	225
Zn	mg/l	0,00	1[183]	0,09	0,03	1	224

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[175] Sn: 3 exceedances (max. 2 mg/l)

[176] pH: 2 values below the ELV (min. 6.2)

[177] pH: 7 values above the ELV (max. 12.7)

[178] CN: 4 exceedances (max. 5.6 mg/l)

[179] Ni: 82 exceedances (max. 63.8 mg/l)

[180] Cu: 14 exceedances (max. 13.9 mg/l)

[181] Cr – total: 2 exceedances (max. 1.5 mg/l)

[182] Ag: 3 exceedances (0.28 mg/l)

[183] Zn: 1 exceedance (1.7 mg/l)

Self-monitoring 2019							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Sn	mg/l	0,00	1[184]	1,00	0,32	1	220
SO_4	mg/l	1026,00	2146,00	1724,48	1324,46	–	29
Conductivity	µS/cm	1115,00	33500,00	11526,50	6235,26	–	220
Q	m^3/d	0,00	356,00	321,40	199,17	–	317

Source: Self-monitoring Collini GmbH, 2019

Table 117: External-monitoring of process wastewater 2017

External-monitoring 2017									
Parameter	**Unit**	**1**	**2**	**3**	**4**	**5**	**6**	**Limit of detection**	**Standard**
TOC	mg/l	18	77	54	13	55	10	1	EN 1484
TN	mg/l	86,4	5	4,7	4	65,5	58,4	0,5	EN 12260
TP	mg/l	345	608	2,3	276	332	59,1	0,05	EN ISO 11885
Cl	mg/l	1370	628	517	575	2710	241	1	EN ISO 10304
HC-Index	mg/l	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	0,05	EN ISO 9377-2

Source: ZT Rolf Boos, 2017

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[184] Sn: 3 exceedances (max. 1.7 mg/l)

Table 118: External-monitoring of process wastewater 2018

		External-monitoring 2018							
Para-meter	Unit	1	2	3	4	5	6	Limit of detection	Standard
TOC	mg/l	181	8,5	4,6	9,3	44	4,5	1	EN 1484
TN	mg/l	13,8	5,9	28,7	19,9	21,7	8,3	0,5	EN 12260
TP	mg/l	564	140	38,1	69,9	247	25,4	0,05	EN ISO 11885
Cl	mg/l	968	221	324	341	350	283	1	EN ISO 10304
HC-Index	mg/l	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	< 0,05	0,05	EN ISO 9377-2

Source: ZT Rolf Boos, 2018

Table 119: External-monitoring of process wastewater 2019

		External-monitoring 2019							
Para-meter	Unit	1	2	3	4	5	6	Limit of detection	Standard
TOC	mg/l	110	13	49	140	55	43	1	EN 1484
TN	mg/l	15	12,2	222	23	12,6	4,9	0,5	EN 12260
TP	mg/l	487	118	48,8	284	275	241	0,05	EN ISO 11885
Cl	mg/l	553	557	4000	5010	1360	232	1	EN ISO 10304
HC-Index	mg/l	< 0,05	<0,05	<0,05	<0,05	<0,05	0,05	0,05	EN ISO 9377-2

Source: ZT Rolf Boos, 2019

Table 120: External-monitoring of process wastewater 2017–2019

External-monitoring 2017–2019							
Parameter	**Unit**	**03.03.2017**	**06.04.2018**	**14.03.2019**	**ELV**	**Limit of detection**	**Standard**
Cr – total	mg/l	0,102	0,101	0,652	0,5	0,01	EN ISO 11885:2009
Cr(VI)	mg/l	< 0 ,050	0,09	< 0,050	–	0,05	EN ISO 18412:2006
CN – free	mg/l	< 0,0020	0,003	0,007	0,1	0,002	EN ISO 14403-2:2012
Cu	mg/l	0,023	0,18	< 0,010	0,5	0,01	EN ISO 11885:2009
Ni	mg/l	0,26	0,36	0,24	0,5	0,01	EN ISO 11885:2009
Ag	mg/l	< 0 ,010	< 0,010	< 0,010	0,1	0,01	EN ISO 11885:2009
Zn	mg/l	< 0,010	0,1	< 0,010	1	0,01	EN ISO 11885:2009
Sn	mg/l	< 0,010	1,37	0,21	1	0,01	EN ISO 11885:2009
SO_4	mg/l	969	1.040	714	–	1	EN ISO 10304-1:2009
pH		7,9	6,9	7,4	6,5–9,5	0,1	EN ISO 12523:2012

Source: ZT Rolf Boos, 2019

5.3 References

AEV Oberflächenbehandlung, BGBl. II Nr. 44/2002: Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Begrenzung von Abwasseremissionen aus der Behandlung von metallischen Oberflächen (AEV Oberflächenbehandlung), BGBl. II Nr. 44/2002

Environmental report Collini GmbH, 2019: Umwelterklärung der Collini GmbH Wien, Umweltdaten 2018

Laboraturium Umweltanalytik (2017): Bericht über die Messung der Emissionskonzentrationen von Schwebestaub sowie Chrom- und Nickelverbindungen im Schwebestaub an der Ausblasung der gefassten und gereinigten Abluft der Bäderabsaugungen der Collini Wien GmbH, Laboratorium Umweltanalytik GmbH, 2017

Laboraturium Umweltanalytik (2018): Emissionsmessung der BARA der Collini Wien GmbH, Laboratorium Umweltanalytik GmbH, 2018

ZT Rolf Boos (2017-2019): Untersuchung Abwasserprobe, Ziviltechnik Büro Rolf Boos, 2017-2019

STM BREF (2006): Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Surface Treatment of Metals and Plastics, European Commission, 2006

6 Doka GmbH

Doka GmbH is an expert in formwork technology. On the premise Amstetten an electroplating plant (acid zinc) and a cathodic dip-paint coating plant (CDC) is operated, next to other plants which are not relevant for this study. The coating plants are in-house coating plants, thus no external work pieces are coated on the premise. Both the electrolytic zinc coating and the CDC plant are IED plants.

Environmental Management System
Doka GmbH has an according to ISO 14001 certified environmental management system implemented.

6.1 Technical description

In the following the two relevant processes, i.e. electrolytic coating and CDC, are described separately.

Electroplating

- Acid zinc
- Passivation with Cr(III) and Cr(VI)

Pre-treatment
Pre-treatment comprises pickling, chemical aqueous (soak) degreasing, electrolytic degreasing and etching. After each process step rinsing is applied. Which and how many pre-treatment steps are passed depends on the work piece and the destined use of the work piece.

Electroplating
The coated work pieces are out of steel. The work pieces are coated with zinc in acid zinc electrolytes. The electrolytes contain zinc and chloride. The electrolytes are operated at room temperature. The work pieces pass the individual treatment steps on jigs or in drums.

After zinc electroplating the work pieces pass chromium conversion (passivation). Depending on the destined use of the work piece it passes either chromium conversion containing Cr(VI) or Cr(VI)-free chromium conversion. Predominantly workpieces that need a colored highlighting for a certain function are passivated with Cr (VI).

The entire electroplating unit (including pre- and post-treatment) is built into a collection tray.

Rinsing
After each process step the work piece is rinsed. Multiple stage counterflow rinsing units consisting of two or three steps are used in order to minimise water use. Excess water from the rinsing unit is fed back into the electroplating baths or into the degreasing baths. After zinc electroplating and chromium conversion the work piece passes three rinsing units out of which one is operated in a closed loop (using ion-exchangers). Excess rinsing water (which cannot be re-applied in process tanks), regenerates from the ion-exchanger and concentrates (e.g. from pickling) are sent in separate streams to the wastewater treatment plant. The streams are separated into acid/alkaline and Cr(VI) containing wastewater.

Waste gas treatment
Edge exhausts are installed at the edges of the pickling baths, electrolytic degreasing and the zinc electrolyte tanks. The extracted air passes an alkaline scrubber (NaOH) in order to minimise HCl emissions.

Bath life span
The process baths are regularly monitored and controlled in the in-house laboratory. This enables an accurate dosing of the needed chemicals and avoids excess use of chemicals. Iron hydroxide sludge is removed from the zinc electrolytes by filters in order to expand the process bath’s life span.

Process wastewater
Treated wastewater is discharged indirectly. Wastewaters from the electroplating unit are collected in separate streams, i.e. acidic/alkaline and Cr(VI) containing, and sent to the wastewater treatment plant (WWTP). Rejects from the pickling baths are collected separately in containers to enable a targeted use in the WWTP, e.g. for neutralising of alkaline wastewater. Wastewater from the on-site batch galvanising plant, i.e. excess

rinsing water, is also treated in the same WWTP but accounts for a smaller fraction of the total wastewater quantity.

- The WWTP consists of the following:
- Buffer tank for alkaline/acidic concentrates
- Buffer tank for Cr(VI) containing concentrates
- Buffer tank for the continuous-flow neutralisation
- Continuous-flow neutralisation with aeration tank and sludge sedimentation tank
- Batch neutralisation
- Filter press (sludge dewatering)
- Final neutralisation and pH end control

Continuous-flow neutralisation:
Wastewater from the ion exchanger from the rinsing unit and excess water from one rinsing bath is treated in the continuous-flow neutralisation. Via pH-monitoring the appropriate amount of sodium hydroxide solution and sodium carbonate solution is added automatically into the continuous-flow neutralisation. After neutralisation the treated wastewater is sent into an aeration tank where iron(II)hydroxide is oxidised into iron(III)hydroxide. Furthermore, a flocculation agent is added to facilitate the subsequent sedimentation. Sedimentation is carried out in a sedimentation tank. The accruing sludge is sent to the filter press (sludge dewatering). The clear water is sent to the final neutralisation step and pH end control before being discharged into the sewer.

Batch neutralisation:
Wastewater from pickling, degreasing, electroplating, passivation and rinsing are treated in the batch neutralisation unit. Wastewater containing Cr(VI) are collected in an individual stream. In the batch neutralisation unit the pH value is lowered to 2.5 using HCl or excess pickling solution. Cr(VI) gets reduced into Cr(III) by adding bisulphite. Once Cr(VI) reduction is completed (using rapid testers) the pH value is increased to 9 – 10 by adding sodium hydroxide and/or lime milk. This triggers the precipitation of the metals contained in the wastewater. It is important that the pH value is held stable for an appropriate time frame of ca. 20 minutes to ensure that the precipitation of metals is completed. After batch neutralisation, the wastewater is sent to the filter press. The dewatered sludge is disposed by external operators. The clear water is sent to the final neutralisation step and pH end control before being discharged into the sewer.

Final neutralisation:
In the final neutralisation step the pH value can be adjusted (if necessary) using HCl or NaOH.

Cathodic dip-paint coating (CDC)

In the CDC plant raw and zinc coated (hot dip coated, batch galvanised or electroplated) work pieces get coated. The CDC plant consists of the following parts:

- Pre-treatment
- CDC
- Dryer and cooling zone
- Automated jigs
- Wastewater treatment
- Exhaust air treatment
- Collection tray and chemicals storage

The entire CDC unit is enclosed. During normal operating conditions workers do not need to enter the enclosed CDC unit. Chemical dosing is usually automatic. Manual dosing can be done from outside the enclosed CDC unit.

Pre-treatment
Pre-treatment is carried out in dip and spray baths. Depending on the requirements for the certain workpiece the following pre-treatment steps can be applied:

- Alkaline degreasing (dip and spray)
- Acid pickling
- Activation with metal salt solution (for improving the zinc phosphate layer)
- Zinc phosphating (for corrosion protection and adhesive primer for the CDC layer)

After each pre-treatment step the work piece is rinsed. Multiple stage counterflow rinsing units consisting of two or three steps are used in order to minimise water use. For rinsing, water from the communal grid or desalinated water is used. Before the workpiece enters the CDC step it is rinsed with desalinated water.

Cathodic dip paint coating (CDC)
Paint particles dispersed in a water-based solution are deposited on immersed work

pieces under the influence of an electric field. The water is usually desalinated. Binding agents are added into the solution but need to be made water soluble with organic acids. The solvent content of a CDC paint is typically in the range of 2 – 4 %. The coating delivers corrosion protection as the combination of paint resin and deposition process create a very resistant film. In CDC the workpiece acts as cathode and the anodes are positioned in the process tank. (STS BREF Final Draft, 2019)

Separate CDC tanks (for different colours) with volumes of approx. 50 m^3 and an operation temperature of maximum 35 °C are in use. After the CDC step the workpiece passes three desalinated rinsing steps. Non-deposited paint particles are sent back into the CDC process bath.

Drying & cooling

After rinsing the electrodeposited paint film is cured in a drying oven at around 180 °C for about one hour. In order to reduce energy consumption the drying oven is isolated and has separate entrance and exit doors. The oven is charged with natural gas.

After drying the workpiece needs to be cooled down in a cooling unit. The cooling unit has ventilation with an air volume flow of about 70,000 m^3/h.

Waste gas treatment

Exhaust air inside the fully enclosed CDC plant is extracted via 4 ventilators of which each has a capacity of 15,000 m^3/h. The collected air is emitted over the rooftop.

The CDC process baths are equipped with exhaust air edge-extraction with a capacity of 1,500 m^3/h each. The collected air is sent to the drying oven.

The exhaust air from the drying oven is collected and sent to a RTO for reducing organic compounds. The combustion chamber temperature of the RTO is min. 750 °C. Temperature monitoring of the combustion chamber is carried out continuously. Waste heat from the RTO is used in the drying oven and to heat up water. This accounts approximately for 650 kW of recuperated heat.

Wastewater treatment

Treated wastewater is discharged indirectly. Wastewaters from the CDC plant are collected in separate streams, i.e. acidic/alkaline and wastewater containing paint, and sent to the wastewater treatment plant (WWTP). Wastewater from the CDC plant is treated in a separate WWTP. Rejects from the pickling baths are collected in containers to enable a targeted use in the WWTP, e.g. for neutralising of alkaline wastewater.

The WWTP consists of the following:

- Buffer tank for alkaline and acidic concentrates
- Buffer tank for paint containing concentrates
- Batch neutralisation
- Filter press (sludge dewatering)
- Sand filter
- Ion exchanger
- pH end control

Batch neutralisation:
In the batch neutralisation unit the pH value is lowered to ≤ 2.5 using HCl or excess pickling solution. Subsequently lime milk is added which triggers the precipitation of the metals contained in the wastewater. The pH value increases to 9 – 10 during precipitation. It is important that the pH value is held stable for ca. 20 minutes to ensure that the precipitation of metals is completed. For better sludge formation, iron-(III)-chloride can be added. For better sludge sedimentation, flocculation agents can be added.

Sludge dewatering:
After batch neutralisation, the wastewater is sent to a buffer tank for sludge dewatering. The settled sludge is dewatered using a filter press. The dewatered sludge is disposed by external operators. The accruing water from sludge dewatering is sent to the final treatment step. Clear water from the sludge dewatering buffer tank is pumped directly to the final treatment step.

Final treatment (sand filter, ion exchanger, pH end control):
Clear water from the sludge dewatering buffer tank and water from sludge dewatering is filtered in a sand filter before being treated in ion exchangers. Subsequently the treated wastewater passes pH end control and gets discharged into the sewer. In case that the pH value is not within the prescribed range, the discharge into the sewer is automatically stopped and an alarm is triggered.

6.2 Current consumption and emission levels

Electroplating

Specific consumption – electroplating

The specific energy and water consumption per m² of electroplated surface varies due to the requirements for the work piece and the shape of the work piece. Lowering energy and water consumption, whilst maintaining the required product quality, is in the interest of the operator, wherefore consumption parameters are monitored at several process steps. In general approximately 3.4 – 4.6 kWh/m² and 0.04 – 0.05 m³/m² (water) are consumed (per m² electroplated surface).

Generated residues from electroplating or linked to electroplating activities are listed in Table 121. The quantity of residues are from 2018.

Table 121: Residues linked to electroplating 2018

Type	Category	Unit	Quantity	Origin
Iron hydroxide (Sludge from neutralisation)	hazardous	t	69.54	WWTP
Acids, acid mixtures	hazardous	t	9.5	Pickling
Bases	hazardous	t	17.94	Degreasing
Concentrates containing metal salts (sludge from electroplating baths)	hazardous	t	0.4	Electroplating

Source: Doka, own recordings

Emissions to air – electroplating

Edge exhausts are installed at the edges of the pickling baths, electrolytic degreasing and the zinc electrolyte tanks. The extracted air passes an alkaline scrubber (NaOH) in order to minimise HCl emissions. The exhaust air unit has a capacity of 40,000–50,000 m³/h.

HCl emissions have to be monitored every five years by an accredited testing institute. The ELV is 30 mg/Nm³. The monitoring frequency and the ELV are prescribed in permit (12-B-9210).

Table 122 presents the monitoring results from 10.09.2015. The measurements were conducted during normal operating conditions. The calculated volume flow was 15,000 m³/h.

Table 122: Monitoring results of HCl emissions to air; 0 °C, 1013 mbar, dry exhaust air

Unit	HCl	ELV	Sampling period	Standard
mg/Nm³	3.2	30	Half hour measurement	ÖN EN 1911
mg/Nm³	4.0	30	Half hour measurement	ÖN EN 1911
mg/Nm³	3.8	30	Half hour measurement	ÖN EN 1911
mg/Nm³	3.7	30	Average – calculated	Calculated

Source: MAPAG, 2015

Emissions to water – electroplating

Treated process wastewater is discharged indirectly via the communal WWTP. Monitoring has to be conducted using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit. Minimum monitoring frequencies for self-monitoring (performed by operator) and external-monitoring are prescribed by permit (AMW2-BA-0446-048). Emission limit values (ELV) are prescribed by permit (AMW2-BA-0446/056).

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

On-site wastewater treatment consists of:

- Buffer tank for alkaline/acidic concentrates
- Buffer tank for Cr(VI) containing concentrates
- Buffer tank for the continuous-flow neutralisation
- Continuous-flow neutralisation with aeration tank and sludge sedimentation tank
- Batch neutralisation
- Filter press (sludge dewatering)
- Final neutralisation and pH end control

A detailed description of the on-site WWTP is presented in chapter 6.1.

Emissions to water from electroplating and batch galvanising are described in the following tables. In Table 123 the minimum monitoring frequencies and ELVs prescribed by permit are presented and compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. In Table 124, Table 125 & Table 126 the self-monitoring recordings of treated process wastewater are presented. Table 127 presents the results from external-monitoring of treated process wastewater for the years 2017, 2018 & 2019.

Table 123: Emission limit values for the process wastewater from electroplating and batch galvanising in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006) [185]	Ordinance (indirect discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Water quantity (Q)	m³/d	43.3	–	–	Every working day	Annually
pH		6.5–10.0	–	6.5–10.0	Every working day	Annually
Lead (Pb)	mg/l	0.5	0.05–0.5	0.5	Every working day	Annually
Chromium – total (Cr)	mg/l	0.5	0.1–2.0	0.5	Every working day	Annually
Cr(VI)	mg/l	0.1	0.1–0.2	0.1	Every working day	Annually
Copper (Cu)	mg/l	0.5	0.2–2.0	0.5	Every working day	Annually
Nickel (Ni)	mg/l	0.5	0.2–2.0	0.5	Every working day	Annually
Zinc (Zn)	mg/l	2.0	0.2–2.0	1.0[186]	Every working day	Annually
COD	mg/l	–	–	–	–	Annually
BOD_5	mg/l	–	–	–	–	Annually

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[185] Discharge to public sewer or surface water from jig, barrel, small scale coil, automotive, PCB and other activities not large scale steel coil

[186] For wastewaters from electroplating or batch galvanising the ELV is 2.0 mg/l

Source: Permit AMW2-BA-0446-0; Permit AMW2-BA-0446/056; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 124: Self-monitoring of treated process wastewater 2016

Self-monitoring 2016							
Parameter	**Unit**	**Daily min.**	**Daily max.**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Cr total	mg/l	0.00	0.45	0.19	0.05	0.50	148.00
Cr(VI)	mg/l	0.00	0.00	0.00	0.00	0.10	11.00
Cu	mg/l	0.00	0.40	0.04	0.02	0.50	148.00
Ni	mg/l	0.00	0.32	0.19	0.09	0.50	148.00
Pb	mg/l	0.00	0.34	0.06	0.01	0.50	148.00
pH		6.50	9.35	8.77	8.17	6.5–10.0	148.00
Zn	mg/l	0.00	1.90	0.35	0.10	2.00	148.00

Source: Self-monitoring Doka, 2016

Table 125: Self-monitoring of treated process wastewater 2017

Self-monitoring 2017							
Parameter	**Unit**	**Daily min.**	**Daily max.**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Cr total	mg/l	0.00	0.30	0.20	0.06	0.50	145.00
Cr(VI)	mg/l	0.00	0.01	0.00	0.00	0.10	53.00
Cu	mg/l	0.00	0.14	0.07	0.02	0.50	145.00
Ni	mg/l	0.00	0.04	0.04	0.01	0.50	145.00
Pb	mg/l	0.00	0.10	0.04	0.01	0.50	144.00
pH		7.71	9.29	9.00	8.56	6.5–10.0	145.00
Zn	mg/l	0.00	0.60	0.10	0.04	2.00	145.00

Source: Self-monitoring Doka, 2017

Table 126: Self-monitoring of treated process wastewater 2018

Self-monitoring 2018							
Parameter	**Unit**	**Daily min.**	**Daily max.**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Cr total	mg/l	0.00	0.24	0.18	0.10	0.50	168.00
Cr(VI)	mg/l	0.00	0.00	0.00	0.00	0.10	25.00
Cu	mg/l	0.00	0.07	0.00	0.00	0.50	168.00
Ni	mg/l	0.00	0.13	0.07	0.01	0.50	168.00
Pb	mg/l	0.00	0.04	0.02	0.00	0.50	168.00
pH		6.68	9.10	8.95	8.61	6.5–10.0	168.00
Zn	mg/l	0.00	1.38	0.12	0.04	2.00	168.00

Source: Self-monitoring Doka, 2018

Measurements below the limit of detection are represented by the value 0.00 mg/l in the self-monitoring records.

Table 127: External-monitoring of process wastewater from electroplating and batch galvanising

External-monitoring 2017 & 2018						
Parameter	**Unit**	**27.09.2017**	**09.10.2018**	**Standard**	**ELV Permit**	**Limit of detection**
Q	m³/d	23.3	36		43.3	
T	°C	19.4	20.1	DIN 38404-4	–	
pH		8.7	8.6	DIN EN ISO 10523	6.5–10.0	0
Pb	mg/l	< 0.01	< 0.01	EN ISO 11885	0.5	0.01
Cr total	mg/l	< 0.01	< 0.01	EN ISO 11885	0.5	0.01
Cr (VI)	mg/l	< 0.05	< 0.05	EN ISO 18412	0.1	0.05
Cu	mg/l	< 0.01	< 0.01	EN ISO 11885	0.5	0.01
Ni	mg/l	< 0.01	< 0.01	EN ISO 11885	0.5	0.01

External-monitoring 2017 & 2018

Parameter	Unit	27.09.2017	09.10.2018	Standard	ELV Permit	Limit of detection
Zn	mg/l	0.019	0.02	EN ISO 11885	2.0	0.01
COD	mg/l	254	353	ÖNORM M 6265	–	10
BOD_5	mg/l	35	64	EN 1899-1	–	3

External-monitoring 2019

Parameter	Unit	16.09.2019	Standard	ELV Permit	Limit of detection
Q	m^3/d			43.3	
T	°C	25.5	DIN 38404-4	–	
pH		9	DIN EN ISO 10523	6.5–10.0	0
Pb	mg/l	< 0.001	EN ISO 17294-2	0.5	0.001
Cr total	mg/l	< 0.001	EN ISO 17294-2	0.5	0.001
Cr (VI)	mg/l	< 0.05	EN ISO 18412	0.1	0.05
Cu	mg/l	< 0.001	EN ISO 17294-2	0.5	0.001
Ni	mg/l	0.002	EN ISO 17294-285	0.5	0.001
Zn	mg/l	0.023	EN ISO 17294-2885	2.0	0.01
COD	mg/l	286	ÖNORM M 6265	–	10
BOD5	mg/l	57	EN 1899-1	–	3

Source: Agrolab Austria GmbH, 2017–2019

Cathodic dip-paint coating (CDC)

Specific consumption – CDC

The specific energy and water consumption per m² of cathodic dip-paint coated surface varies due to the requirements for the work piece and the shape of the work piece. Lowering energy and water consumption, whilst maintaining the required product quality, is in the interest of the operator, wherefore consumption parameters are monitored at several process steps. In general approximately 2 – 3.5 kWh/m² and 0.02 – 0.03 m^3/m^2 (water) are consumed (per m² coated surface).

Table 128: Residues linked to electroplating 2019

Type	Category	Unit	Quantity	Origin
:Sludge from zinc phosphating	hazardous	t	4.9	Zinc phosphating
Acids, acid mixtures	hazardous	t	165	Pickling, activation, zinc phosphating (cleaning)
Bases	hazardous	t	92	Degreasing
Paint sludge	hazardous	t	0.37	CDC
Sludge from WWTP	Non-hazardous	t	60.4	WWTP

Source: Doka, own recordings

Emissions to air – CDC

Exhaust air inside the fully enclosed CDC plant is extracted via 4 ventilators of which each has a capacity of 15,000 m^3/h. The collected air is emitted over the rooftop. The CDC process baths are equipped with exhaust air edge-extraction with a capacity of 1,500 m^3/h each. The collected air is sent to the drying oven.

The exhaust air from the drying oven is collected and sent to a RTO. Waste heat from the RTO is used in the drying oven and to heat up water (approx. 650 kW).

The combustion chamber temperature of the RTO has to be at least 750 °C and has to be monitored continuously, as prescribed by permit AMW2-BA-0446/043.

The ELVs for CO, NOx, TVOC and dust are set by permit AMW2-BA-0446/043. Monitoring has to be carried out at least all 3 years.

Table 129 presents the monitoring results from 24.09.2019. The measurements were conducted during normal operation conditions. The calculated volume flow was 3,200 m^3/h (at standard conditions; corresponds to 6,100 m^3/h at operating conditions).

Table 129: Monitoring results of emissions to air; 0 °C, 1013 mbar, dry exhaust air

Half-hour measurement	O_2 vol. %	CO mg/Nm³	NO_x mg/Nm³	TVOC mg/Nm³	Dust mg/Nm³
1	19.5	24	40	2	< 1
2	19.6	9	34	< 2	< 1
3	19.5	22	36	< 2	< 1
Average	19.5	18	37	< 2	< 1
ELV		100	100	20	5

Source: MAPAG, 2019; AMW2-BA-0446/043

Emissions to water – CDC

Treated process wastewater is discharged indirectly via the communal WWTP. Monitoring has to be conducted using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit. Minimum monitoring frequencies for self-monitoring (performed by operator) and external-monitoring are prescribed by permit. Emission limit values (ELV) are prescribed by permit (AMW2-BA-0446/043).

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

On-site wastewater treatment consists of:

- Buffer tank for alkaline and acidic concentrates
- Buffer tank for paint containing concentrates
- Batch neutralisation
- Filter press (sludge dewatering)
- Sand filter
- Ion exchanger
- pH end control

A detailed description of the on-site WWTP is presented in chapter 6.1.

Emissions to water from CDC are described in the following tables. In Table 130 the minimum monitoring frequencies and ELVs prescribed by permit are presented and compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. In Table 131, Table 132 & Table 133 the self-monitoring recordings of treated process wastewater are presented. Table 134 presents the results from external-monitoring of treated process wastewater for the years 2017, 2018 & 2019.

Table 130: Emission limit values for the process wastewater from CDC in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)[187]	Ordinance (indirect discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Water quantity (Q)	m³/d	106.4	–	–	Daily	Annually
Temperature (T)	°C	35	–	35	Daily	Annually
pH		6.5–10.0	–	6.5–10.0	Daily	Annually
Zinc	mg/l	1.0	0.2–2.0[188]	1.0	Daily	Annually
Chromium – total (Cr)	mg/l	0.5	0.1–2.0	0.5	Daily	Annually
Copper (Cu)	mg/l	0.5	0.2–2.0	0.5	Daily	Annually
Nickel (Ni)	mg/l	0.5	0.2–2.0	0.5	Daily	Annually
Lead (Pb)	mg/l	0.5	0.05–0.5	0.5	Daily	Annually
Fluoride (F)	mg/l	20	10–20	20	Daily	Annually
Nitrite (NO_2-N)	mg/l	10	–	10	Daily	Annually
Sum of hydrocarbons	mg/l	15	–	15	–	Annually
CSB	mg/l	–	–	–	–	Annually
BOD_5	mg/l	–	–	–	–	Annually

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[187] Discharge to public sewer or surface water from jig, barrel, small scale coil, automotive, PCB and other activities not large scale steel coil

[188] For wastewaters from electroplating or batch galvanising the ELV is 2.0 mg/l

Source: Permit AMW2-BA-0446/043; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 131: Self-monitoring of treated process wastewater 2017

Self-monitoring 2017							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Cr total	mg/l	0.00	0.29	0.14	0.05	0.50	64
Cu	mg/l	0.00	0.16	0.16	0.04	0.50	64
F	mg/l	0.00	20.00	10.00	4.38	20.00	64
Ni	mg/l	0.00	0.26	0.12	0.04	0.50	64
NO_2-N	mg/l	0.00	3.04	3.04	1.20	10.00	61
Pb	mg/l	0.00	0.10	0.10	0.04	0.50	64
pH		6.65	9.97	8.62	7.49	6.5–10.0	64
Temp.	°C	21.00	28.00	27.00	24.01	35°C	62
Zn	mg/l	0.00	0.13	0.07	0.01	1.0	64

Source: Self-monitoring Doka, 2017

Table 132: Self-monitoring of treated process wastewater 2018

Self-monitoring 2018							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Cr total	mg/l	0.04	0.23	0.15	0.09	0.50	81
Cu	mg/l	0.00	0.00	0.00	0.00	0.50	81
F	mg/l	0.00	10.50	10.01	4.55	20.00	80
Ni	mg/l	0.00	0.40	0.12	0.05	0.50	81
NO_2-N	mg/l	0.00	4.57	3.04	1.26	10.00	79
Pb	mg/l	0.00	0.06	0.03	0.00	0.50	81
pH		6.91	9.85	8.58	7.74	6.5–10.0	81

Self-monitoring 2018 Parameter	Unit	Daily min	Daily max	95 Percentile	Annual average	ELV Permit	Number of samples
Temp.	°C	19.90	28.20	27.00	24.22	35°C	80
Zn	mg/l	0.00	0.09	0.03	0.01	1.00	81

Source: Self-monitoring Doka, 2018

Table 133: Self-monitoring of treated process wastewater 2019

Self-monitoring 2019 Parameter	Unit	Daily min	Daily max	95 Percentile	Annual average	ELV Permit	Number of samples
Cr total	mg/l	0.00	0.32	0.16	0.08	0.50	95
Cu	mg/l	0.00	0.03	0.01	0.00	0.50	95
F	mg/l	0.30	13.59	10.90	6.80	20.00	95
Ni	mg/l	0.00	0.49	0.19	0.06	0.50	95
NO_2-N	mg/l	0.00	6.09	3.04	0.86	10.00	95
Pb	mg/l	0.00	0.12	0.05	0.01	0.50	95
pH		6.38	9.42	8.63	7.63	6.5–10.0	95
Temp.	°C	18.00	32.00	26.88	24.08	35°C	93
Zn	mg/l	0.00	0.19	0.06	0.01	1.00	95

Source: Self-monitoring Doka, 2018

Measurements below the limit of detection are represented by the value 0.00 mg/l in the self-monitoring records.

Table 134: External-monitoring of process wastewater from CDC

External-monitoring 2017 & 2018

Parameter	Unit	27.09.2017	09.10.2018	Standard	ELV Permit	Limit of detection
Q	m^3/d	26.0	37.0		43.3	
T	°C	23.1	23.0	DIN 38404-4	–	
pH		7.8	8.5	DIN EN ISO 10523	6.5–10.0	0
Pb	mg/l	< 0.01	< 0.01	EN ISO 11885	0.5	0.01
Cr total	mg/l	< 0.01	< 0.01	EN ISO 11885	0.5	0.01
Cu	mg/l	< 0.01	0.013	EN ISO 11885	0.5	0.01
Ni	mg/l	0.04	0.17	EN ISO 11885	0.5	0.01
Zn	mg/l	< 0.01	0.01	EN ISO 11885	2.0	0.01
F	mg/l	8.7	10.4	EN ISO 10304-1	15	0.05
NO_2-N	mg/l	7.39	2.6	EN 26777	10	0.01
COD	mg/l	357	419	ÖNORM M 6265	–	10
BOD_5	mg/l	136	138	EN 1899-1	–	3
Sum of hydrocarbons (2017)	mg/l	0.17	–	DIN 38409-18	15	0.1
Sum of hydrocarbons (2018)	mg/l	–	< 0.05	EN ISO 9377-2	15	0.05

External-monitoring 2019

Parameter	Unit	17.09.2019	Standard	ELV Permit	Limit of detection
Q	m^3/d	17.2		43.3	
T	°C	25.9	DIN 38404-4	–	
pH		6.7	DIN EN ISO 10523	6.5–10.0	0
Pb	mg/l	< 0.001	EN ISO 17294-2	0.5	0.001
Cr total	mg/l	0.016	EN ISO 17294-2	0.5	0.001
Cu	mg/l	< 0.001	EN ISO 17294-2	0.5	0.001
Ni	mg/l	0.44	EN ISO 17294-2	0.5	0.001

External-monitoring 2017 & 2018						
Parameter	**Unit**	**27.09.2017**	**09.10.2018**	**Standard**	**ELV Permit**	**Limit of detection**
Zn	mg/l	< 0.01		EN ISO 17294-2	2.0	0.01
F	mg/l	5.7		EN ISO 10304-1	15	0.05
NO_2-N	mg/l	3.2		EN 26777	10	0.01
COD	mg/l	1130		ÖNORM M 6265	–	10
BOD_5	mg/l	406		EN 1899-1	–	3
Sum of hydrocarbons	mg/l	0.14		EN ISO 9377-2	15	0.05
Q	m^3/d	17.2			43.3	
T	°C	25.9		DIN 38404-4	–	

Source: Agrolab Austria GmbH, 2017–2019

6.3 References

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STM BREF (2006): Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Surface Treatment of Metals and Plastics, European Commission, 2006

STS BREF, Final Draft (2019): Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Surface Treatment Using Organic Solvents including Wood and Wood Products Preservation with Chemicals, Final Draft, European Commission, 2019

7 Henkel Beiz-& Elektropoliertechnik Betriebs-GmbH

Henkel Beiz- und Elektropoliertechnik is a specialist in chemical and electrochemical surface treatment of metals. Henkel Beiz- und Elektropoliertechnik operates facilities in Germany, Hungary and Austria. On the premise Waidhofen (AT) pickling, electropolishing is carried out. The plant is an IED plant (Annex I 2.6).

7.1 Technical description

On the premise Waidhofen (AT) electropolishing and pickling of precious metals is carried out. In the following the processes are described.

Electropolishing

Electropolishing is a commonly used electrochemical method for smoothing, polishing, deburring and cleaning various metals, generally steel, stainless steel, copper and its alloys and aluminium and its aluminium alloys. It is widely used in food equipment, surgical equipment and implants, the pharmaceutical, paper, pulp and food industries, as well as in automotive and architectural applications. Electropolishing removes a fine surface layer electrolytically, and is often used in cases where very smooth and bright finishes are needed. In electropolishing, the workpiece (anode) is immersed in electrolyte and electric current (usually DC) is connected between the workpiece and the cathode. The workpiece becomes polarised and metal ions start to diffuse to the cathode, and metal is removed from the anode. The reaction can be controlled by adjusting bath and process parameters and by choosing the metal or alloy being electropolished. (STM BREF, 2006)

In these electropolishing processes, different electrolytes are used. Electrolytes are usually mixtures of various acids (sulphuric acid, chromic acid, citric acid, and/or phosphoric acid) and sometimes organic compounds (such as glycerine, tartaric acid or diethyleneglycolmonobutylether) are added. (STM BREF, 2006)

On the premise Waidhofen, work pieces of various size are electropolished. Furthermore, pipes are electropolished (inside and outside).

During electropolishing of stainless steels, hydrogen is formed, which mixes with oxygen at the solution surface. If the free flow off is prohibited and an ignition by a spark is possible, this can produce an explosion.

Pickling of precious metals

Pickling is a chemical metal-stripping procedure used to brighten and/or remove oxides from metallic surface. Prior to pickling the work pieces needs to be degreased. During the pickling process disturbed or adhering layers, such as scale, oxide films and other corrosion products of the metal, are removed by chemical reaction with an acid based pickling agent. In order to remove strong oxide layers effectively, specified acid concentrations, temperature and pickling times must be adhered to. Hydrochloric or sulphuric acids are normally used. In special cases nitric, hydrofluoric or phosphoric acid, or mixtures of acids are used. (STM BREF, 2006)

During pickling some erosion of the metallic surface is desirable, but excessive attack of the acid on the work piece is unwanted. Hydrogen is usually formed during pickling. The attack can be reduced by using so-called pickling inhibitors. These also cause an inhibition of hydrogen development, thus minimising so-called hydrogen (or pickling) embrittlement, caused by entrapment of hydrogen in the metal crystalline structure at the surface. (STM BREF, 2006)

The concentration of the ions of the dissolved metal increase in the pickling solution while the strength of the free acid declines. The acid consumption associated with the dissolution of metal and metal oxide can be supplemented by adding fresh pickling solution. However, this technique is limited by the constantly increasing metal content. A maximum iron content of 8 % is recommended for sulphuric acid, 12 % for hydrochloric acid and 2.5 % for phosphoric acid. When the limiting concentrations are reached, the pickling solution is disposed of completely or partly. (STM BREF, 2006)

The workpieces to be pickled must be completely grease-free, otherwise uneven pickling will occur as the acid attacks grease-free areas only. The use of wetting agents accelerates the pickling procedures as the workpieces are wetted better and more quickly. Iron materials can be de-rusted and descaled in so-called acid degreasing agents without prior degreasing. The commercial acid degreasing agents contain mixtures of wetting agents and emulsifying agents, which can support the emulsification of fats and oils in strong acid media. (STM BREF, 2006)

Process tanks need to be equipped with fume extraction to remove generated aerosols and hydrochloric acid gas and nitrous oxides. Spent pickling solutions require either treatment and disposal through an effluent treatment system or disposal as liquid wastes.

Rinsing

After each process step the work piece is rinsed. Eco-rinse units and multiple stage counterflow rinsing units consisting of two or three steps are used in order to minimise water use.

Waste gas

Edge exhausts are installed at the edges of the process baths. The collected waste gas is treated with a demister before being emitted via stack.

Process wastewater

Treated process wastewater is discharged directly into the river Thaya. The WWTP consists of the following:

- Buffer tank
- Batch neutralisation
- pH adjustment with lime milk
- flocculation agent
- Sedimentation
- 2 basins
- Chamber filter press
- Final neutralisation
- Sand filter
- Ion exchange resin

7.2 Current consumption and emission levels

Waste generation

Generated residues are listed in Table 135. The quantity of residues are from 2016. Cr(VI) containing concentrates do not accrue as waste anymore, as Cr(VI) use has been phased out in 2017.

In 2018 an analysis of the metal hydroxide sludge from wastewater treatment has been done. The measurements have been compared to ELVs from the ordinance on landfills. Table 136 and Table 137 present the results of the analysis.

Table 135: Generated waste 2016

Type	Unit	Quantity	Origin	hazardous
Industrial waste	t	7.05	Entire production	no
Scrap iron	t	0.149	Electro polishing; workshop (repair shop)	no
Acid mixtures	t	36.4	Electropolishing	yes
Metal hydroxide sludge	t	127.5	WWTP	no
Concentrate – Cr(VI) containing	t	9.29	Electropolishing	yes

Source: Henkel, own recordings

Table 136: Analysis of metal hydroxide sludge 2018

Analysis of metal hydroxide sludge					
Parameter	**Unit**	**Measurement**	**ELV – Ordinance on landfills**	**% of ELV**	**Assessment**
Cr – total	mg/kg dry material	5100	8000	63.80%	relevant
Cu	mg/kg dry material	1010	5000	20.20%	relevant
Ni	mg/kg dry material	1340	2000	67.00%	relevant

Source: MAPAG, 2018

Table 137: Analysis of eluates from metal hydroxide sludge 2018

Analysis of eluates					
Parameter	**Unit**	**Measurement**	**ELV – Ordinance on landfills**	**% of ELV**	**Assessment**
pH		7.6	6–13	–	relevant
Conductivity	mS/m	386	–	–	–
Total dissolved solids	mg/kg dry material	4000	100000	40%	relevant
Molybdenum (Mo)	mg/kg dry material	19.4	30	64.70%	relevant
Ni	mg/kg dry material	9.2	40	23.00%	relevant
Nitrite	mg/kg dry material	74	1000	7.40%	not critical
SO_4	mg/kg dry material	18900	25000	75.60%	relevant

Source: MAPAG, 2018

Emissions to air

Waste gas is collected (edge exhausts at process baths) and treated with a demister before being emitted via stack.

Table 138 – Table 140 present the monitoring results from 25.11.2010. The measurements were conducted during normal operating conditions. At the time work pieces out of chrome-nickel-steel were treated. Three half-hourly measurements were done. In the tables below the averages of the three half-hourly measurements are presented. Measurement results were compared to ELVs from TA Luft (2002).

Table 138: Monitoring results of emissions to air from electropolishing (pipe unit); 0 °C, 1013 mbar, dry exhaust air

Electropolishing – pipe unit				
Parameter	**Unit**	**Average (3 half-hourly measurements)**	**ELV (TA Luft 2002)**	**Standard**
Q	Nm³/h	410	–	–
Concentrations				
H_2SO_4	mg/Nm³	< 0.9	1	ISO 21438-2
SO_x	mg/Nm³	1.4	350	VDI 2462
Loads				
H_2SO_4	g/h	0.37	–	calculated
SO_x	g/h	0.57	1800	calculated

Source: Rettensteiner, 2010

Table 139: Monitoring results of emissions to air from electropolishing; 0 °C, 1013 mbar, dry exhaust air

Electropolishing				
Parameter	**Unit**	**Average (3 half-hourly measurements)**	**ELV (TA Luft 2002)**	**Standard**
Q	Nm³/h	850	–	–
Concentrations				
H_2SO_4	mg/Nm³	< 0.7	1	ISO 21438-2
SO_x	mg/Nm³	< 0.4	350	VDI 2462
H_3PO_4	mg/Nm³	< 0.7	–	ISO 21438-2
Loads				
H_2SO_4	g/h	< 0.6	–	calculated
SO_x	g/h	< 0.3	1800	calculated

Electropolishing				
Parameter	**Unit**	**Average (3 half-hourly measurements)**	**ELV (TA Luft 2002)**	**Standard**
H_3PO_4	g/h	< 0.35	–	calculated

Source: Rettensteiner, 2010

Table 140: Monitoring results of emissions to air from electropolishing; 0 °C, 1013 mbar, dry exhaust air

Pickling				
Parameter	**Unit**	**Average (3 half-hourly measurements)**	**ELV (TA Luft 2002)**	**Standard**
Q	Nm^3/h	8230		–
Concentrations				
HNO_3	mg/Nm^3	< 0.8	–	ISO 21438-2
NO	mg/Nm^3	2.7	–	VDI 2456
NO_2	mg/Nm^3	4.7	–	VDI 2456
NO_x	mg/Nm^3	8.8	350	VDI 2456
HF	mg/Nm^3	0.51	3	VDI 2470-1
Loads				
HNO_3	g/h	< 6.6	–	calculated
NO	g/h	22.2	–	calculated
NO_2	g/h	59.3	–	calculated
NO_x	g/h	81.5	1800	calculated
HF	g/h	4.2	15	calculated

Source: Rettensteiner, 2010

Emissions to water

Treated process wastewater is discharged directly into the river Thaya. Monitoring has to be conducted using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit. Minimum monitoring frequencies for self-monitoring (performed by operator) and external-monitoring are prescribed by permit. Emission limit values (ELV) are prescribed by permit.

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

The WWTP consists of:

- Buffer tank
- Batch neutralisation
  - pH adjustment with lime milk
  - flocculation agent
- Sedimentation
  - 2 basins
- Chamber filter press
- Final neutralisation
- Sand filter
- Ion exchange resin

Emissions to water are described in the following tables. In Table 141 the minimum monitoring frequencies and ELVs prescribed by permit are presented and compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. In Table 142 – Table 144 the self-monitoring recordings of treated process wastewater are presented. Table 145 – Table 147 present the results from external-monitoring of treated process wastewater for the years 2018, 2019 & 2020.

Table 141: Emission limit values for the process wastewater in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)	Ordinance (direct discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Q	m^3/d	30	–	–	–	Yearly
TSS	mg/l	50	5–30	30[189]	–	Yearly
Settleable substances	ml/l	0.3	–	–	–	Yearly
pH		6.5–9.0	–	6.5–9.0	Weekly	Yearly
Cadmium (Cd)	mg/l	0.1	0.1–0.2	0.1	–	Yearly
Chromium total	mg/l	0.5	0.1–2.0	0.5	Weekly	Yearly
Cr(VI)	mg/l	0.1	0.1–0.2	0.1	Weekly (if Cr total is higher than 0,1)	Yearly
Copper (Cu)	mg/l	0.5	0.2–2.0	0.5	–	Yearly
Nickel (Ni)	mg/l	0.5	0.2–2.0	0.5	Weekly	Yearly
Zinc (Zn)	mg/l	1	0.2–2.0	1	–	Yearly
COD	mg/l	100	100–500	100	Weekly	Yearly
POX	mg/l	0.1	–	–	–	Yearly

Source: NUA Umwelt, 2018; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Cr(VI) concentration in the process wastewater needs to be measured if Cr – total is above 0.1 mg/l in the effluent.

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[189] TSS emissions to water from wastewater containing mainly suspended inorganic solids can be up to 50 mg/l according to the general ordinance on wastewater emissions

Measurements above the ELV or exceedances occurred during start-up phase after company holidays.

Table 142: Self-monitoring of process wastewater 2018

Self-monitoring 2018							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
pH		6.61	8.43	8.32	7.53	6.5 – 9.0	53
COD	mg/l	65.50	99.40	98.40	91.76	100.0	53
Ni	mg/l	0.17	0.47	0.43	0.37	0.5	61
Cr – total	mg/l	0.05	0.47	0.22	0.10	0.5	53
Cr (VI)	mg/l	0.04	0.09	0.09	0.06	0.1	11
TOC	mg/l	48.60	122.00	85.24	73.79	–	52

Source: Henkel, own recordings

Table 143: Self-monitoring of process wastewater 2019

Self-monitoring 2019							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
pH		6.50	7.94	7.81	7.42	6.5–9.0	53
COD	mg/l	75.30	98.30	97.07	90.89	100.0	54
Ni	mg/l	0.27	0.47	0.45	0.38	0.5	54
Cr – total	mg/l	0.03	0.21	0.08	0.06	0.5	53
TOC	mg/l	42.40	66.30	65.84	58.93	–	53

Source: Henkel, own recordings

Table 144: Self-monitoring of process wastewater 2020

Self-monitoring 2020							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
pH		6.83	7.81	7.71	7.38	6.5–9.0	56
COD	mg/l	59.10	99.30	98.54	90.01	100.0	55
Ni	mg/l	0.31	0.44	0.43	0.38	0.5	60
Cr	mg/l	0.03	0.22	0.08	0.07	0.5	53
TOC	mg/l	50.80	67.90	66.00	61.57	–	53

Source: Henkel, own recordings

Table 145: External-monitoring of process wastewater 2018

Parameter	Unit	12.09.2018	ELV	Standard
pH		7	6.5–9.0	EN ISO 10523
Settleable substances	ml/l	< 0.1	0.3	ÖNORM M6271
TSS	mg/l	37	50	ÖNORM M6274
Cd	mg/l	0.009	0.1	EN ISO 17294-2
Cr – total	mg/l	0.12	0.5	EN ISO 17294-2
Cr(VI)	mg/l	< 0.05	0.1	colorimetric – on-site
Cu	mg/l	0.051	0.5	EN ISO 17294-2
Ni	mg/l	0.5	0.5	EN ISO 17294-2
Zn	mg/l	0.02	1	EN ISO 17294-2
POX	mg/l	< 0.0 1	0.1	E DEV H25
AOX	mg/l	0.03	–	EN ISO 9562
COD	mg/l	97	100	ÖNORM M6265

Source: NUA Umwelt, 2018

Table 146: External-monitoring of process wastewater 2019

Parameter	Unit	03.10.2019	ELV	Standard
pH		6.9	6.5–9.0	EN ISO 10523
Settleable substances	ml/l	< 0.1	0.3	ÖNORM M6271
TSS	mg/l	10	50	ÖNORM M6274
Cd	mg/l	0.004	0.1	EN ISO 17294-2
Cr – total	mg/l	0.08	0.5	EN ISO 17294-2
Cr(VI)	mg/l	< 0.05	0.1	colorimetric – on-site
Cu	mg/l	0.041	0.5	EN ISO 17294-2
Ni	mg/l	0.5	0.5	EN ISO 17294-2
Zn	mg/l	0.02	1	EN ISO 17294-2
POX	mg/l	< 0.01	0.1	E DEV H25
AOX	mg/l	0.03	–	EN ISO 9562
COD	mg/l	< 15	100	ÖNORM M6265

Source: NUA Umwelt, 2019

Table 147: External-monitoring of process wastewater 2020

Parameter	Unit	29.11.2020	ELV	Standard
pH		7.4	6.5–9.0	EN ISO 10523
Settleable substances	ml/l	< 0.1	0.3	ÖNORM M6271
TSS	mg/l	6.6	50	ÖNORM M6274
Cd	mg/l	0.002	0.1	EN ISO 17294-2
Cr – total	mg/l	0.084	0.5	EN ISO 17294-2
Cr(VI)	mg/l	< 0.05	0.1	colorimetric – on-site
Cu	mg/l	0.018	0.5	EN ISO 17294-2

Parameter	Unit	29.11.2020	ELV	Standard
Ni	mg/l	0.37	0.5	EN ISO 17294-2
Zn	mg/l	< 0.1	1	EN ISO 17294-2
POX	mg/l	< 0.01	0.1	E DEV H25
AOX	mg/l	0.12	–	EN ISO 9562
COD	mg/l	22	100	ÖNORM M6265

Source: NUA Umwelt, 2020

7.3 References

AEV Oberflächenbehandlung, BGBl. II Nr. 44/2002: Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Begrenzung von Abwasseremissionen aus der Behandlung von metallischen Oberflächen (AEV Oberflächenbehandlung), BGBl. II Nr. 44/2002

MAPAG (2018): Prüfbericht Metallhydroxidschlamm der Firma Henkel, MAPAG, 2018

NUA Umwelt (2018-2020): Prüfbericht über die Abwasseruntersuchung der Firma Henkel, NUA Umwelt, 2018-2020

Rettensteiner (2010): Prüfbefund über die Emissionen aus relevanten Anlagen der Firma Henkel, Arno Rettensteiner, 2010

STM BREF (2006): Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Surface Treatment of Metals and Plastics, European Commission, 2006

STS BREF, Final Draft (2019): Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Surface Treatment Using Organic Solvents including Wood and Wood Products Preservation with Chemicals, Final Draft, European Commission, 2019

8 Lahner KG

Lahner KG Oberflächentechnik is a specialist sub-contractor (jobbing shop) offering a variety of different types of electroplating and coatings for various work pieces, i.e.

- Hard chromium plating
- Nickel electroplating
- Acid zinc electroplating
- Anodising
- Phosphating layer conversion coatings

8.1 Technical description

In the following the different types of electroplating and coating taken place on site are described below.

Hard chromium plating

Hard chromium plating is a functional coating that consists of heavy deposits (thick layer) to ensure high resistance to mechanical and wear damage. Hard chromium electrolytes are based on Cr(VI) and different catalysts i.e. sulphuric acid, hexafluorosilicates, methanesulfonic acid. For significant improving of the corrosion protection the work piece can be (electro)plated with e.g. nickel before hard chromium plating or hard chromium plating can be varied resulting in duplex or triplex hard chromium layers.

Hexavalent chromium has adverse health effects, causing skin and mucus membrane irritation and certain cancers (STM BREF, 2006). Aerosols are generated from Cr(VI) process solutions by a significant hydrogen evolution at the cathode. Thus workplace health and safety regulations require measures to meet maximum allowable concentrations. For meeting these regulations, fume suppressants are used to reduce the amount of aerosol. Fume suppressants were usually based on PFOS which is toxic and persistent (STM RBEF, 2006).

Today the use of PFOS-free fume suppressants is state of the art.

At Lahner KG a PFOS-free fume suppressant is in use.

Cr (VI) is also soluble at a wide range of pH-values, contributing to high aquatic toxicity (STM BREF, 2006). Therefore it must be reduced to trivalent chromium first before precipitating in wastewater treatment plants. Solid sodium disulfite ((Na2S2O5) forming with water into sodium hydrogen sulfite) is typically used for the reduction of Cr (VI) to Cr (III). At Lahner KG Cr (VI) reduction is done using sodium dithionite (Na2S2O4) due to the low concentration of Cr (VI) in the wastewater. Further, the use of sodium hydrogen sulfite increases the salinity of the wastewater.

Pre-treatment

Work pieces which undergo hard chromium plating have a significant dimension and are moved by a crane system. Cleaning is done manually by applying organic solvents, alkaline solutions or preferably lime (Viennese lime). Etching is done with diluted sulphuric acid or straight in the hard chromium process bath.

Hard chromium plating

Hard chromium plating is carried out in three baths. The baths are covered by a lid and equipped with edge exhaust air extraction. Rinsing is done above the process bath, so that the process solution re-enters into the process bath

Rinsing

In a first step the work piece is rinsed above the process bath. Depending on the product requirements and the size (geometry) of the work piece, it can be further rinsed in static rinsing units.

Closing the loop

Rinsing water from the static rinsing unit, as well as the rinsing water from rinsing above the process bath re-enters the process bath, so that evaporation losses of the process solution are compensated. Refilling the static rinse units is done with fresh water. Water from the exhaust air scrubbers from hard chromium plating re-enters the process bath as well. These measures enable a closed loop in hard chromium plating of almost 95 % depending on the shape of the work piece and the temperature of the process bath.

Waste gas treatment

Exhaust air is extracted at the edges of the process baths. Exhaust air from hard chromium plating is sent through an exhaust air scrubber. The thereof resulting wastewater is sent back into the chromium process bath.

Fume suppressants

Dosing of fume suppressants (for the reduction of aerosols) is demand-orientated and not based on the production flow, as fume suppressants also oxidize in the process bath when electroplating is not taking place. Demand-orientated dosing is done by analysing the droplets in the aerosol. At Lahner KG a PFOS free fume suppressant is in use.

Acid zinc electroplating

The acid zinc electroplating unit is fully automatized. Work pieces are transported via jigs.

The production process of zinc electroplating consists in general of the following:

Pre-treatment:

- Degreasing
- Pickling
- Electrolytically assisted degreasing
- Descaling (Deoxidation)
- Acid zinc electroplating
- Chromium III conversion coating

Pre-treatment

Pre-treatment consists of alkaline degreasing, etching with HCl, electrolytically assisted degreasing and descaling (deoxidation). Alkaline degreasing is done above room temperature between 40 – 60 °C. Electrolytically assisted degreasing removes the remains of unwanted residues from the surface, which remain trapped in the micro-roughness of the work piece’s surface.

These residues are removed by the electrolytic formation of H_2 gas at the surface of the cathode and of O_2 gas at the surface of the anode. (STM BREF, 2006) The work piece can be connected as anode or cathode.

Before entering zinc electroplating the work piece passes descaling with hydrochloric acid.

Acid zinc electroplating

After pre-treatment the work piece is zinc electroplated. Zinc is carried out in acid zinc electrolytes, which give bright decorative layers.

For providing corrosion resistance comparable with alkaline zinc electrolytes, post-treatment is required.

Acid zinc electrolytes contain typically zinc chloride, potassium chloride, boric acid and organic brighteners and wetting agents (STM BREF, 2006).

The solution has a good conductivity and high cathode efficiency leading to a lower energy demand than alkaline zinc electrolytes (STM BREF, 2006).

Chromium conversion coating

After zinc electroplating the work pieces pass chromium III conversion solution (passivation). Chromium conversion coatings enhance corrosion protection, preventing the zinc surface to form white rust. For further improving the corrosion resistance, organic sealing can be applied if required

Rinsing

After each process step rinsing is applied. Multiple stage counterflow rinsing units are used. A fraction of excess water re-enters the process bath to compensate for drag-out and evaporation losses. The remaining fraction is treated with ion exchange resins and is reused in the rinsing unit.

Waste gas treatment

Exhaust air is extracted at the edges of the process baths. Exhaust air from the pickling baths is treated in alkaline (NaOH) scrubbers which have been installed in 2019.

Bath life span

The process baths are regularly monitored and controlled. This enables an accurate dosing of the needed chemicals and avoids excess use of chemicals. Iron hydroxide sludge is removed from the zinc electrolytes by filters in order to expand the process bath's life span.

Nickel electroplating

Nickel and its salts have adverse health effects (STM BREF, 2006). Aerosols and airborne particles can arise from electroplating as well as from plant and solution maintenance operations. Due to a high electricity yield of the process bath and the use of wetting agents, the discharge of aerosols and airborne particles from electroplating is relatively low.

Nickel electroplating improves both the resistance of work pieces to corrosion, wear and abrasion, and provides a smooth, highly reflective coating. Nickel is also a good base coat for subsequent electroplated coatings, such as chromium, gold, silver, etc. At Lahner KG nickel electroplated work pieces can be further coated with decorative chromium.

The nickel electroplating is fully automatized. Work pieces are transported via jigs. Both steel and non-ferrous metals can be treated.

The production process of nickel electroplating consists in general of the following:

- Pre-treatment:
    - Degreasing
    - Etching
    - Electrolytically assisted degreasing
    - Activation
- Nickel electroplating
- Decorative chromium

Pre-treatment

Pre-treatment consists of alkaline degreasing, etching with HCl, electrolytically assisted degreasing and activation.

Electrolytically assisted degreasing removes the remains of unwanted residues from the surface, which remain trapped in the micro-roughness of the work piece's surface.

These residues are removed by the electrolytic formation of H_2 gas at the surface of the cathode and of O_2 gas at the surface of the anode (STM BREF, 2006). The work piece can be connected as anode or cathode.

Before entering nickel electroplating the work piece passes activation.

Nickel electroplating & decorative chromium

Nickel electroplating is carried out in Watts-type nickel solutions. The electrolyte is operated above room temperature (50 – 60 °C) and consists typically of nickel sulphate, nickel chloride and boric acid (STM BREF, 2006). Wetting agents and organic brighteners are usually added to reduce gas bubble retention on the nickel surface and enhance brightness of the coating (STM BREF, 2006).

After nickel electroplating decorative chromium electroplating can be applied if required by the client.

Rinsing

After each process step rinsing is applied. Multiple stage counterflow rinsing units are used. A fraction of excess water re-enters the process bath to compensate for drag-out and evaporation losses. The remaining fraction is treated with ion exchange resins and is reused in the rinsing unit.

Waste gas treatment

Exhaust air is extracted at the edges of the process baths. No abatement technique is installed for exhaust air treatment.

Bath life span

The process baths are regularly monitored and controlled. This enables an accurate dosing of the needed chemicals and avoids excess use of chemicals. Regular monitoring and maintenance Watts-type nickel solutions can have an almost indefinite working life (STM BREF, 2006).

Phosphating layer conversion coating

Phosphating layer conversion coating is a chemical process where a zinc-phosphate layer is formed. The rough surface gained through numerous capillaries makes phosphate layers a perfect base coat for further surface treatment operations such as painting, oiling, etc.

The phosphating solutions are generally applied by spraying or by immersion. At Lahner KG the solution is applied by immersion.

In general the phosphating process consists of:

- Degreasing
- Pickling
- Acceleration
- Phosphate layer forming

After alkaline degreasing pickling is applied. During pickling, metal oxides are dissolved by the acid.

The pickling reaction can be accelerated by oxidising agents. After pickling and acceleration, phosphate layer forming takes place. Metal dissolution in the pickling reaction results in a significant increase of the pH value close to the metal surface. Consequently, the equilibrium constant for the precipitation reaction is exceeded and zinc phosphate is precipitated as the metal surface offers favourable nucleation sites. Once the metal surface is covered, the reaction ceases.

Rinsing
After each process step, rinsing is applied. Multiple stage counterflow rinsing units are used.

Waste gas treatment
Exhaust air is extracted at the edges of the process baths. No abatement technique is installed for exhaust air treatment.

Anodising of aluminium

Anodising of metals is an electrolytic surface oxidation process resulting in an oxide layer, which is firmly attached to the work piece, providing corrosion protection. In anodising, the work piece is (as the name indicates) connected as the anode. During the anodising process the negatively charged anion migrates to the anode where it is discharged with a loss of one or more electrons. The metal reacts with the oxygen of the anion and a layer of oxide forms on the surface. (STM BREF, 2006)

Aluminium is predominantly anodised, with alumina (Al_2O_3) formed at the surface. (STM BREF, 2006). Magnesium, titanium, tantalum and niobium can be also anodised. At Lahner KG only aluminium is anodised.

Aluminium is typically anodised in sulphuric acid electrolytes (STM BREF, 2006).

Oxide layers from anodising are mainly transparent wherefore the work piece remains its metallic look. Pre-treatment determines the final look of the anodised work piece.

The work piece can be coloured by dipping them into organic dyes. Paint particles will settle in the pores of the oxide layer. At Lahner KG work pieces can be coloured in two different colours.

To increase corrosion resistance and to retain surface colouring, sealing is applied to the anodised work piece. Sealing can be carried out in hot or cold processes. At Lahner KG hot water sealing is applied.

With hot sealing, the pores in the oxide layer are closed by hydrating the aluminium oxide to bohemite (AlO(OH)): the pores are closed by the increased volume of the bohemite structure. The sealing process is carried out by dipping the anodised parts in hot or boiling (minimum 96°C) deionised water. (STM BREF, 2006)

Work pieces are moved by a crane system. The anodising unit is fully automatized.

The production process of anodising consists in general of the following:

- Mechanical pre-treatment
    - Grinding
    - Brushing
    - Polishing
- Chemical pre-treatment
    - Degreasing
    - Pickling
    - Descaling (Deoxidation)
- Anodising
- Colouring
- Hot water sealing

Mechanical & chemical pre-treatment

Depending on the requirements of the client grinding, brushing and/or polishing can be applied. Usually for decorative applications of the anodised work piece a combination of mechanical pre-treatment is applied, as pre-treatment decides the final appearance of the anodised work piece.

Chemical pre-treatment consists of alkaline degreasing, etching and descaling.

Anodising

Anodising of aluminium is done in sulphuric acid electrolytes, which is the most common technique for anodising of aluminium. The temperature of the electrolyte is typically between 15 and 30 °C. Also hard anodising is carried out at Lahner KG. Hard anodising results in thicker oxide layers for better corrosion resistance. For hard anodising, the electrolyte has to be operated below 5 °C. Even though with special electrolytes, hard anodising at 10 °C is possible. Hard anodised layers are normally not sealed.

Colouring

Colouring of the anodised work piece can be done by dip dyeing. Paint particles will settle in the pores of the oxide layer. At Lahner KG work pieces can be coloured in two different colours.

Hot sealing

After dip dyeing hot sealing is applied to increase corrosion resistance and to retain surface colouring. The sealing process is carried out by dipping the anodised parts in hot or boiling (minimum 95- 96 °C) deionised water (STM BREF, 2006).

Rinsing

After each process step rinsing is applied. Multiple stage counterflow rinsing units are used. A fraction of excess water re-enters the process bath to compensate for drag-out and evaporation losses. The remaining fraction is treated with ion exchange resins and is reused in the rinsing unit.

Waste gas treatment

Exhaust air is extracted at the edges of the process baths. No abatement technique is installed for exhaust air treatment.

Bath life span

The process baths are regularly monitored and controlled. This enables an accurate dosing of the needed chemicals and avoids excess use of chemicals.

Process wastewater

Treated wastewater is discharged indirectly. Process wastewater is collected in separate streams, i.e. acidic chromate containing wastewater and alkaline wastewater. Used concentrates from process baths are disposed by authorised waste disposal companies.

The WWTP consists of:

- Chromate treatment
- Neutralisation
- Sludge dewatering

Chromate treatment

Cr(VI) has to be reduced to Cr(III) as Cr(VI) is difficult to precipitate.

At Lahner KG Cr(VI) reduction is done by using sodium dithionite. Reduction by sodium dithionite does not require lowering the pH value below 2.5.

Neutralisation

Subsequently precipitation of heavy metals follows. The pH value is increased to 8.5 – 9.0 by adding lime milk or NaOH.

If the targeted pH value is exceeded HCl is added. Dosing of NaOH and HCl is automatic, depending on the monitored pH value. It is important that the pH value is stable for an appropriate time frame of ca. 20 minutes to ensure that the precipitation of metals is completed. Flocculation agents can be added. For the precipitation of fluoride and the reduction of sulphate calcium hydroxide or calcium chloride is added.

Sludge dewatering

After batch neutralisation, the wastewater is sent to the filter press. The dewatered sludge is disposed by external operators. The clear water is sent to pH end control before being indirectly discharged.

A renewal of the WWTP is planned for the end of 2020. The principle of the WWTP is kept whilst dimension and security measures (pipe-in-pipe, catch basins, etc.) are enhanced.

8.2 Current consumption and emission levels

Due to the big variety of electroplated products (regarding size, shape, quality requirements, etc.) representative specific consumption parameters cannot be derived.

Waste generation

Generated waste from electroplating is listed in Table 148. The quantity of wastes are from 2018. Used process solutions are also disposed of externally.

Table 148: Waste generated from electroplating 2018

Type	Unit	Quantity	Origin	Treatment
Pickling solution	t	72.18	Production process	Authorised waste disposal company
Solutions from phosphating layer conversion coating	t	3.28	Production process	Authorised waste disposal company
Degreasing solution	t	95.78	Production process	Authorised waste disposal company
Solution from chromium conversion coating (blue passivation)	t	1.86	Production process	Authorised waste disposal company
Activation solution	t	2.98	Production process	Authorised waste disposal company
Anodising (black colouring)	t	10.36	Production process	Authorised waste disposal company
Anodising solution	t	5.68	Production process	Authorised waste disposal company
Anodising (colouring baths)	t	3.14	Production process	Authorised waste disposal company
Cr (VI) solution	t	5.52	Production process	Authorised waste disposal company
Chromium conversion coating (Cr (VI) containing)	t	2.98	Production process	Authorised waste disposal company

Type	Unit	Quantity	Origin	Treatment
Metal hydroxide sludge	t	20	WWTP	Authorised waste disposal company

Source: Lahner KG, own recordings, 2018

Emissions to air

Edge exhausts are installed at the edges of the process baths. Exhaust air from the pickling baths of zinc electroplating is treated with alkaline scrubbers. Exhaust air from hard chromium plating is sent through an exhaust air scrubber The thereof resulting wastewater is sent back into the chromium process bath.

There are no permit requirements regarding emissions to air. Nevertheless Lahner KG commissioned an emissions to air monitoring in 2020 and 2018.

In December 2019 alkaline scrubbers for treating exhaust air from the pickling baths of the zinc electroplating unit have been installed. Table 149 presents the monitoring results from 09.01.2020. The measurements were conducted during normal operating conditions. The calculated volume flow was 1,800 Nm³/h (dry).

Table 149: Monitoring results of emissions to air from pickling – zinc electroplating, 0 °C, 1013 mbar, dry exhaust air

Parameter	Unit	Half-hour average	Half-hour average	Half-hour average	Standard
Cr(VI)	mg/Nm³	< 0.001	< 0.001	< 0.001	EN 14385
Cr – total	mg/Nm³	< 0.001	< 0.001	< 0.001	EN 14385
HCl	mg/Nm³	< 0.5	1.2	< 0.5	EN 1911

Source: MAPAG, 2020

Table 150 presents the monitoring results from 27.09.2018. The measurements were conducted during normal operating conditions. The calculated volume flow was 21,400 m³/h.

Table 150: Monitoring results of emissions to air; 0 °C, 1013 mbar, dry exhaust air

Parameter	Unit	Hard chromium plating	Pickling – zinc electroplating	Process bath – zinc electroplating	Standard	Sampling duration
Cr(VI)	mg/Nm³	< 0.001	< 0.001	< 0.001	DIN 38405	60 min
Cr – total	mg/Nm³	0.005	< 0.001	0.002	ÖNORM EN 14385	60 min
HCl	mg/Nm³	< 0.5	4.7	< 0.5	ÖNORM EN 1911	60 min

Source: MAPAG, 2018

Emissions to water

Treated process wastewater is discharged indirectly. Monitoring has to be conducted using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit. Minimum monitoring frequencies for self-monitoring (performed by operator) and external-monitoring are prescribed by permit. Emission limit values (ELV) are prescribed by permit.

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

The on-site WWTP consists of:

- Chromate treatment
- Neutralisation
- Sludge dewatering

A detailed description of the on-site WWTP is presented in chapter 8.1.

Emissions to water are described in the following tables. In Table 151 the minimum monitoring frequencies and ELVs prescribed by permit are presented and compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. In Table 152, Table 153 & Table 154 the self-monitoring recordings of treated process wastewater are presented. Table 155 presents the results from external-monitoring of treated process wastewater for the years 2017, 2018 & 2019.

Table 151: Emission limit values for the process wastewater from electroplating in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006) [190]	Ordinance (indirect discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Water quantity (Q)	m³/d	40	–	–		Annually
pH		6.5–10.0	–	6.5–10.0	–	Annually
TSS	mg/l	150	–	30	–	Annually
Lead (Pb)	mg/l	0.5	0.05–0.5	0.5	–	Annually
Cadmium (Cd)	mg/l	0.1	0.1–0.2	0.1	–	Annually
Chromium – total (Cr)	mg/l	0.5	0.1–2.0	0.5	–	Annually
Cr(VI)	mg/l	0.1	0.1–0.2	0.1	Per batch of treated wastewater	Annually
Copper (Cu)	mg/l	0.5	0.2–2.0	0.5	Per batch of treated wastewater	Annually
Nickel (Ni)	mg/l	0.5	0.2–2.0	0.5	Per batch of treated wastewater	Annually
Zinc (Zn)	mg/l	2.0	0.2–2.0	1.0[191]	Per batch of treated wastewater	Annually
Cyanide (CN)	mg/l	0.1	0.01–0.2	0.1	–	Annually
Fluoride (F)	mg/l	20	–	20	Per batch of treated wastewater	Annually

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[190] Discharge to public sewer or surface water from jig, barrel, small scale coil, automotive, PCB and other activities not large scale steel coil

[191] For wastewaters from electroplating or batch galvanising the ELV is 2.0 mg/l

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)[190]	Ordinance (indirect discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Sulphate (SO4)	mg/l	2000	–	–	Per batch of treated wastewater	Annually
AOX	mg/l	0.5	–	1.0	–	Annually
Hydrocarbon index	mg/l	15.0	–	15.0	–	Annually

Source: Permit 9-W-9890/19; Permit MDW2-WA-064/008; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 152: Self-monitoring of treated process wastewater 2017

Self-monitoring 2017							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Cr (VI)	mg/l	0.002	0.098[192]	0.037	0.013	0.1	801
Zn	mg/l	0.000	1.97[193]	1.142	0.368	2	801
Cu	mg/l	0.000	0.50[194]	0.285	0.081	0.5	801
F	mg/l	0.018	20.0[195]	17.23	6.15	20	801
SO_4	mg/l	58.1	1999.0[196]	1552.0	776.0	2000	801
Ni	mg/l	0.001	0.487	0.29	0.11	0.5	801

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[192] Two measurements above the ELV but no exceedance due to “4 out of 5” rule (0.134 mg/l; 0.129 mg/l)
[193] One exceedance (4.28 mg/l); two measurements above the ELV but no exceedance due to “4 out of 5” rule (2.02 mg/l; 2.08 mg/l)
[194] Three measurements above the ELV but no exceedance due to “4 out of 5” rule (0.601 mg/l; 0.525 mg/l; 0.553 mg/l)
[195] Nine measurements above the ELV but no exceedance due to “4 out of 5” rule (20.7 mg/l; 20.8 mg/l; 20.5 mg/l; 20.8 mg/l; 20.8 mg/l; 20.6 mg/l; 20.8 mg/l; 22.2 mg/l; 23 mg/l)
[196] Seven measurements above the ELV but no exceedance due to “4 out of 5” rule (2055 mg/l; 2127 mg/l; 2064 mg/l; 2285 mg/l; 2024 mg/l; 2056 mg/l; 2018 mg/l)

Source: Self-monitoring Lahner KG, 2017

Table 153: Self-monitoring of treated process wastewater 2018

Self-monitoring 2018							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Cr (VI)	mg/l	0.001	0.100	0.0393	0.013	0.1	938
Zn	mg/l	0.002	1.970	1.205	0.372	2	938
Cu	mg/l	0.000	0.478[197]	0.2885	0.085	0.5	938
F	mg/l	0.000	19.9[198]	16.7	6.51	20	938
SO_4	mg/l	56.400	1995[199]	1542.25	798.1	2000	938
Ni	mg/l	0.003	0.488[200]	0.29	0.12	0.5	938

Source: Self-monitoring Lahner KG, 2018

Table 154: Self-monitoring of treated process wastewater 2019

Self-monitoring 2019							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Cr (VI)	mg/l	0.000	0.087	0.043	0.013	0.1	805
Zn	mg/l	0.000	1.970[201]	1.328	0.423	2	805

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[197] One measurement above the ELV but no exceedance due to “4 out of 5” rule (0.555 mg/l)

[198] Ten measurements above the ELV but no exceedance due to “4 out of 5” rule (20.8 mg/l; 20.3 mg/l; 21.2 mg/l; 20.3 mg/l; 21.6 mg/l; 22.2 mg/l; 20.3 mg/l; 20.5 mg/l; 20.1 mg/l; 21.5 mg/l)

[199] Three measurements above the ELV but no exceedance due to “4 out of 5” rule (2496 mg/l; 2029 mg/l; 2001 mg/l; 2023 mg/l; 2015 mg/l)

[200] Five measurements above the ELV but no exceedance due to “4 out of 5” rule (0.512 mg/l; 0.516 mg/l; 0.543 mg/l; 0.507 mg/l; 0.554 mg/l)

[201] Seven measurements above the ELV but no exceedance due to “4 out of 5” rule (2.05 mg/l; 2.11 mg/l; 2.33 mg/l; 2.01 mg/l; 2.05 mg/l; 2.06 mg/l; 2.09 mg/l)

Self-monitoring 2019							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Cu	mg/l	0.000	0.500[202]	0.293	0.089	0.5	805
F	mg/l	0.088	24.0[203]	19.6	8.28	20	805
SO4	mg/l	0.000	1990.0[204]	1667.0	879.0	2000	805
Ni	mg/l	0.001	0.489[205]	0.357	0.142	0.5	805

Source: Self-monitoring Lahner KG, 2019

Measurements below the limit of detection are represented by the value 0.00 mg/l in the self-monitoring records.

Measurements have to be performed before discharging of a treated wastewater batch. Batches are discharged several times during a day, leading to a high number of measurements.

Table 155: External-monitoring of process wastewater 2017, 2018, 2019

External-monitoring 2017–2019						
Parameter	**Unit**	**18.12.2017**	**04.12.2018**	**12.11.2019**	**Standard**	**ELV**
Q	m^3/d	26	9.4	16		40

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[202] Four measurements above the ELV but no exceedance due to “4 out of 5” rule (0.526 mg/l; 0.51 mg/l; 0.511 mg/l; 0.512 mg/l)

[203] 34 measurements above the ELV but no exceedance due to “4 out of 5” rule (21.4 mg/l; 20.3 mg/l; 23.6 mg/l; 20.9 mg/l; 23.1 mg/l; 23.2 mg/l; 23.8 mg/l; 23.2 mg/l; 23.7 mg/l; 22.6 mg/l; 20.4 mg/l; 20.5 mg/l; 20.6 mg/l; 20.4 mg/l; 21.0 mg/l; 20.2 mg/l; 22.2 mg/l; 20.2 mg/l; 21.2 mg/l; 20.1 mg/l; 21.8 mg/l;; 23.5 mg/l; 20.5 mg/l; 21.4 mg/l; 20.3 mg/l; 20.4 mg/l; 21.3 mg/l; 21.9 mg/l; 20.5 mg/l; 21.8 mg/l; 20.9 mg/l; 23.7 mg/l; 24.0 mg/l; 20.6 mg/l) Three exceedances as more than one out of five consecutive measurements were above the ELV (21.6 mg/l; 20.5 mg/l; 22.0 mg/l)

[204] 13 measurements above the ELV but no exceedance due to “4 out of 5” rule (2155 mg/l; 2247 mg/l; 2007 mg/l; 2083 mg/l; 2035 mg/l; 2668 mg/l; 2206 mg/l; 2231 mg/l; 2091 mg/l; 2150 mg/l; 2341 mg/l; 2464 mg/l; 2287 mg/l)

[205] Three measurements above the ELV but no exceedance due to “4 out of 5” rule (0.543 mg/l; 0.514 mg/l; 0.534 mg/l)

External-monitoring 2017–2019						
Parameter	**Unit**	**18.12.2017**	**04.12.2018**	**12.11.2019**	**Standard**	**ELV**
pH		8.4	8.3	9.2	DIN EN ISO 10523	6.5-10
Fluoride	mg/l	14.5	<5	8.09	EN ISO 10304-1	20
Sulphate	mg/l	603	1500	825	EN ISO 10304-1	2000
TSS	mg/l	13	21	11	DIN 38409. Teil 2	150
Lead	mg/l	< 0.1	< 0.1	< 0.1	EN ISO 11885	0.5
Cadmium	mg/l	0.0047	< 0.004	< 0.004	EN ISO 11885	0.1
Chromium – total	mg/l	0.3	0.49	< 0.04	EN ISO 11885	0.5
Copper	mg/l	0.1	0.1	< 0.04	EN ISO 11885	0.5
Nickel	mg/l	< 0.1	0.13	< 0.1	EN ISO 11885	0.5
Zinc	mg/l	0.43	0.49	< 0.2	EN ISO 11885	2
Chromium (VI)	mg/l	< 0.005	< 0.01	< 0.01	DIN 38405. Teil 24	0.1
COD	mg/l	188	692	122	DIN 38409. Teil 41	-
Cyanide	mg/l	0.002	< 0.002	< 0.002	EN ISO 14403-2	0.1
Total Phosphorus	mg/l	0.175	0.88	0.088	EN ISO 6878	-
AOX	mg/l	< 0.02	0.037	0.16	EN ISO 9562	0.5
Hydrocarbon index	mg/l	< 0.1	0.077	0.07	EN ISO 9377-2	15

Source: MAPAG, 2017-2019

8.3 References

AEV Oberflächenbehandlung, BGBl. II Nr. 44/2002: Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Begrenzung von Abwasseremissionen aus der Behandlung von metallischen Oberflächen (AEV Oberflächenbehandlung), BGBl. II Nr. 44/2002

MAPAG (2017 – 2019): Prüfbericht Untersuchung der Abwasserreinigungsanlage, MAPAG, 2017 – 2019

MAPAG (2018): Prüfbericht Luftmessung, MAPAG, 2018

MAPAG (2020): Prüfbericht Luftmessung, MAPAG, 2018

Permit 9-W-9890/19: Bescheid, 9-W-9890/19, BH Mödling, 2001

Permit MDW2-WA-064/008: Bescheid, MDW2-WA-064/008, BH Mödling, 2009

STM BREF (2006): Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Surface Treatment of Metals and Plastics, European Commission, 2006

9 MACO Salzburg – Mayer & Co Beschläge GmbH

MACO is an international company that is specialized in the production of fittings, locks, etc. In the production facilities Salzburg and Trieben, in-house surface treatment units are operated. On the premise Salzburg, zinc electroplating, cathodic dip-paint coating (CDC) and powder coating is carried out. MACO Salzburg is an IED plant.

Environmental Management System
MACO Salzburg has an according to ISO 14001 certified environmental management system implemented.

9.1 Technical description

Surface treatment processes operated at MACO Salzburg are:

- Alkaline zinc electroplating
- Cathodic dip-paint coating (CDC)
- Powder coating

Work pieces to be coated are fittings, locks, etc. out of zinc, steel or aluminium alloys.

Alkaline zinc electroplating

Several zinc electroplating lines are operated at MACO Salzburg. Zinc electroplating is done in rack and barrel systems. Process steps consist of:

- Pre-treatment
- Alkaline cyanide-free zinc electroplating
- Cr(III) conversion coating

Pre-treatment
In a first step the work pieces are degreased in alkaline solutions (NaOH). Subsequently

the work pieces are pickled in acidic solutions (HCl). In between process steps rinsing is applied.

Zinc electroplating

Zinc electroplating is carried out in alkaline cyanide-free electrolytes. The process solution contains in general zinc oxide and sodium hydroxide or potassium hydroxide (STM BREF, 2006). After zinc electroplating the work piece passes rinsing, first in an eco-rinse (to minimize drag-out) and then in multiple counter-flow cascade rinsing units.

Cr(III) conversion coating

After zinc electroplating the work pieces pass chromium conversion (passivation). Only trivalent chromium conversion coatings are applied at MACO Salzburg. Thus the environmental or health problems associated with hexavalent chromium can be avoided. Passivation is done to enhance the corrosion protection, e.g. avoiding the formation of white rust on zinc.

Cathodic dip-paint coating (CDC)

Process steps consist of:

- Degreasing
- Conversion coating
- CDC
- Drying

Degreasing

Before passing CDC the work pieces need to be cleaned and degreased. Degreasing is done in several steps with alkaline solutions above room temperature.

Conversion coating

Subsequently a conversion coating, either chromium conversion coating or zinc phosphate layer conversion coating, is applied, The rough surface gained through numerous capillaries makes phosphate layers a perfect base coat for further surface treatment operations such as painting, oiling, etc. The phosphating solutions are in general applied by spraying or by immersion. Main components of the phosphating solution are zinc, nickel, manganese, phosphates, nitrite (oxidising agent), nitrates and fluorides. Alternatively, chromium conversion coatings can be applied.

Cathodic dip-paint coating (CDC)

Paint particles dispersed in a water-based solution are deposited on immersed work pieces under the influence of an electric field. The water is usually desalinated. Binding agents are added into the solution but need to be made water soluble with organic acids. The solvent content of a CDC paint is typically in the range of 2 – 4 %. The coating delivers corrosion protection as the combination of paint resin and deposition process create a very resistant film. In CDC the workpiece acts as cathode and the anodes are positioned in the process tank. (STS BREF Final Draft, 2019)

Drying

After rinsing the electrodeposited paint film is cured in a drying oven at around 180 °C for about one hour. In order to reduce energy consumption the drying oven is isolated and has separate entrance and exit doors. The oven is charged with heating oil extra light (low-sulphur content, max. 50mg/kg).

Powder coating

Process steps consist of:

- Degreasing
- Phosphating layer conversion coating
- Powder coating

Between each pre-treatment process step rinsing is applied.

Powder coating

Powder coatings are solvent-free systems that require electrostatic application procedures. Powder coatings are typically based on acrylic resins with either an acid or an anhydride. The main film-forming agents are polyester or epoxy resins. The powder particles are normally applied by electrostatic charging in spray guns or a cloud chamber and are then attracted to the earthed substrate. To cure, the material is heated in a convection oven where it melts and fuses into a film. (STS BREF, 2020)

Powder coating is a dry process, thus no wastewater is produced. Pre-treatment for powder coating can, however, be water based and produce wastewater emissions. Powder coatings are solvent-free systems, thus VOC emissions to air are less of a concern (than in conventional varnishing operations). During curing, VOC can be emitted.

Rinsing

After each process step the work piece is rinsed. Multiple stage counter flow rinsing units consisting of two or three steps are used in order to minimise water use. Excess water from the rinsing unit is fed back into the electroplating baths or into the degreasing baths. After zinc electroplating the work piece is first rinsed in an eco-rinse and subsequently in a multiple stage counter flow rinsing unit.

After CDC excess material is removed by rinsing. The rinsing water is treated with ultrafiltration. Thereof gained CDC material re-enters the CDC process. The ultrafiltrated rinsing water is re-used as rinsing water in a counter flow cascade.

Waste gas

The electroplating lines are equipped with edge exhausts. Collected waste gas is treated in alkaline wet scrubbers (NaOH).

Waste gas from the WWTP and zinc release is collected and emitted via stacks without emission abatement being applied.

Pre-treatment steps from powder coating are equipped with edge exhausts. Collected waste gas is treated in alkaline scrubbers (NaOH).

Waste gas from CDC pre-treatment is collected with edge exhausts. Waste gas from CDC tank is collected with hood suction. The drying oven is equipped with a dedicated suction system.

Bath life span

The process baths are regularly monitored and controlled in the in-house laboratory. This enables an accurate dosing of the needed chemicals and avoids excess use of chemicals. In order to prolong bath life span, impurities are filtered out from process baths.

Process wastewater

Treated wastewater is discharged directly into the river Salzach. Wastewater is collected in separate streams, i.e.:

- Rinsing water (recirculated)
- Rinsing water (acidic or alkaline)
- Acidic concentrates

- Alkaline concentrates
- Concentrates containing nitrates
- Spent concentrates from sealing

Wastewater treatment consists in general of:

- Neutralisation
- Sand filtration
- Ion exchange resins
- Chamber filter presses

In the following the treatment of the individual wastewater streams are discussed in detail.

Rinsing water (recirculated)

Rinsing water which is recirculated in the process is collected in a buffer tanks and treated with

- Sand filter
- Ion exchange resins

Treated rinsing water re-enters the process. Eluates are sent to batch neutralisation.

Rinsing water (acidic or alkaline)

Treatment of acidic and alkaline rinsing water consists of:

- Neutralisation (continuous flow)
  - Lowering pH value to 2.5 by adding HCl
  - Increasing pH value to 8.5 – 9 with lime milk
- Flocculation
- Sedimentation
- Chamber filter press

Wastewater from the chamber filter press is sent to the final treatment unit.

Acidic and alkaline concentrates, concentrates containing nitrates

Treatment of acidic and alkaline concentrates, together with eluates from recirculated rinsing water treatment, consists of:

- Dedicated buffer tanks (for each wastewater stream)
- Batch neutralisation
  - Lowering the pH value to 3 – 4 (keeping pH value stable for at least 10 min.)
  - Increasing the pH value to 8.5 – 9 (keeping pH value stable for at least 10 min.)
- Flocculation
- Sedimentation
- Chamber filter press

Wastewater from the chamber filter press is sent to the final treatment unit.

Final treatment unit

In the final treatment unit pre-treated alkaline and acidic rinsing waters, as well as alkaline, acidic, nitrate containing concentrates are treated. Treatment consist of:

- Pre-neutralisation
- Sand filtration
- Ion exchange resins
- End control (pH adjustment)

Spent concentrates from sealing

Sealing enhances corrosion protection. Spent sealing concentrates are collected separately and treatment consists of:

- Buffer tank
- Neutralisation
  - Lowering pH value to 2 – 3 (polymers are precipitated)
- Chamber filter press
- Neutralisation (wastewater from chamber filter press)
  - Increasing pH value to 7 with NaOH (Silicates are precipitated)
- Evaporator

- Distillate is combined with wastewater stream “nitrate containing concentrates”
- Eluate (silicate containing solution) is collected and disposed via external disposal companies

9.2 Current consumption and emission levels

Waste generation

Generated waste is listed in Table 156. The waste quantities are from 2015.

Table 156: Waste generation 2015

Type of waste	Quantity [t]	Classification
Sludge from process bath maintenance	27.68	
Sludge from WWTP	164.06	hazardous
Acids. acid mixtures	28.54	hazardous
Bases and alkaline mixtures	40.32	hazardous
Ion exchange resins	5.68	hazardous
Concentrates containing metal salts	159.90	hazardous
Waste oil	10.57	hazardous
Drill and grinding emulsions	10.78	hazardous
Waste from oil separator	32.25	hazardous
Oil-water mixtures	48.68	hazardous
Mixtures containing solvents	0.25	hazardous
Solvent-water mixtures	17.90	hazardous
Sludge containing solvents	0.04	hazardous
Paint and varnish sludge	24.30	hazardous
Iron and steel scrap	2569.02	
Aluminium	1.52	
Zinc	68.58	
Copper	3.24	

Source: MACO, own recordings

Emissions to air

Emissions to air are monitored with three consecutive half-hourly measurements. The measurements presented in the tables below are the averages of the three half-hourly measurements and relate to 0 °C, 1013 mbar, dry exhaust air. Emissions to air measurements are compared to the ELVs according to the German TA-Luft or the Austrian Ordinance for VOC emitting plants (VAV).

The electroplating lines are equipped with edge exhausts. Collected waste gas is treated in alkaline wet scrubbers (NaOH). Emissions to air measurements are presented in Table 157 – Table 160. The exhaust air volume flows were 12,775 Nm³/h (zinc rack line, scrubber 1), 6,910 Nm³/h (zinc rack line, scrubber 2), 10,262 Nm³/h (zinc drum line 1) and 16,368 Nm³/h (drum line 2).

Table 157: Zinc electroplating – rack line, wet scrubber 1, average of 3 half-hourly measurements

Parameter	Unit	Average (3 half-hourly m.) 03.09.2020	ELV (TA-Luft)
Cr – total	mg/Nm³	< 0.005	1
Cr – total	g/h	< 0.06	5
Dust	mg/Nm³	0.2	20
Dust	g/h	2.85	200
Zn	mg/Nm³	0.015	–
Zn	g/h	0.19	–

Source: Kaufmann, 2020

Table 158: Zinc electroplating – rack line, wet scrubber 2, average of 3 half-hourly measurements

Parameter	Unit	Average (3 half-hourly m.) 03.09.2020	ELV (TA-Luft)
Cr – total	mg/Nm³	< 0.005	1
Cr – total	g/h	< 0.03	5

Parameter	Unit	Average (3 half-hourly m.) 03.09.2020	ELV (TA-Luft)
Dust	mg/Nm³	0.4	20
Dust	g/h	2.97	200
Zn	mg/Nm³	0.024	–
Zn	g/h	0.17	–

Source: Kaufmann, 2020

Table 159: Zinc electroplating, drum line 1, wet scrubber, average of 3 half-hourly measurements

Parameter	Unit	Average (3 half-hourly m.) 04.05.2010	ELV (TA-Luft)
Cr – total	mg/Nm³	< 0.001	1
Cr – total	g/h	< 0.03	5
Dust	mg/Nm³	0.2	20
Dust	g/h	2.97	200
Zn	mg/Nm³	0.144	–
Zn	g/h	1.483	–
Cu	mg/Nm³	0.003	0.5
Cu	g/h	0.034	2.5

Source: Kaufmann, 2010

Table 160: Zinc electroplating, drum line 2, wet scrubber, average of 3 half-hourly measurements

Parameter	Unit	Average (3 half-hourly m.) 26.05.2009	ELV (TA-Luft)
Cr – total	mg/Nm³	0.007	1
Cr – total	g/h	0.11	5

Parameter	Unit	Average (3 half-hourly m.) 26.05.2009	ELV (TA-Luft)
Dust	mg/Nm³	0.2	20
Dust	g/h	3.34	200
Zn	mg/Nm³	0.02	–
Zn	g/h	0.4	–
Cu	mg/Nm³	<0.01	0.5
Cu	g/h	<0.09	2.5

Source: Kaufmann, 2009

Waste gas from the WWTP and zinc release is collected and emitted via stacks without emission abatement being applied. The waste gas volume flow was 8,659 Nm³/h.

Table 161: WWTP and zinc release, average of 3 half-hourly measurements

Parameter	Unit	Average (3 half-hourly m.) 26.05.2009	ELV (TA-Luft)
Cr – total	mg/Nm³	<0.01	1
Cr – total	g/h	<0.08	5
Dust	mg/Nm³	0.4	20
Dust	g/h	3.27	200
Zn	mg/Nm³	0.04	–
Zn	g/h	0.38	–
Cu	mg/Nm³	<0.01	0.5
Cu	g/h	<0.08	2.5

Source: Kaufmann, 2009

Waste gas from CDC pre-treatment is collected with edge exhausts. Waste gas from CDC tank is collected with hood suction. The drying oven is equipped with a dedicated suction system. The waste gas volume flow was 6,862 Nm³/h.

Table 162: CDC, average of 3 half-hourly measurements

Process step	Parameter	Unit	Average (3 half-hourly m.) 03.09.2020	ELV (VAV)
Pre-treatment baths	VOC	mg/Nm³	1.3	150
	VOC	g/h	8.96	–
	Dust	mg/Nm³	0.3	5
	Dust	g/h	2.36	–
CDC	VOC	mg/Nm³	1.9	150
	VOC	g/h	15.99	–
	Dust	mg/Nm³	0.4	5
	Dust	g/h	3.63	–
Drying oven	VOC	mg/Nm³	22.6	150
	VOC	g/h	13.33	–
	Dust	mg/Nm³	0.4	5
	Dust	g/h	0.26	–

Source: Kaufmann, 2020

Pre-treatment steps from powder coating are equipped with edge exhausts. Collected waste gas is treated in alkaline scrubbers (NaOH). The waste gas volume flow was 2,964 Nm³/h.

Table 163: Powder coating pre-treatment, wet scrubber, average of 3 half-hourly measurements

Parameter	Unit	Average (3 half-hourly m.) 13.11.2007	ELV (TA-Luft)
Cr – total	mg/Nm³	<0.1	1
Cr – total	g/h	<0.296	5
Dust	mg/Nm³	0.2	20
Dust	g/h	0.593	200

Parameter	Unit	Average (3 half-hourly m.) 13.11.2007	ELV (TA-Luft)
Zn	mg/Nm³	<0.1	–
Zn	g/h	0.296	–
Ni	mg/Nm³	<0.1	0.5
Ni	g/h	0.296	2.5

Source: Kaufmann, 2007

Table 164: Powder coating drying oven, average of 3 half-hourly measurements

Parameter	Unit	Average (3 half-hourly m.) 08.11.2011
VOC	mg/Nm³	1.8
VOC	g/h	2.4
Dust	mg/Nm³	0.3
Dust	g/h	0.35

Source: Kaufmann, 2011

Emissions to water

Treated wastewater is discharged directly into the river Salzach. Monitoring has to be conducted using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit. Minimum monitoring frequencies for self-monitoring (performed by operator) and external-monitoring are prescribed by permit. Emission limit values (ELV) are prescribed by permit.

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

Wastewater is collected in separate streams, i.e.:

- Rinsing water (recirculated)
- Rinsing water (acidic or alkaline)
- Acidic concentrates

- Alkaline concentrates
- Concentrates containing nitrates
- Spent concentrates from sealing

Wastewater treatment consists in general of:

- Neutralisation
- Sand filtration
- Ion exchange resins
- Chamber filter presses

A detailed description of the on-site WWTP is presented in chapter 9.1.

Emissions to water are described in the following tables. In Table 165 the minimum monitoring frequencies and ELVs prescribed by permit are presented and compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. In Table 166 – Table 172 the self-monitoring recordings of treated process wastewater are presented. Table 169 – Table 171 present the results from external-monitoring of treated process wastewater for the years 2017, 2018 & 2019. Table 172 presents the monitoring standards from external-monitoring.

Table 165: Emission limit values for the process wastewater in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)	Ordinance (direct discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
T	°C	35	–	30	cont.	all 3 months
TSS	mg/l	30	5–30	30	–	all 3 months
pH		6.5–9.0	–	6.5–9.0	cont.	all 3 months
Cr – total	mg/l	0.5	0.1–2.0	0.5	–	all 3 months
Fe	mg/l	2	0.1–5.0	2	–	all 3 months

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)	Ordinance (direct discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Zn	mg/l	2	0.2–2.0	2	–	all 3 months
TP	mg/l	2	0.5–10	2	–	all 3 months
COD	mg/l	200	100–500	200	–	all 3 months
AOX	mg/l	1	–	1	–	all 3 months
Low volatile lipophilic substances	mg/l	20	–	20	–	all 3 months
Sum of hydrocarbons	mg/l	5	–	–	–	all 3 months
TSS	g/d	18000	–	–	–	all 3 months
Cr – total	g/d	300	–	–	–	all 3 months
Fe	g/d	1200	–	–	–	all 3 months
Zn	g/d	1200	–	–	–	all 3 months
TP	g/d	1200	–	–	–	all 3 months
COD	g/d	120000	–	–	–	all 3 months
AOX	g/d	600	–	–	–	all 3 months
Low volatile lipophilic substances	g/d	12000	–	–	–	all 3 months
Sum of hydrocarbons	g/d	3000	–	–	–	all 3 months
Q	m^3/d	600	–	–	cont.	all 3 months

Source: Permit 01/01/23717/1999/070; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 166: Self-monitoring of treated process wastewater 2017

Self-monitoring 2017						
Parameter	**Unit**	**Daily min.**	**Daily max.**	**Annual average**	**ELV Permit**	**Number of samples**
pH		6.5[206]	8.91	7.8	6.5–9.0	242
COD	mg/l	13	162	59.59	200	243
Cr – total	mg/l	0.01	0.05	0.05	0.5	243
Zn	mg/l	0.1	1.92	0.64	2	243
Fe	mg/l	0.02	0.1	0.09	2	243
F	mg/l	2.1	5	3.82	10	243

Source: Self-monitoring MACO, 2017

Table 167: Self-monitoring of treated process wastewater 2018

Self-monitoring 2018						
Parameter	**Unit**	**Daily min.**	**Daily max.**	**Annual average**	**ELV Permit**	**Number of samples**
pH		7.11	8.91	7.93	6.5–9.0	255
COD	mg/l	19	162	74.45	200	255
Cr – total	mg/l	0	0.5[207]	0.05	0.5	255
Zn	mg/l	0.17	2[208]	0.85	2	255
Fe	mg/l	0.01	1	0.11	2	255
F	mg/l	1.2	9.7	3.72	10	255

Source: Self-monitoring MACO, 2018

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[206] pH: One exceedance (1.81)

[207] Cr-total: One exceedance (0.65 mg/l)

[208] Zn: One exceedance (7 mg/l)

Table 168: Self-monitoring of treated process wastewater 2019

Self-monitoring 2019						
Parameter	**Unit**	**Daily min.**	**Daily max.**	**Annual average**	**ELV Permit**	**Number of samples**
pH		6.8	8.65	7.71	6.5–9.0	242
COD	mg/l	5	120	52.95	200	243
Cr – total	mg/l	0.01	0.11	0.05	0.5	243
Zn	mg/l	0.1	2[209]	0.55	2	243
Fe	mg/l	0.01	0.46	0.09	2	243
F	mg/l	0.1	5	3.48	10	243

Source: Self-monitoring MACO, 2019

Table 169: External-monitoring of process wastewater

External-monitoring 2017							
Parameter	**Unit**	**07.02.2017**	**23.06.2017**	**29.09.2017**	**09.11.2017**	**ELV Permit**	**Limit of detection**
TSS	mg/l	2	4	6	< 2	30	2
COD	mg/l	63	58	72	49	200	15
DOC	mg/l	17	12	14	19	–	0.5
Cr – total	mg/l	< 0.01	< 0.01	< 0.01	< 0.01	0.5	0.01
Fe	mg/l	< 0.02	0.03	0.02	0.04	2	0.02
TP	mg/l	< 0.08	0.98	< 0.08	< 0.08	2	0.08
Zn	mg/l	0.34	0.08	0.55	0.53	2	0.02
AOX	mg/l	< 0.02	< 0.02	0.02	0.02	1	0.02
Hydrocarbon Index	mg/l	< 0.1	< 0.1	< 0.1	0.1	5	0.1

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[209] Zn: One exceedance (4.68 mg/l)

External-monitoring 2017							
Parameter	**Unit**	**07.02.2017**	**23.06.2017**	**29.09.2017**	**09.11.2017**	**ELV Permit**	**Limit of detection**
Low volatile lipophilic substances	mg/l	< 1	1	4	< 1	20	1

Source: Institut Fresenius, 2017–2019

Table 170: External-monitoring of process wastewater

External-monitoring 2018							
Parameter	**Unit**	**21.02.2018**	**21.06.2018**	**24.09.2018**	**11.10.2018**	**ELV Permit**	**Limit of detection**
TSS	mg/l	5	2	< 2	5	30	2
COD	mg/l	43	58	44	130	200	15
DOC	mg/l	16	22	14	43	–	0.5
Cr – total	mg/l	< 0.01	< 0.01	< 0.01	< 0.01	0.5	0.01
Fe	mg/l	0.4	< 0.02	0.03	0.13	2	0.02
TP	mg/l	< 0.08	< 0.08	< 0.08	0.1	2	0.08
Zn	mg/l	0.75	0.18	0.34	1.2	2	0.02
AOX	mg/l	0.09	0.06	0.04	0.03	1	0.02
Hydrocarbon Index	mg/l	< 0.1	< 0.1	0.1	< 0.1	5	0.1
Low volatile lipophilic substances	mg/l	1	< 1	27	5	20	1

Source: Institut Fresenius, 2017–2019

Table 171: External-monitoring of process wastewater

External-monitoring 2019							
Parameter	**Unit**	**14.03.2019**	**13.06.2019**	**28.08.2019**	**20.11.2019**	**ELV Permit**	**Limit of detection**
TSS	mg/l	<2	<2	< 2	< 2	30	2
COD	mg/l	67	38	< 15	39	200	15
DOC	mg/l	22	17	2.9	15	–	0.5
Cr – total	mg/l	< 0.01	< 0.01	< 0.01	< 0.01	0.5	0.01
Fe	mg/l	< 0.02	< 0.02	< 0.02	< 0.02	2	0.02
TP	mg/l	< 0.08	< 0.08	< 0.08	< 0.08	2	0.08
Zn	mg/l	0.49	0.65	0.91	0.12	2	0.02
AOX	mg/l	< 0.02	0.02	0.02	0.03	1	0.02
Hydrocarbon Index	mg/l	< 0.1	< 0.1	< 0.1	< 0.1	5	0.1
Low volatile lipophilic substances	mg/l	4	2	2	34	20	1

Source: Institut Fresenius, 2017–2019

Table 172: Applied monitoring standards, external-monitoring

Parameter	Standard
TSS	DIN 38409-2-2
COD	DIN 38409-41
DOC	DIN EN 1484
Cr – total	DIN EN ISO 11885
Fe	DIN EN ISO 11885
TP	DIN EN ISO 11885
Zn	DIN EN ISO 11885
AOX	DIN EN ISO 9562

Parameter	Standard
Hydrocarbon Index	DIN EN ISO 9377-2
Low volatile lipophilic substances	DIN 38409-56

Source: Institut Fresenius, 2017–2019

9.3 References

AEV Oberflächenbehandlung, BGBl. II Nr. 44/2002: Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Begrenzung von Abwasseremissionen aus der Behandlung von metallischen Oberflächen (AEV Oberflächenbehandlung), BGBl. II Nr. 44/2002

Institut Fresenius (2017-2019): Prüfbericht Institut Fresenius, 2017-2019

Kaufmann (2020): Prüfbericht, Technisches Büro für Umwelttechik, Dipl.-Ing. Horst Kaufmann, 2020

Permit 01/01/23717/1999/070: Wasserrechtliche Bewilligung, 01/01/23717/1999/070, MA Stadt Salzburg

STM BREF (2006): Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Surface Treatment of Metals and Plastics, European Commission, 2006

STS BREF, Final Draft (2019): Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Surface Treatment Using Organic Solvents including Wood and Wood Products Preservation with Chemicals, Final Draft, European Commission, 2019

10 MACO Trieben – Mayer & Co Beschläge GmbH

MACO is an international company that is specialized in the production of fittings, locks, etc. In the production facilities Salzburg and Trieben, in-house surface treatment units are operated. On the premise Trieben, zinc electroplating and anodizing of aluminium is carried out. MACO Trieben is an IED plant.

Environmental Management System
MACO Trieben has an according to ISO 14001 certified environmental management system implemented.

10.1Technical description

Surface treatment processes operated at MACO Trieben are:

- Alkaline zinc electroplating
- Anodizing
- Cathodic dip-paint coating

Work pieces to be coated are fittings, locks, etc. out of zinc, steel or aluminium alloys.

Alkaline zinc electroplating

Several zinc electroplating lines are operated at MACO Trieben. Zinc electroplating is done in rack and barrel systems. Process steps consist of:

- Pre-treatment
- Alkaline cyanide-free zinc electroplating
- Chromium conversion coating

Pre-treatment

Pre-treatment consists of degreasing, pickling, electrolytically assisted degreasing and activation.

Zinc electroplating

Zinc electroplating is carried out in alkaline cyanide-free electrolytes. The process solution contains in general zinc oxide and sodium hydroxide or potassium hydroxide (STM BREF, 2006).

Chromium conversion coating

After zinc electroplating the work pieces pass chromium conversion (passivation). Until the end of the year 2020, both trivalent and hexavalent chromium conversion coatings were applied at MACO Trieben. From 2021 on only Cr(III) passivation is carried out at MACO Trieben. Passivation is done to enhance the corrosion protection, e.g. avoiding the formation of white rust on zinc.

Anodizing of aluminium

Anodising of metals is an electrolytic surface oxidation process resulting in an oxide layer, which is firmly attached to the work piece, providing corrosion protection. In anodising, the work piece is (as the name indicates) connected as the anode. During the anodising process, the negatively charged anion migrates to the anode where it is discharged with a loss of one or more electrons. The metal reacts with the oxygen of the anion and a layer of oxide forms on the surface. (STM BREF, 2006)

At MACO Trieben aluminium is anodized. The anodizing process consists of:

- Pre-treatment
  - Activation
  - Pickling
  - Degreasing
  - Electropolishing
- Anodizing
- Colouring
- Sealing

Pre-treatment

‘Pre-treatment consists of activation with diluted sulphuric acid, pickling with sodium hydroxide (NaOH), degreasing and electropolishing. The degreasing solution contains sodium carbonates (NaCO3), sodium bicarbonate (NaHCO3), borates, phosphates and surfactants. The electropolishing bath contains sulphuric acid and phosphoric acid.

Anodising

Anodising of aluminium is done in sulphuric acid electrolytes, which is the most common technique for anodising of aluminium. The temperature of the electrolyte is typically between 15 and 30 °C.

Colouring

The work piece can be coloured in different ways, e.g. immersion colouring, electrolytic colouring, interference colouring or integral colouring. At MACO Trieben electrolytic colouring and immersion colouring is used.

Sealing

To increase corrosion resistance and to retain surface colouring, sealing is applied to the anodised work piece. Sealing can be carried out in hot or cold processes. At MACO Trieben hot water sealing is applied.

With hot sealing, the pores in the oxide layer are closed by hydrating the aluminium oxide to bohemite (AlO(OH)), the pores are closed by the increased volume of the bohemite structure. The sealing process is carried out by dipping the anodised parts in hot or boiling deionised water. (STM BREF, 2006)

Cathodic dip-paint coating (CDC)

The CDC unit is fully automatic. Already electroplated and passivated fittings are processed in the CDC unit. The CDC unit is fully encapsulated.

Process steps consist of:

- Degreasing
- Conversion coating
- CDC
- Drying

Degreasing

Before passing CDC the work pieces need to be cleaned and degreased. Degreasing is done in several steps with alkaline solutions above room temperature.

Conversion coating

Subsequently a conversion coating, either chromium conversion coating or zinc phosphate layer conversion coating, is applied, The rough surface gained through numerous capillaries makes phosphate layers a perfect base coat for further surface treatment operations such as painting, oiling, etc. The phosphating solutions are in general applied by spraying or by immersion. Main components of the phosphating solution are zinc, nickel, manganese, phosphates, nitrite (oxidising agent), nitrates and fluorides. Alternatively chromium conversion coatings can be applied. At MACO Trieben, both, Cr(VI) and Cr(III) conversion coatings are used.

Cathodic dip-paint coating (CDC)

Paint particles dispersed in a water-based solution are deposited on immersed work pieces under the influence of an electric field. The water is desalinated. Binding agents are added into the solution but need to be made water soluble with organic acids. The solvent content of a CDC paint is typically in the range of 2 – 4 %. The coating delivers corrosion protection as the combination of paint resin and deposition process create a very resistant film. In CDC the workpiece acts as cathode and the anodes are positioned in the process tank. (STS BREF Final Draft, 2019)

Drying

After rinsing the electrodeposited paint film is cured in a drying oven at around 150 °C for about one hour. In order to reduce energy consumption the drying oven is isolated and has separate entrance and exit doors. The oven is charged with natural gas.

Rinsing

After each process step the work piece is rinsed. Multiple stage counter flow rinsing units consisting of two or three steps are used in order to minimise water use. Excess water from the rinsing unit is fed back into the process baths. After zinc electroplating the work piece is first rinsed in an eco-rinse and subsequently in a multiple stage counter flow rinsing unit.

In order to reduce the quantity of excess rinsing water a vacuum evaporator is used. The distillate is re-used as rinsing water, the retentate is disposed as waste via an external waste company. Concentrates not suitable for the on-site WWTP are also treated in the vacuum evaporator unit and subsequently disposed as waste.

Certain rinsing steps require desalinated water. A reverse osmosis unit is operated on site. In order to recirculate desalinated water from rinsing pre-treatment via ion-exchange resins is carried out.

Waste gas

Process baths are covered and equipped with edge exhausts. Collected waste gas is treated in alkaline wet-scrubbers.

The CDC unit is encapsulated. Waste gas is collected via a general ventilation system and edge exhausts. The collected waste gas is treated in wet scrubbers.

Bath life span

The process baths are regularly monitored and controlled in the in-house laboratory. This enables an accurate dosing of the needed chemicals and avoids excess use of chemicals. In order to prolong the bath life span, impurities are filtered out from process baths.

Degreasing baths are equipped with oil-separators.

Retardation units are used to prolong the life-span of anodizing baths. A retardation unit consists of anion ion exchange resins through which the anodizing solution is sent to reduce the concentration of aluminium in the process solution (which accrues during the anodizing process).

The colouring baths (anodising), as well as the hot sealing baths, are continuously filtered.

Process baths for zinc phosphate conversion coatings for CDC are equipped with sludge filters and presses.

Surfactants

Surfactants are used in several process baths (e.g. degreasing, pickling, etc.). At MACO Trieben only surfactants with a biodegradability > 80 %, according to the OECD Guidelines for Testing of Chemicals (Section 3 Environmental Fate and Behavior, Number 301 Ready Biodegradability), are used.

Process wastewater

MACO Trieben operates dedicated WWTPs for different processes. Process wastewater from anodising and electroplating is discharged directly into the river Palten. Process wastewater from CDC is (due to the high COD concentration) discharged indirectly.

Anodising:

Rinsing water re-circulation unit

Rinsing water from anodizing needs to be treated to be re-used in the process. Treatment consists of:

Sand filtration

- Ion exchange resins (cathionic and anionic)
- Wastewater from anodizing

Wastewater from anodizing is collected in separate streams (alkaline and acidic) and treated in a dedicated WWTP. Treatment consists of:

- Neutralisation
  - Batch neutralization
  - Continuous flow neutralization
- Flocculation
- Sedimentation
- Chamber filter press
- Final neutralization
- Sand filtration
- Ione exchange resin

Electroplating

Rinsing water re-circulation unit

Rinsing water from electroplating needs to be treated to be re-used in the process. Treatment consists of:

- Sand filtration
- Ion exchange resins (cathionic and anionic)

Wastewater from electroplating

Wastewater from electroplating is treated in two identical dedicated WWTPs.

Wastewater from electroplating is collected in separate streams, i.e.:

- Rinsing water and concentrates containing chromium and eluates
- Rinsing water
- Concentrates acidic
- Concentrates alkaline
- Spent acids
- Wastewater from brightening

Wastewater treatment consists of:

- Cr(VI) reduction (with $FeCl_2$)
- Neutralisation
    - Batch neutralization
    - Continuous flow neutralisation (for less contaminated wastewaters)
- Flocculation
- Sedimentation
- Chamber filter press
- Final neutralisation
- Sand filtration
- Ion exchange resins

Wastewater from CDC

- Wastewater from CDC is collected in separate streams, i.e.:
    - Wastewater from degreasing and zinc phosphate conversion coating
    - Rinsing water
- Concentrates
    - Wastewater from chromium conversion coating
    - Rinsing water containing Cr(VI)
- Concentrates
- Wastewater from CDC

Wastewater from waste gas treatment

Wastewater from degreasing, conversion coating processes and waste gas treatment is treated by:

- Cr(VI) reduction (with $FeCl_2$)
- Neutralisation
- Flocculation
- Sedimentation
- Chamber filter press
- Nitrite oxidation (with H_2O_2)
- Final neutralisation
- Filtration
- Activated carbon filter
- Ion exchange resin

Wastewater from CDC is treated by:

- Alkalisation with spent alkaline wastewater
- Flocculation
- Filtration
- Vacuum evaporation

The distillate from vacuum evaporation is treated in the above described WWTP. The remaining concentrate is disposed as waste by an external waste company.

10.2 Current consumption and emission levels

Emissions to air

Emissions to air from zinc electroplating have to be monitored all three years by an accredited institute. ELVs are prescribed by permit. Emissions to air are monitored with three consecutive half-hourly measurements. The measurements presented in the tables below are the averages of the three half-hourly measurements and relate to 0 °C, 1013 mbar, dry exhaust air.

The electroplating lines are equipped with edge exhausts. Collected waste gas is treated in wet scrubbers. Emissions to air measurements are presented in Table 173 – Table 179.

Table 173: Zinc electroplating – rack line 1, average of 3 half-hourly measurements

Zinc electroplating – rack line 1			
Parameter	**Unit**	**Average (3 half-hourly m.)**	**ELV Permit**
Co	mg/Nm³	<0.005	0.05
Cr(VI)	mg/Nm³	<0.01	0.05
Cr – total	mg/Nm³	<0.01	1
HCl	mg/Nm³	5.44	10
Dust	mg/Nm³	0.3	20
TVOC	mg/Nm³	<1.0	50
Aerosols	mg/Nm³	2.21	10

Mass flow (dry) 24,011 Nm³/h

Source: Kaufmann, 2020

Table 174: Zinc electroplating – rack line 2, average of 3 half-hourly measurements

Zinc electroplating – rack line 2			
Parameter	**Unit**	**Average (3 half-hourly m.)**	**ELV Permit**
Co	mg/Nm³	<0.005	0.05
Cr(VI)	mg/Nm³	<0.01	0.05
Cr – total	mg/Nm³	<0.01	1
HCl	mg/Nm³	8.75	10
Dust	mg/Nm³	0.3	20
TVOC	mg/Nm³	<1.0	50
Aerosols	mg/Nm³	5.61	10

Mass flow (dry) 17,477 Nm³/h

Source: Kaufmann, 2020

Table 175: Zinc electroplating, rack line 3, average of 3 half-hourly measurements

Zinc electroplating – rack line 3			
Parameter	**Unit**	**Average (3 half-hourly m.)**	**ELV Permit**
Co	mg/Nm³	<0.005	0.05
Cr(VI)	mg/Nm³	<0.01	0.05
Cr – total	mg/Nm³	<0.01	1
HCl	mg/Nm³	2.3	10
Dust	mg/Nm³	0.2	20
TVOC	mg/Nm³	<1.0	50
Aerosols	mg/Nm³	7.39	10

Mass flow (dry) 30,754 Nm³/h

Source: Kaufmann, 2020

Table 176: Zinc electroplating, drum line 1, average of 3 half-hourly measurements

Zinc electroplating – drum line 1			
Parameter	**Unit**	**Average (3 half-hourly m.)**	**ELV Permit**
Co	mg/Nm³	<0.005	0.05
Cr(VI)	mg/Nm³	<0.01	0.05
Cr – total	mg/Nm³	0.09	1
HCl	mg/Nm³	1.44	10
Dust	mg/Nm³	0.3	20
TVOC	mg/Nm³	<1.0	50
Aerosols	mg/Nm³	2.62	10

Mass flow (dry) 14,973 Nm³/h

Source: Kaufmann, 2020

Table 177: Zinc electroplating, drum line 2, average of 3 half-hourly measurements

Zinc electroplating – drum line 2			
Parameter	**Unit**	**Average (3 half-hourly m.)**	**ELV Permit**
Co	mg/Nm³	<0.005	0.05
Cr(VI)	mg/Nm³	<0.01	0.05
Cr – total	mg/Nm³	0.007	1
HCl	mg/Nm³	0.33	10
Dust	mg/Nm³	0.3	20
TVOC	mg/Nm³	<1.0	50
Aerosols	mg/Nm³	1.98	10
Mass flow (dry) 27,491 Nm³/h			

Source: Kaufmann, 2020

Table 178: Zinc electroplating, drum line 3, average of 3 half-hourly measurements

Zinc electroplating – drum line 3			
Parameter	**Unit**	**Average (3 half-hourly m.)**	**ELV Permit**
Co	mg/Nm³	<0.005	0.05
Cr(VI)	mg/Nm³	<0.01	0.05
Cr – total	mg/Nm³	0.014	1
HCl	mg/Nm³	0.53	10
Dust	mg/Nm³	0.3	20
TVOC	mg/Nm³	<1.0	50
Aerosols	mg/Nm³	8.7	10
Mass flow (dry) 28,889 Nm³/h			

Source: Kaufmann, 2020

Table 179: Zinc electroplating, drum line 4, average of 3 half-hourly measurements

Zinc electroplating – drum line 4			
Parameter	**Unit**	**Average (3 half-hourly m.)**	**ELV Permit**
Co	mg/Nm³	<0.005	0.05
Cr(VI)	mg/Nm³	<0.001	0.05
Cr – total	mg/Nm³	<0.001	1
HCl	mg/Nm³	0.36	10
Dust	mg/Nm³	0.2	20
TVOC	mg/Nm³	<1.0	50
Aerosols	mg/Nm³	0.57	10

Mass flow (dry) 32,518 Nm³/h

Source: Kaufmann, 2020

Emissions to water

MACO Trieben operates several WWTPs. Process wastewater from anodising and electroplating is discharged directly into the river Palten. Process wastewater from CDC is (due to the high COD concentration) discharged indirectly.

Monitoring has to be conducted using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit. Minimum monitoring frequencies for self-monitoring (performed by operator) and external-monitoring are prescribed by permit. Emission limit values (ELV) are prescribed by permit.

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

Wastewater from Cathodic dip-paint coating (CDC)

Wastewater from CDC is collected in separate streams, i.e.:

- Wastewater from degreasing and zinc phosphate conversion coating
  - Rinsing water
  - Concentrates

- Wastewater from chromium conversion coating
  - Rinsing water containing Cr(VI)
  - Concentrates
- Wastewater from CDC
- Wastewater from waste gas treatment

Wastewater from degreasing, conversion coating processes and waste gas treatment is treated by:

- Cr(VI) reduction (with $FeCl_2$)
- Neutralisation
- Flocculation
- Sedimentation
- Chamber filter press
- Nitrite oxidation (with H_2O_2)
- Final neutralisation
- Filtration
- Activated carbon filter
- Ion exchange resin

Wastewater from CDC is treated by:

- Alkalisation with spent alkaline wastewater
- Flocculation
- Filtration
- Vacuum evaporation

The distillate from vacuum evaporation is treated in the above described WWTP. The remaining concentrate is disposed as waste by an external waste company.

Table 180: CDC – Emission limit values for the process wastewater in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface

treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

CDC Parameter	Unit	ELV Permit – CDC	BAT-AEL (BREF 2006)	Ordinance (indirect discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Q	m³	30				3x per year
Temperature (T)	°C	30		35		3x per year
Total Suspended Solids (TSS)	mg/l	30		150		3x per year
pH-Wert		6.5–9.0		6.5–10.0	cont.	3x per year
Aluminium (Al)	mg/l	3		Limited by TSS		3x per year
Zink (Zn)	mg/l	2	0.2–2.0	1	weekly	3x per year
Iron (Fe)	mg/l	2		Limited by TSS		3x per year
Chromium-VI (Cr(VI))	mg/l	0.1	0.1–0.2	0.1	every batch	3x per year
Chromium (Cr) total	mg/l	0.5	0.1–2.0	0.5		3x per year
Nickel (Ni)	mg/l	0.5	0.2–2.0	0.5		3x per year
Nitrite (NO_2)	mg/l	1.5		10		3x per year
Ammonia (NH_4-N)	mg/l	20		200		3x per year
Fluoride (F)	mg/l	20		20		3x per year
COD	mg/l	1000			weekly	3x per year
Low volatile lipophilic substances	mg/l	20		100		3x per year
Hydrocarbon Index	mg/l	5		15		3x per year
Sum of anionic and	mg/l	5				3x per year

CDC						
Parameter	**Unit**	**ELV Permit – CDC**	**BAT-AEL (BREF 2006)**	**Ordinance (indirect discharge)**	**Min. monitoring frequency self-monitoring**	**Min. monitoring frequency external-monitoring**
non-ionic surfactants						

Source: Permit 4.1-102/11; Permit BHLI-21533/2019-13; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 181: Self-monitoring of CDC process wastewater 2020

Self-monitoring 2020 – CDC							
Parameter	**Unit**	**Daily min.**	**Daily max.**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Q	m³/d	0.00	22.40	10.26	1.46	115	259
pH		7.05	8.37	7.85	7.32	6.5–9.0	237
COD	mg/l	0.00	831.00	693.00	136.81	1000	26
Cr(VI)	mg/l	0.00	0.08	0.08	0.02	0.1	26
Zn	mg/l	0.00	1.31	1.03	0.46	2	26

Source: Self-monitoring MACO, 2020

Table 182: Self-monitoring of CDC process wastewater 2019

Self-monitoring 2019 – CDC							
Parameter	**Unit**	**Daily min.**	**Daily max.**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Q	m³/d	0.00	29.50	28.50	16.22	115	255
pH		7.06	8.87	8.56	8.04	6.5–9.0	243
COD	mg/l	0.00	985.00	916.00	548.33	1000	51
Cr(VI)	mg/l	0.00	0.08	0.08	0.03	0.1	51

Self-monitoring 2019 – CDC							
Parameter	**Unit**	**Daily min.**	**Daily max.**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Zn	mg/l	0.00	1.65	1.48	0.70	2	51

Source: Self-monitoring MACO, 2019

Table 183: Self-monitoring of CDC process wastewater 2018

Self-monitoring 2018 – CDC							
Parameter	**Unit**	**Daily min.**	**Daily max.**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Q	m³/d	0.00	28.10	23.38	13.77	115	255
pH		7.01	8.32	8.01	7.43	6.5–9.0	242
COD	mg/l	0.00	750.00	697.50	231.86	1000	51
Cr(VI)	mg/l	0.00	0.09	0.08	0.04	0.1	51
Zn	mg/l	0.00	1.81	1.69	0.70	2	51

Source: Self-monitoring MACO, 2018

Table 184: External-monitoring of CDC process wastewater

External-monitoring 2020 – CDC					
Parameter	**Unit**	**30.06.2020**	**29.09.2020**	**15.12.2020**	**ELV**
Q	m³/d	CDC not operating	CDC not operating	8.5	30
T	°C			23.4	30
pH	–			8	6.5–9.0
TSS	mg/l			5.6	30
Cr(VI)	mg/l			0.053	0.1
NO_2-N	mg/l			0.87	1.5
Al	mg/l			0.019	3

External-monitoring 2020 – CDC					
Parameter	**Unit**	**30.06.2020**	**29.09.2020**	**15.12.2020**	**ELV**
Zn	mg/l			0.3	2
Ni	mg/l			0.16	0.5
Cr – total	mg/l			0.076	0.5
Fe	mg/l			0.027	2
F	mg/l			7.33	20
NH_4-N	mg/l			0.027	20
COD	mg/l			53	1000
SO_4	mg/l			70	–
TP	mg/l			0.13	–
TN	mg/l			36.6	–
low volatile lipophilic substances	mg/l			18	20
HC-Index	mg/l			0.28	5
Surfactants anionic	mg/l			0.6	–
Surfactants non-ionic	mg/l			3.6	–
Surfactants total	mg/l			4.2	5

Source: Clug, 2020

Table 185: External-monitoring of CDC process wastewater

External-monitoring 2019 – CDC					
Parameter	**Unit**	**20.03.2019**	**27.06.2019**	**11.12.2019**	**ELV**
Q	m^3/d	19.5	13.8	18.4	30
T	°C	23.2	26.4	22.1	30
pH	–	8.59	8.55	8.8	6.5–9.0

External-monitoring 2019 – CDC					
Parameter	**Unit**	**20.03.2019**	**27.06.2019**	**11.12.2019**	**ELV**
TSS	mg/l	4.8	22	18.4	30
Cr(VI)	mg/l	<0.015	0.06	0.027	0.1
NO_2-N	mg/l	0.4	0.65	0.93	1.5
Al	mg/l	0.043	0.081	0.021	3
Zn	mg/l	0.11	0.15	0.18	2
Ni	mg/l	<0.001	<0.001	< 0.001	0.5
Cr – total	mg/l	0.047	0.14	0.049	0.5
Fe	mg/l	0.092	0.3	0.23	2
F	mg/l	<0.10	<0.10	< 0.50	20
NH_4-N	mg/l	0.44	1.43	2.25	20
COD	mg/l	861	261	579	1000
SO_4	mg/l	30.8	65.6	67	–
TP	mg/l	0.047	0.026	0.054	–
TN	mg/l	16.1	51.3	59.1	–
low volatile lipophilic substances	mg/l	4	5	< 1.0	20
HC-Index	mg/l	<0.08	<0.08	< 0.08	5
Surfactants anionic	mg/l	3.6	1.87	1.7	–
Surfactants non-ionic	mg/l	1.25	0.43	0.69	–
Surfactants total	mg/l	4.85	2.3	2.39	5

Source: Clug, 2019

Table 186: External-monitoring of CDC process wastewater

External-monitoring 2018 – CDC					
Parameter	**Unit**	**22.03.2018**	**28.06.2018**	**19.12.2018**	**ELV**
Q	m^3/d	12.6	12.5	12.4	30
T	°C	21.7	24.2	21.3	30
pH	–	7.85	8.05	7.98	6.5–9.0
TSS	mg/l	2.6	11.3	11.6	30
Cr(VI)	mg/l	<0.015	0.05	0.068	0.1
NO_2-N	mg/l	0.015	0.43	0.24	1.5
Al	mg/l	0.015	0.037	0.012	3
Zn	mg/l	0.11	0.081	0.18	2
Ni	mg/l	<0.001	<0.001	<0.001	0.5
Cr – total	mg/l	0.15	0.047	0.24	0.5
Fe	mg/l	0.43	0.096	0.8	2
F	mg/l	<0.01	<0.1	0.1	20
NH_4-N	mg/l	0.54	1.72	0.63	20
COD	mg/l	18	185	84	1000
SO_4	mg/l	50.2	46.6	52.7	–
TP	mg/l	0.09	0.18	0.24	–
TN	mg/l	5.12	75.4	34.9	–
low volatile lipophilic substances	mg/l	4.9	1.07	< 1.0	20
HC-Index	mg/l	0.16	0.1	< 0.08	5
Surfactants anionic	mg/l	0.37	2.95	2	–
Surfactants non-ionic	mg/l	<0.1	0.15	0.41	–
Surfactants total	mg/l	0.37	3.1	2.41	5

Source: Clug, 2018

Wastewater from Anodising

Wastewater from anodizing is collected in separate streams (alkaline and acidic) and treated in a dedicated WWTP. Treatment consists of:

- Neutralisation
  - Batch neutralization
  - Continuous flow neutralization
- Flocculation
- Sedimentation
- Chamber filter press
- Final neutralization
- Sand filtration
- Ione exchange resin

Table 187: Anodising – Emission limit values for the process wastewater in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Anodising						
Parameter	**Unit**	**ELV Permit – Anodising**	**BAT-AEL (BREF 2006)**	**Ordinance (direct discharge)**	**Min. monitoring frequency self-monitoring**	**Min. monitoring frequency external-monitoring**
Q	m³/d	115				3x per year
Temperature (T)	°C	30		30		3x per year
Settleable substances	ml/l	0,3				3x per year
Total Suspended Solids (TSS)	mg/l	30	5–30	30		3x per year
pH		6,5–9,0		6,5–9,0	cont.	3x per year
Aluminium (Al)	mg/l	3	1–10	3		3x per year

Anodising						
Parameter	**Unit**	**ELV Permit – Anodising**	**BAT-AEL (BREF 2006)**	**Ordinance (direct discharge)**	**Min. monitoring frequency self-monitoring**	**Min. monitoring frequency external-monitoring**
Iron (Fe)	mg/l	2	0,1–5,0	2		3x per year
Copper (Cu)	mg/l	0,5	0,2–2,0	0,5	weekly	3x per year
Tin (Sn)	mg/l	1	0,2–2,0	1	weekly	3x per year
Nickel (Ni)	mg/l		0,2–2,0	0,5		3x per year
Sulphate (SO_4)	mg/l	3000				3x per year
COD	mg/l	100	100–500	100	weekly	3x per year
Low volatile lipophilic substances	mg/l	20		20		3x per year
Sum of Hydrocarbons	mg/l	5	1–5	5		3x per year
Sum of anionic and non-ionic surfactants	mg/l	5				3x per year
AOX	mg/l	1		1		3x per year

Source: Permit 4.1-102/11; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 188: Self-monitoring of anodising process wastewater 2020

Self-monitoring 2020 – anodising							
Parameter	**Unit**	**Daily min.**	**Daily max.**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Q	m^3/d	0.00	114.20	74.66	36.52	115	259
pH		7.04	8.26	7.92	7.58	6.5–9.0	237
Cu	mg/l	0.00	0.10	0.01	0.01	0.5	52
COD	mg/l	0.00	89.00	85.58	48.97	100	52
Sn	mg/l	0.00	0.98	0.85	0.31	1	52

Source: Self-monitoring MACO, 2020

Table 189: Self-monitoring of anodising process wastewater 2019

Self-monitoring 2019 – anodising							
Parameter	**Unit**	**Daily min.**	**Daily max.**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Q	m^3/d	0.00	103.40	82.35	39.94	115	255
pH		7.03	8.38	7.92	7.51	6.5–9.0	243
Cu	mg/l	0.00	0.10	0.05	0.01	0.5	51
COD	mg/l	0.00	87.40	85.60	52.82	100	51
Sn	mg/l	0.00	0.57	0.31	0.08	1	51

Source: Self-monitoring MACO, 2019

Table 190: Self-monitoring of anodising process wastewater 2018

Self-monitoring 2018 – anodising							
Parameter	**Unit**	**Daily min.**	**Daily max.**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Q	m^3/d	0.00	113.50	61.86	37.78	115	255
pH		7.01	7.88	7.45	7.23	6.5–9.0	241
Cu	mg/l	0.00	0.02	0.01	0.01	0.5	51
COD	mg/l	0.00	92.00	90.30	53.60	100	51
Sn	mg/l	0.00	0.27	0.12	0.03	1	51

Source: Self-monitoring MACO, 2018

Table 191: External-monitoring of anodising process wastewater

External-monitoring 2020 – Anodising					
Parameter	**Unit**	**30.06.2020**	**29.09.2020**	**15.12.2020**	**ELV**
Q	m^3/d	33	37.8	45.9	115
T	°C	24.9	23.9	20.4	30
pH	–	7.8	7.5	7.47	6.5–9.0
TSS	mg/l	23	17.9	16	30
S^{2-}	mg/l	< 0.025	< 0.025	0.035	0.1
Al	mg/l	2.44	0.26	0.23	3
Cu	mg/l	0.0015	0.001	0.004	0.5
Fe	mg/l	< 0.01	0.02	0.02	2
Sn	mg/l	< 0.001	< 0.001	< 0.001	1
COD	mg/l	27	< 15	23	100
AOX	mg/l	0.59	0.22	0.29	1
low volatile lipophilic substances	mg/l	< 1	1	15	20
HC-Index	mg/l	< 0.08	< 0.08	< 0.08	5
Surfactants anionic	mg/l	0.98	0.33	0.65	–
Surfactants non-ionic	mg/l	2.9	0.14	1.94	–
Surfactants total	mg/l	3.88	0.47	2.69	5
SO_4	mg/l	790	1300	530	3000
TP	mg/l	0.008	0.051	0.028	–
TN	mg/l	2.5	1.27	1.53	–

Source: Clug, 2020

Table 192: External-monitoring of anodising process wastewater

External-monitoring 2019 – Anodising					
Parameter	**Unit**	**20.03.2019**	**27.06.2019**	**11.12.2019**	**ELV**
Q	m^3/d	32.2	42.6	23.2	115
T	°C	20.8	25.3	19.3	30
pH	–	7.22	8.41	7.8	6.5–9.0
TSS	mg/l	13.2	11.2	25.9	30
S^{2-}	mg/l	<0.025	<0.025	< 0.025	0.1
Al	mg/l	0.034	0.34	2.62	3
Cu	mg/l	0.0057	<0.0010	< 0.001	0.5
Fe	mg/l	0.051	<0.010	0.15	2
Sn	mg/l	<0.001	<0.0010	< 0.001	1
COD	mg/l	37	36	19	100
AOX	mg/l	0.093	0.056	0.22	1
low volatile lipophilic substances	mg/l	7	9	< 1.0	20
HC-Index	mg/l	<0.08	< 0.08	0.17	5
Surfactants anionic	mg/l	0.73	1.08	0.53	–
Surfactants non-ionic	mg/l	<0.20	3.35	3.12	–
Surfactants total	mg/l	0.73	4.43	3.65	5
SO_4	mg/l	237	1810	990	3000
TP	mg/l	0.095	0.16	0.016	–
TN	mg/l	3.55	2.22	0.8	–

Source: Clug, 2019

Table 193: External-monitoring of anodising process wastewater

External-monitoring 2018 – Anodising					
Parameter	**Unit**	**22.03.2018**	**28.06.2018**	**19.12.2018**	**ELV**
Q	m^3/d	30.9	50.3	45.7	115
T	°C	22.2	24.9	19.7	30
pH	–	7.02	7.4	7.36	6.5–9.0
TSS	mg/l	7.47	15.9	9.93	30
S^{2-}	mg/l	<0.025	0.058	< 0.025	0.1
Al	mg/l	0.05	0.041	0.3	3
Cu	mg/l	<0.001	<0.001	< 0.001	0.5
Fe	mg/l	0.077	0.04	0.082	2
Sn	mg/l	<0.001	0.0019	<0.001	1
COD	mg/l	51	38	52	100
AOX	mg/l	0.14	0.13	0.12	1
low volatile lipophilic substances	mg/l	3.6	< 1.0	< 1.0	20
HC-Index	mg/l	0.1	0.11	< 0.08	5
Surfactants anionic	mg/l	0.53	0.54	0.57	–
Surfactants non-ionic	mg/l	0.39	0.25	1.41	–
Surfactants total	mg/l	0.92	0.79	1.98	5
SO_4	mg/l	277	1220	1140	3000
TP	mg/l	0.16	0.49	0.17	–
TN	mg/l	4.76	2.82	3.71	–

Source: Clug, 2018

Wastewater from Electroplating

Wastewater from electroplating is treated in two identical dedicated WWTPs.

Wastewater from electroplating is collected in separate streams, i.e.:

- Rinsing water and concentrates containing chromium and eluates
- Rinsing water
- Concentrates acidic
- Concentrates alkaline
- Spent acids
- Wastewater from brightening

Wastewater treatment consists of:

- Cr(VI) reduction (with $FeCl_2$)
- Neutralisation
  - Batch neutralization
  - Continuous flow neutralisation (for less contaminated wastewaters)
- Flocculation
- Sedimentation
- Chamber filter press
- Final neutralisation
- Sand filtration
- Ion exchange resins

Table 194: Zn Electroplating – Emission limit values for the process wastewater in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Electroplating **Parameter**	**Unit**	**ELV Permit – Zn Electroplating**	**BAT-AEL (BREF 2006)**	**Ordinance (direct discharge)**	**Min. monitoring frequency self-monitoring**	**Min. monitoring frequency external-monitoring**
Q	m³/d	465				3x per year
Temperature (T)	°C	30		30		3x per year
Settleable substances	ml/l	0.3				3x per year
Total Suspended Solids (TSS)	mg/l	30	5–30	30		3x per year
pH		6.5–9.0		6.5–9.0	cont.	3x per year
Aluminium (Al)	mg/l		1–10	3		3x per year
Chromium total (Cr)	mg/l	0.5	0.1–2.0	0.5		3x per year
Chromium-VI (Cr(VI))	mg/l	0.1	0.1–0.2	0.1	weekly	3x per year
Cobalt (Co)	mg/l	1		1		3x per year
Iron (Fe)	mg/l	2	0.1–5.0	2		3x per year
Copper (Cu)	mg/l	0.5	0.2–2.0	0.5	weekly	3x per year
Zinc (Zn)	mg/l	2	0.2–2.0	1[210]	weekly	3x per year
Fluoride (F)	mg/l	20	10–20	20		3x per year
Nitrite (NO_2)	mg/l	1.5		1.5		3x per year
Sulphite (SO_3)	mg/l	1				3x per year

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[210] The ELV for Zn is 2.0 mg/l for process wastewater from galvanising or batch galvanising

Electroplating						
Parameter	**Unit**	**ELV Permit – Zn Electroplating**	**BAT-AEL (BREF 2006)**	**Ordinance (direct discharge)**	**Min. monitoring frequency self-monitoring**	**Min. monitoring frequency external-monitoring**
COD	mg/l	200	100–500	100[211]	weekly	3x per year
Low volatile lipophilic substances	mg/l	20		20		3x per year
Sum of Hydrocarbons	mg/l	5	1–5	5		3x per year
Sum of anionic and non-ionic surfactants	mg/l	5				3x per year
AOX	mg/l	1		1		3x per year

Source: Permit 4.1-102/11; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 195: Self-monitoring of electroplating process wastewater 2020

Self-monitoring 2020 – electroplating							
Parameter	**Unit**	**Daily min.**	**Daily max.**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Q	m^3/d	0.00	441.20	431.61	340.35	465	259
pH		6.78	7.97	7.71	7.29	6.5–9.0	237
Cu	mg/l	0.00	0.25	0.05	0.01	0.5	52
COD	mg/l	0.00	199.00	194.00	146.29	200	52
Cr(VI)	mg/l	0.00	0.10	0.06	0.02	0.1	52
Zn	mg/l	0.00	1.95	1.88	1.43	2	52

Source: Self-monitoring MACO, 2020

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[211] The ELV for COD is 200 mg/l for process wastewater from galvanising

Table 196: Self-monitoring of electroplating process wastewater 2019

Self-monitoring 2019 – electroplating							
Parameter	**Unit**	**Daily min.**	**Daily max.**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Q	m^3/d	0.00	434.00	430.65	343.38	465	255
pH		6.97	8.41	7.81	7.36	6.5–9.0	243
Cu	mg/l	0.00	0.02	0.02	0.01	0.5	51
COD	mg/l	0.00	193.00	182.00	139.63	200	51
Cr(VI)	mg/l	0.00	0.05	0.03	0.01	0.1	51
Zn	mg/l	0.00	1.91	1.87	1.54	2	51

Source: Self-monitoring MACO, 2019

Table 197: Self-monitoring of electroplating process wastewater 2018

Self-monitoring 2018 – electroplating							
Parameter	**Unit**	**Daily min.**	**Daily max.**	**95 Percentile**	**Annual average**	**ELV Permit**	**Number of samples**
Q	m^3/d	0.00	441.80	424.32	330.86	465	255
pH		7.01	8.08	7.80	7.31	6.5–9.0	241
Cu	mg/l	0.00	0.01	0.01	0.01	0.5	51
COD	mg/l	0.00	196.00	190.50	152.65	200	51
Cr(VI)	mg/l	0.00	0.08	0.06	0.02	0.1	51
Zn	mg/l	0.00	1.91	1.88	1.37	2	51

Source: Self-monitoring MACO, 2018

Table 198: External-monitoring of electroplating process wastewater

External-monitoring 2020 – Electroplating					
Parameter	**Unit**	**30.06.2020**	**29.09.2020**	**15.12.2020**	**ELV**
Q	m^3/d	432.8	404	316	465
T	°C	25.2	24.9	23.6	30
pH	–	7.3	7.3	7	6.5–9.0
TSS	mg/l	25.7	25.6	16.9	30
Cr(VI)	mg/l	< 0.015	< 0.015	0.015	0.1
SO_3	mg/l	< 0.5	< 0.1	< 0.1	1
NO_2-N	mg/l	0.33	0.093	0.51	1.5
Zn	mg/l	0.83	1.63	0.55	2
Cu	mg/l	0.023	0.023	0.035	0.5
Cr – total	mg/l	0.01	0.018	0.006	0.5
Fe	mg/l	0.29	0.98	0.75	2
Co	mg/l	< 0.001	< 0.001	0.001	1
F	mg/l	7.41	2.21	7.51	20
COD	mg/l	130	103	133	200
AOX	mg/l	0.56	0.4	0.58	1
low volatile lipophilic substances	mg/l	< 1	1	13	20
HC-Index	mg/l	< 0.08	< 0.08	< 0.08	5
Surfactants anionic	mg/l	0.47	1.2	2	–
Surfactants non-ionic	mg/l	2.6	3.55	2.38	–
Surfactants total	mg/l	3.07	4.75	4.38	5
SO_4	mg/l	83	77	84	–
TP	mg/l	0.067	0.19	0.13	–
TN	mg/l	80.2	63.5	44.7	–

Source: Clug, 2020

Table 199: External-monitoring of electroplating process wastewater

External-monitoring 2019 – Electroplating					
Parameter	**Unit**	**20.03.2020**	**27.06.2019**	**11.12.2019**	**ELV**
Q	m³/d	384	395	413.8	465
T	°C	25.4	26.5	21.1	30
pH	–	7.64	7.68	7.3	6.5–9.0
TSS	mg/l	18.4	18.7	20.3	30
Cr(VI)	mg/l	<0.015	<0.026	0.055	0.1
SO_3	mg/l	<0.5	<0.5	< 0.5	1
NO_2-N	mg/l	0.44	0.074	0.2	1.5
Zn	mg/l	1.15	1.07	0.89	2
Cu	mg/l	0.0062	0.012	0.0093	0.5
Cr – total	mg/l	0.031	0.032	0.025	0.5
Fe	mg/l	0.056	0.081	0.43	2
Co	mg/l	<0.001	< 0.001	< 0.001	1
F	mg/l	4.84	4.9	5.52	20
COD	mg/l	113	103	146	200
AOX	mg/l	0.32	0.87	0.46	1
low volatile lipophilic substances	mg/l	15	11	< 1.0	20
HC-Index	mg/l	<0.08	< 0.08	< 0.08	5
Surfactants anionic	mg/l	1.56	1.35	1.5	–
Surfactants non-ionic	mg/l	1.06	1.5	1.56	–
Surfactants total	mg/l	2.62	2.85	3.06	5
SO_4	mg/l	182	170	83	–
TP	mg/l	0.19	0.099	0.036	–
TN	mg/l	122	177	85.8	–

Source: Clug, 2019

Table 200: External-monitoring of electroplating process wastewater

External-monitoring 2018 – Electroplating					
Parameter	**Unit**	**22.03.2018**	**28.06.2018**	**19.12.2018**	**ELV**
Q	m^3/d	401.9	399.7	398	465
T	°C	23.8	25.1	22.9	30
pH	–	7.34	7.53	7.41	6.5–9.0
TSS	mg/l	4.8	25.6	11.8	30
Cr(VI)	mg/l	0.033	0.026	0.027	0.1
SO_3	mg/l	0.24	0.26	< 0.5	1
NO_2-N	mg/l	0.26	0.35	0.19	1.5
Zn	mg/l	0.84	0.69	0.7	2
Cu	mg/l	0.0024	0.0016	0.0043	0.5
Cr – total	mg/l	0.03	0.043	0.069	0.5
Fe	mg/l	0.04	0.017	0.23	2
Co	mg/l	0.0032	0.0075	< 0.001	1
F	mg/l	0.14	0.77	4.98	20
COD	mg/l	99	29	90	200
AOX	mg/l	0.58	0.86	0.45	1
low volatile lipophilic substances	mg/l	4.2	<1.0	< 1.0	20
HC-Index	mg/l	0.15	0.16	< 0.08	5
Surfactants anionic	mg/l	1.77	1.79	1.63	–
Surfactants non-ionic	mg/l	1.61	0.65	3.15	–
Surfactants total	mg/l	3.38	2.44	4.78	5
SO_4	mg/l	118	201	130	–
TP	mg/l	0.33	0.14	0.15	–
TN	mg/l	75.2	248	59.2	–

Source: Clug, 2018

Table 201: Monitoring standards external-monitoring

Monitoring standards (external monitoring)	
Parameter	**Standard**
TSS	DIN 38 409 - H 2
AOX	EN ISO 9562
Al	ÖNORM EN ISO 17294-2
NH_4-N	ÖNORM ISO 7150-1
COD	DIN 38 409 - H 44
Cr – total	ÖNORM EN ISO 17294-2
Cr(VI)	EN ISO 17294-2
Fe	ÖNORM EN ISO 17294-2
Conductivity	ÖNORM EN 27888
Fe	DIN EN ISO 10304-1
TP	ÖNORM EN ISO 6878
TN	DIN EN ISO 11905-1
Co	ÖNORM EN ISO 17294-2
HC-Index	ÖNORM EN ISO 9377-2
Cu	ÖNORM EN ISO 17294-2
Ni	ÖNORM EN ISO 17294-2
NO_2-N	EN 26777
pH	DIN 38 404 - C 5
low volatile lipophilic substances	DIN ISO 11349
SO_4	DIN EN ISO 10304-1
S^{2-}	DIN 38 405 - D 26
SO_3	ÖNORM EN ISO 10304-3
T	DIN 38 404 - C 4
Surfactants anionic	ÖNORM EN 903
Surfactants total	Rechnerisch
Surfactants non-ionic	DIN 38 409 - H 23

Monitoring standards (external monitoring)	
Parameter	**Standard**
Zn	ÖNORM EN ISO 17294-2
Sn	ÖNORM EN ISO 17294-2

Source: Clug, 2020

10.3 References

AEV Oberflächenbehandlung, BGBl. II Nr. 44/2002: Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Begrenzung von Abwasseremissionen aus der Behandlung von metallischen Oberflächen (AEV Oberflächenbehandlung), BGBl. II Nr. 44/2002

Clug (2018-2020): Inspektionsbericht, Überprüfung der Abwasserreinigungsanlage, Chemisches Laboratorium für Umwelt und Gesundheit, Trofaiach, 2018-2020

Kaufmann (2020): Prüfbericht,Technisches Büro für Umwelttechik, Dipl.-Ing. Horst Kaufmann, 2020

Permit 4.1-102/11: Wasserrechtliche Bewilligung, 4.1-102/11, BH Liezen

Permit BHLI-21533/2019-13: Wasserrechtliche Bewilligung, BHLI-21533/2019-13, BH Liezen

STM BREF (2006): Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Surface Treatment of Metals and Plastics, European Commission, 2006

STS BREF, Final Draft (2019): Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Surface Treatment Using Organic Solvents including Wood and Wood Products Preservation with Chemicals, Final Draft, European Commission, 2019

11 MAGNA STEYR Fahrzeugtechnik AG & CO KG

Magna Steyr is producing vehicles for different automotive companies. The production of cars can be structured into body in white production, painting and assembly. The production facility in Graz is a plant affected by IED. Certain sub-processes of painting, i.e. pre-treatment, phosphating and e-coating, are affected by IED Annex I activity 2.6.

Environmental Management System
Magna Steyr has a certified environmental management system implemented according to EMAS and ISO 14001.

11.1Technical description

The painting process is structured into the following sub-processes:

- Pre-treatment including Phosphating
- E-coating
- Sealing including underbodycoating
- Primer
- Base coat
- Clear coat
- Cavity preservation

The sub-processes primer, base coat and clear coat are covered by the BREF-STS “Surface Treatment using Solvents” and not further described in this chapter.

Pre-treatment
The car body is cleaned in a body washer where cleaning solutions are sprayed to the car body. Subsequently the car bodies pass spray and dip degreasing. Degreasing is done above room temperature with alkaline cleaning solutions. After a rinsing stage the car body passes a titanium-based activation which enhances phosphating layer conversion.

Phosphating layer conversion coating

Phosphating layer conversion coatings are widely used to treat steel, aluminium and galvanized parts. The rough surface enables adhesion gained through numerous capillaries makes phosphate layers a perfect base layer for the further e-coat process operations such as painting, etc. The phosphating solution is in general applied by dipping. The main components of the phosphating solution are zinc, nickel, manganese, phosphates, nitrite (oxidizing agent), nitrates and fluorides. After phosphating the car body is rinsed by spray and immersion rinsing.

Passivation

To further improve corrosion resistance the car body passes passivation. The chromium-free conversion process is based on an organic zirconium based solution. After passivation the car body is rinsed.

E-coating

Paint particles dispersed in a water-based solution are applied onto the vehicle in a dip process supported by an electric field. Hereby the car body works as the cathode, the anodes are placed at the side tank wall.

The composition of an E-coat bath is a typical emulsion of pigment paste and deionised water. The solvent content is typical lower than 1.5%.

After the E-coat application the car body is rinsed to remove not deposited E-coat material. After the rinse zone the paint film is cured in a drying oven at 180 °C for 20 minutes.

The applied and dried E-coat film offers a very good corrosion protection for out- and inside areas.

Process water

Deionised water is used in the entire pre-treatment and e-coating process to ensure product quality but also to reduce the entry of impurities into the process. This helps maintaining process stability and reducing consumption of chemicals. Water deionisation is done with reverse osmosis.

Rinsing

Rinsing is done after each process step. Both spray and immersion rinsing units are in operation. Rinsing water is recirculated in counter flow cascades. Rinsing water is treated with ion exchange resins. After e-coating the car body is rinsed to remove excess material. The rinsing water is treated with ultrafiltration. The gained e-coat material re-enters the e-coat process. The ultrafiltrated rinsing water is re-used as rinsing water in a counter flow cascade.

Bath life span

Degreasing baths are equipped with oil-water separators. This prolongs the degreasing bath life span and reduces consumption of chemicals. Phosphating baths are equipped with filters to prolong bath life span. The accruing sludge is dewatered with chamber filter presses and disposed by external waste disposal companies.

Waste gas

The entire pre-treatment, phosphating and e-coating unit is encapsulated (tunnel). Waste gas from pre-treatment and phosphating is solvents free, extracted and emitted via dedicated stacks. Waste gas from e-coating is extracted and emitted via dedicated stacks. Waste gas from heat treatment (after e-coating) is extracted, treated with a Thermal Air Oxidizer (TAO) for reducing organic compounds and emitted via stacks. Excess heat from the TAO is used for heat treatment.

Process wastewater

Treated wastewater is discharged indirectly. Wastewater streams from pre-treatment, phosphating and e-coating are collected and treated separately, i.e.:

- Acidic and alkaline concentrates, regenerates and rinsing water
- Wastewater from e-coating
- Wastewater from degreasing

The WWTP consists of a neutralisation unit (where heavy metals are precipitated) and a biological treatment step.

The neutralisation unit consists of:

- Buffer tank
- Neutralisation (heavy metal precipitation, fluoride precipitation)
- Flocculation
- Sedimentation

- Sludge dewatering
- Sand filter
- Ion exchange resin
- Final neutralisation

The biological treatment consists of:

- Buffer tank
- 2 membrane bioreactors
- Sand filter
- Neutralisation
- Ion exchange resin
- Final neutralisation

Acidic and alkaline concentrates, regenerates and rinsing water is treated in the neutralisation unit. Wastewater from e-coating and degreasing is treated in the biological treatment step. Wastewater from the neutralisation unit and the biological treatment unit are merged together before final neutralisation.

Wastewater from reverse osmosis is sent directly into the public sewer.

11.2Current consumption and emission levels

Specific consumption

The specific energy and water consumption per produced car varies due to the product requirements and the shape of the vehicle. Reducing energy and water consumption, whilst maintaining the required product quality, is one of the main goals of the operator, therefore consumption parameters are monitored at several process steps. For pre-treatment, phosphating and e-coating approximately between 200kWh/car and 300kWh/carbody (depends on production shifts) and 0.6 – 0.8 m^3/car (fresh water) are consumed. The amount of recirculated water in the process is approximately double the amount of consumed fresh water. The amount of recirculated water in the process is approximately double the amount of consumed fresh water.

Generated waste from pre-treatment, phosphating and e-coating is listed in Table 202.

Table 202: Waste generation from IED Annex I 2.6 relevant process steps

	Pre-treatment and phosphating			E-coat				
	2019	2018	2017	2019	2018	2017	Unit	Comment
Sludge – phosphating	74781.00	93117.00	50145.00	–	–	–	t/a	hazardous
Oil contaminated waste	9573.00	9794.00	9690.00	–	–	–	t/a	hazardous
Sludge – Oil separator	4040.00	6840.00	15560.00	–	–	–	t/a	hazardous
Varnish contaminated waste	–	–	–	22222.00	22389.00	23855.00	t/a	hazardous
Metal hydroxide sludge	408260.00	478780.00	381720.00	–	–	–	t/a	hazardous

Source: Magna Steyr, own recordings

Emissions to air

The entire pre-treatment, phosphating and e-coating unit is encapsulated (tunnel). Waste gas from pre-treatment and phosphating is solvents free, extracted and emitted via dedicated stacks. Waste gas from e-coating is extracted and emitted via dedicated stacks. Waste gas from heat treatment (after e-coating) is extracted, treated with a Thermal Air Oxidizer (TAO) for reducing organic compounds and emitted via stacks. Excess heat from the TAO is used for heat treatment.

Monitoring requirements for emissions to air from the CDC unit are prescribed by the IED, VOC-Anlagenverordnung and permit. Monitoring has to be conducted all three years by an accredited testing institute.

Table 203 presents the monitoring results from 2016 and 2019. The measurements were conducted during normal operating conditions.

Table 203: Monitoring results of emissions to air from CDC; 0 °C, 1013 mbar, dry exhaust air

Process step	Dust ELV: 5 mg/Nm³ [mg/Nm³]	CO ELV:100 mg/Nm³ [mg/Nm³]	NOx ELV: 100 mg/Nm³ [mg/Nm³]	TVOC ELV: 30 mg/Nm³ [mg/Nm³]
2016 – CDC				
rinsing				2.5
CDC bath				25.0
heat treatment (TAO)	0.2	31.0	45.3	4.7
heat treatment (TAO)	0.2	31.0	46.6	0.7
cooling	0.4			0.3
2019 – CDC				
rinsing				14.0
CDC bath				17.8
heat treatment (TAO)	0.2	51.7	96.8	1.1
heat treatment (TAO)	0.2	29.8	97.2	0.8
cooling	0.4			2.5

Source: Kaufmann, 2016 & 2019

Emissions to water

Treated process wastewater is discharged indirectly. Monitoring has to be conducted using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit. Minimum monitoring frequencies for self-monitoring (performed by operator) and external-monitoring are prescribed by permit. Emission limit values (ELV) are prescribed by permit

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

The WWTP consists of a neutralisation unit (where heavy metals are precipitated) and a biological treatment step.

The neutralisation unit consists of:

- Buffer tank
- Neutralisation (heavy metal precipitation, fluoride precipitation)
- Flocculation
- Sedimentation
- Sludge dewatering
- Sand filter
- Ion exchange resin
- Final neutralisation

The biological treatment consists of:

- Buffer tank
- 2 membrane bioreactors
- Sand filter
- Neutralisation
- Ion exchange resin
- Final neutralisation

A detailed description of the on-site WWTP is presented in chapter 11.1

Emissions to water are described in the following tables. In Table 204 the minimum monitoring frequencies and ELVs prescribed by permit are presented and compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. In Table 205 – Table 208 the self-monitoring recordings of treated process wastewater are presented. Table 209 – Table 212 present the results from external-monitoring of treated process wastewater for the years 2016, 2017, 2018 & 2019.

Only wastewater from activities according to IED Annex I activity 2.6 are treated in the on-site WWTP.

Table 204: Emission limit values for the process wastewater in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)[212]	Ordinance (indirect discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
pH		6.5–9.5	–	6.5–10.0	–	2x per year
Temperature	°C	35	–	35	–	2x per year
TSS	mg/l	150	0.1–2.0	0.5	–	2x per year
Cr(VI)	mg/l	0.1	0.1–0.2	0.1	–	2x per year
Manganese (Mn)	mg/l	0.9	–	–	–	2x per year
Nickel (Ni)	mg/l	0.5	0.2–2.0	0.5	Daily	2x per year
Zinc (Zn)	mg/l	1.1	0.2–2.0	1.0[213]	–	2x per year
Ammonium (NH_4-N)	mg/l	200	–	200	–	2x per year
Fluoride (F)	mg/l	20	–	20	–	2x per year
Sulfate (SO_4)	mg/l	400	–	–	–	2x per year
COD	mg/l	15000 (day) 20000 (night)	–	–	Daily	2x per year
AOX	mg/l	1.0	–	–	–	2x per year
Hydrocarbon Index	mg/l	15	–	15	–	2x per year
Sulphite (SO_3)	mg/l	10	–	–	–	2x per year

Source: Permit A17-EAG-098439/2018/0009, STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

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[212] Discharge to public sewer or surface water from jig, barrel, small scale coil, automotive, PCB and other activities not large scale steel coil

[213] For wastewaters from electroplating or batch galvanising the ELV is 2.0 mg/l

External-monitoring has to be conducted twice a year and is usually done in six month intervals.

Table 205: Self-monitoring of treated process wastewater 2016

Self-monitoring 2016					
Parameter	**Unit**	**Daily min.**	**Annual average**	**Daily max.**	**ELV Permit**
pH	–	6.9	7.4	8.1	6.5–9.5
T	°C	18	21	25	35
Ni	mg/l	0.1	0.2	0.39	0.4
COD	mg/l	25	235	813	15000(day)/20000(night)

Source: Self-monitoring Magna Steyr, 2016

Table 206: Self-monitoring of treated process wastewater 2017

Self-monitoring 2017					
Parameter	**Unit**	**Daily min.**	**Annual average**	**Daily max.**	**ELV Permit**
pH	–	6.9	7.3	8.3	6.5–9.5
T	°C	19	21	25	35
Ni	mg/l	0.1	0.22	0.36	0.4
COD	mg/l	22	167	374	15000(day)/20000(night)
F	mg/l	2	7.8	18	20

Source: Self-monitoring Magna Steyr, 2017

Table 207: Self-monitoring of treated process wastewater 2018

Self-monitoring 2018					
Parameter	Unit	Daily min.	Annual average	Daily max.	ELV Permit
pH	–	6.8	7.5	7.9	6.5–9.5
T	°C	14	21	28	35
Ni	mg/l	0.04	0.15	0.38	0.4
COD	mg/l	29	96	340	15000(day)/20000(night)
F	mg/l	5	11,5	18	20

Source: Self-monitoring Magna Steyr, 2018

Table 208: Self-monitoring of treated process wastewater 2019

Self-monitoring 2019					
Parameter	Unit	Daily min.	Annual average	Daily max.	ELV Permit
pH	–	6.8	7.4	8.5	6.5–9.5
T	°C	16	21	25	35
Ni	mg/l	0.04	0.15	0.33	0.4
COD	mg/l	30	136	1573	15000(day)/20000(night)
F	mg/l	4	12	18	20

Source: Self-monitoring Magna Steyr, 2019

Table 209: External-monitoring of process wastewater

External-monitoring 2016				
Parameter	Unit	M1	M2	ELV Permit
pH		7.20	7.33	6.5–9.5
T	°C	19.2	24.4	35

External-monitoring 2016 Parameter	Unit	M1	M2	ELV Permit
TSS	mg/l	5.7	14.1	150
Conductivity	µS/cm	3108	5566	–
Ni	mg/l	0.032	0.13	0.4
Zn	mg/l	0.006	0.052	1.1
Mn	mg/l	0.06	0.57	0.9
NH_4-N	mg/l	0.084	0.54	200
TP	mg/l	2.2	5.45	–
SO_4	mg/l	25.8	71.5	400
F	mg/l	3.5	4.38	20
COD	mg/l	49	70	15000(day)/ 20000(night)
AOX	mg/l	0.17	0.35	1.0
Hydrocarbon Index	mg/l	<0.08	<0.08	15
SO_3	mg/l	0	0	10

Source: Clug, 2016–2019

Table 210: External-monitoring of process wastewater

External-monitoring 2017 Parameter	Unit	M1	M2	ELV Permit
pH		7.34	7.34	6.5–9.5
T	°C	24.5	26.6	35
TSS	mg/l	10.5	37.3	150
Conductivity	µS/cm	2506	3197	–
Ni	mg/l	0.037	0.062	0.4
Zn	mg/l	0.036	0.067	1.1
Mn	mg/l	0.16	0.57	0.9

External-monitoring 2017				
Parameter	**Unit**	**M1**	**M2**	**ELV Permit**
NH_4-N	mg/l	2.8	9.3	200
TP	mg/l	3.1	5.8	–
SO_4	mg/l	47.8	108	400
F	mg/l	5.5	9.8	20
COD	mg/l	85	96	15000(day)/ 20000(night)
AOX	mg/l	0.15	0.26	1.0
Hydrocarbon Index	mg/l	<0.08	0.55	15
SO_3	mg/l	0	0.67	10

Source: Clug, 2016–2019

Table 211: External-monitoring of process wastewater

External-monitoring 2018				
Parameter	**Unit**	**M1**	**M2**	**ELV Permit**
pH		7.67	7.97	6.5–9.5
T	°C	24.7	28.5	35
TSS	mg/l	1.6	4.6	150
Conductivity	µS/cm	2232	2807	–
Ni	mg/l	0.034	0.051	0.4
Zn	mg/l	0.004	0.012	1.1
Mn	mg/l	0.16	0.19	0.9
NH_4-N	mg/l	9.3	14.4	200
TP	mg/l	4.6	6.0	–
SO_4	mg/l	19.1	171	400
F	mg/l	7.1	10.2	20
COD	mg/l	40	45	15000(day)/ 20000(night)

External-monitoring 2018				
Parameter	**Unit**	**M1**	**M2**	**ELV Permit**
AOX	mg/l	0.12	0.16	1.0
Hydrocarbon Index	mg/l	<0.08	0.1	15
SO_3	mg/l	0	0	10

Source: Clug, 2016–2019

Table 212: External-monitoring of process wastewater

External-monitoring 2019				
Parameter	**Unit**	**M1**	**M2**	**ELV Permit**
pH		8.02	8.15	6.5–9.5
T	°C	23.6	24.2	35
TSS	mg/l	2.4	11.3	150
Conductivity	µS/cm	2409	3623	–
Ni	mg/l	0.01	0.019	0.4
Zn	mg/l	0.008	0.020	1.1
Mn	mg/l	0.029	0.13	0.9
NH_4-N	mg/l	6.3	9.1	200
TP	mg/l	8.7	15.7	–
SO_4	mg/l	77	81.3	400
F	mg/l	8.1	12.1	20
COD	mg/l	55	71	15000(day)/ 20000(night)
AOX	mg/l	0.06	0.17	1.0
Hydrocarbon Index	mg/l	<0.08	0.13	15
SO_3	mg/l	0	0	10

Source: Clug, 2016–2019

TSS values from external monitoring represent the measures of the treated wastewater stream. A wastewater stream with high COD load (which stems from varnishing and e-coating; in the following refered to as "high COD load") is sent without treatment to the communal wastewater treatment plant (as the communal WWTP is equipped to treat this wastewater stream). The discharge is done at certain times where there is a general low COD load of the communal WWTP. The external monitoring values for TSS from this wastewater stream were:

- 2019: 58 mg/l, 61 mg/l
- 2020: 59 mg/l, 59 mg/l, 37 mg/l, 73 mg/l, 28 mg/l, 50 mg/l, 107 mg/l, 92 mg/l, 74 mg/l, 77 mg/l
- 2021: 124 mg/l, 18 mg/l, 100 mg/l, 88 mg/l, 66 mg/l

Aluminium emissions are limited through the emission limit value for TSS (which is accordance with the national ordinance on wastewater emissions from surface treatment activities). Hence, aluminium emissions are not monitored. In the course of this study, aluminium emissions from the wastewater stream "high COD load" were measured. The measured values are presented below. The wastewater stream "high COD load" is sent without further treatment to the communal WWTP (at times when the general COD load of the WWTP is low).

- 3.11.2021: 4.28 mg/l, 7.5 mg/l, 2.38 mg/l, 6.24 mg/l, 8.78 mg/l
- 9.11.2021: 11.4 mg/l, 13.9 mg/l, 4.92 mg/l, 5.91 mg/l, 8.01 mg/l

11.3 References

AEV Oberflächenbehandlung, BGBl. II Nr. 44/2002: Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Begrenzung von Abwasseremissionen aus der Behandlung von metallischen Oberflächen (AEV Oberflächenbehandlung), BGBl. II Nr. 44/2002

Clug (2016-2019): Chemisches Laboratorium für Umwelt und Gesundheit, clug Trofaiach, Überprüfung der Abwasserreinigungsanlage, 2017-2019

Permit (A17-EAG-098439/2018/0009): Wasserrechtliche Bewilligung, Kenntnisnahme Änderung der Abwasserreinigungsanlage, A17-EAG-098439/2018/0009, Stadt Graz

STM BREF (2006): Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Surface Treatment of Metals and Plastics, European Commission, 2006

STS BREF, BAT Conclusions December 2020: Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Surface Treatment Using Organic Solvents including Wood and Wood Products Preservation with Chemicals, Final Draft, European Commission, 2019

12 Miba Gleitlager Austria GmbH-Laakirchen

Miba Gleitlager Austria GmbH Laakirchen Site is exclusively electroplating bearings from own production. The bearings are produced on site. The bearings are produced for various applications such as heavy duty truck engines, high speed diesel & gas engines, locomotive engines, 4 stroke medium speed diesel & gas engines, 2 stroke engines, compressors & gas turbines.

Approximately 600 employees are working on site in 3-shift operation. The Miba group is an international company with production sites in North- and South-America, Asia and Europe. The electroplating installation in Laakirchen is not an IED-installation.

Environmental Management System
Miba Gleitlager Austria GmbH Laakirchen Site has an according to ISO 14001 certified environmental management system implemented.

12.1Technical description

Bearing production
The aluminium and bronze bearing alloys are molten from raw and recycled materials and casted into steel pipes. After that the work piece undergoes mechanical treatment consisting of cutting via water jets, stamping and pressing, numerical control (NC) turning, grinding and NC milling.

Pre-treatment – degreasing
After mechanical treatment the bearings are coated using an electrolytic process. Prior to the galvanising step the work piece is degreased using perchloroethylene. The degreasing unit is fully closed. After degreasing the bearings pass aqueous cleaning. The process solution is strong alkaline or mild alkaline, depending on the alloy. Work pieces which pass mild alkaline cleaning undergo additional acid pickling. Work pieces which pass strong alkaline cleaning undergo descaling.

Electroplating – core activity

The bearings are thereafter electroplated with three functional layers. The first layer consists of nickel. Watts-type nickel solutions are used for nickel plating. Typically Watt's-type nickel solutions consist of nickel sulphate (240 – 375 g/l), nickel chloride (35 – 60 g/l) and boric acid (30 – 45 g/l) (STM BREF, 2006). Although higher concentrated nickel electrolytes can also be used. Operating temperatures can range from 25 °C to 70 °C, a range between 50 °C to 60 °C is more common though (STM BREF, 2006). The pH is normally 3.5 – 4.5 (STM BREF, 2006). For the second, tribological layer, the bearing is electroplated in acidic fluoroborate electrolytes. Depending on the destined application the bearing is coated with lead-tin-copper alloys or tin-copper-antimony alloys. In a final electroplating step the bearing gets coated with tin in acidic fluoroborate electrolytes, methanesulfonic acid or alkaline tin (stannate) electrolytes. 2 out of the 7 tin baths are operated above room temperature.

Certain workpieces can be electroplated with an optional copper-tin coating in cyanide bronze electrolytes. Typically the concentration in cyanide bronze electrolytes is 4 – 10 g/l tin as stannate (salts of stannic acid), 4 – 20 g/l copper, 1 – 4 g/l zinc and 6 – 70 g/l potassium cyanide (STM BREF, 2006). The process bath is operated above room temperature (approximately 60 °C).

The semicircled bearings pass the electrolytes stacked on a round tower. The anode is in the centre of the tower.

Electroplating – rinsing

After each process bath the work piece is rinsed in rinsing baths. Multiple stage counterflow rinsing units consisting of three steps are used in order to minimise water use. Counterflow rinsing means that the fresh water is fed into the rinsing unit in opposite direction of the work piece passing the rinsing steps. Thus the first rinsing step, that the work piece enters, is the least fresh (highest contaminated) one. Excess water is passed in counterflow (from the third to the first rinsing step) and extracted from the first rinsing step. The extracted rinsing water is regenerated by ion exchangers and fed back (as fresh water) into the rinsing unit. Regenerated nickel is recycled into the nickel solution.

Electroplating – waste gas treatment

Edge exhausts are installed at the edges of the process tanks. Additionally the production halls are equipped with exhaust air suction units. In order to abate emissions to air the exhaust air is sent through scrubbers before being merged into one stack and emitted over the roof of the installation. The exhaust air unit was renewed in 2018 and has a capacity of 50,000 m^3/h. The exhaust air unit is equipped with a heat exchanger.

Degreasing – waste gas treatment
The enclosed degreasing unit (perchloroethylene) is equipped with an activated carbon filter.

Electroplating – recycling and residues
Solid metal residues are collected separately and externally recycled. Solid metal residues from electroplating are trimming waste from anodes, worn out anodes, anode mud, test pieces and rejects.

Due to the low content of recyclable materials, sludge from electroplating wastewater treatment is not reused (not economically viable). The water content of sludge is reduced by 70 % via filter presses. The predominant fraction of the dry substance consists of calcium hydroxide, sulphate, phosphate, fluoride, aluminate and silicate. The minor fraction consists of iron hydroxide and heavy metal hydroxides (such as lead, tin, zinc, copper, nickel and antimony). The dewatered sludge still contains high amounts of pore water with an increased concentration of tetrafluorbic acid.

Regenerated nickel from the rinsing units is recycled into the nickel solution in order to extend the process bath lifetime. Certain acids and acid mixtures are treated in the vacuum distillation unit of the WWTP and recycled. Metal residues from mechanical preparation of the bearings are recycled in the non-ferrous metals processing unit.

The lifespan of the process baths is prolonged (almost unlimited) through frequent monitoring in the in-house laboratory, continuous conditioning, filtration and selective cleaning.

Electroplating – energy efficiency
The temperature of heated process baths are lowered if not in operation in order to reduce the energy demand. Heated process tanks are not covered.

Process wastewater
Process wastewater is treated in an on-site wastewater treatment plant (WWTP) before being discharged into the sewer and sent to the communal WWTP (indirect discharge). Process wastewater is separately collected in seven individual streams, being:

- Concentrates (electroplating baths)
- Complexing agents (EDTA, cyanides)
- Nickel rinse water
- Wastewater from sulphuric acid (H_2SO_4) etching
- Excess water from rinsing units (destined for discharge)
- Rinsing water (destined for re-use)
- Wastewater containing oils and greases

Wastewater stream 1 (Batch treatment of active baths): Wastewaters from electroplating baths are treated via precipitation. Precipitation is carried out in a batch process. This enables adjusting the pH value for optimising precipitation of the metals in the wastewater. Calcium hydroxide ($Ca(OH)_2$) is added as a precipitation agent and also for pH adjustment. Also, CaCl2 and flocculation agent is added to the wastewater to reduce the concentration of free fluoride and sulphate in the wastewater. The treated wastewater (clear water) enters wastewater stream 5. The sludge is collected in a tank before being de-watered in a chamber filter press. The de-watered sludge is subsequently externally disposed by an authorized waste disposal company. The accruing wastewater from de-watering enters wastewater stream 5.

Wastewater stream 2: Wastewater containing complexing agents is treated via UV radiation together with the oxidising agent hydrogen peroxide (H_2O_2) in order to destroy EDTA and CN complexes. Subsequently the treated wastewater enters wastewater stream 1.

Wastewater stream 3: Wastewater from rinsing after nickel electroplating is collected in a buffer tank and treated in a vacuum evaporator with vapour compression. The distillate is re-used in the production. The nickel concentrate is regenerated via selective plating cathodes (plating out) and recycled into the production process (process bath). The nickel plating out is necessary as the nickel process solutions suffer from increasing metal concentration (Zn & Fe).

Wastewater stream 4: Wastewater from sulphuric acid etching is collected in a buffer tank before being treated in a vacuum evaporator with vapour compression. The sulfuric acid concentrate is collected and recycled by an external disposal company. The distillate is further treated in wastewater stream 5.

Wastewater stream 5 (Rinses & Pretreated active baths): Excess water from rinsing units which is destined for being discharged is treated together with wastewater from water jet cutters, from direct cooling from the on-site foundry and complexing agents free regenerates from wastewater stream 6 and treated wastewater from wastewater stream 1. In a first step the pH value is adjusted with hydrogen chloride (HCl) before passing precipitation with calcium hydroxide ($Ca(OH)_2$) and NaAlOH4 (for the SO_4^{2-}-precipitation). After the precipitation some flocculation agent is added. The sludge is removed via the sedimentation step. Subsequently the pH value of the clear water gets adjusted again and the wastewater sent through sand filters and ion-exchangers. The regenerate of the ion-exchanger enters wastewater stream 5. The treated wastewater is in a final step neutralised and after a final control discharged into the sewer. (With this treatment process there are still some not removed compounds in the treated wastewater (BF_4^-, BO_3^{3-}, NO_3^-; NO_2^-& organic components. NO_3^-; NO_2^-& organic components are treated in the communal wastewater treatment process. BF_4^- & BO_3^{3-} will be emitted with the wastewater).

Wastewater stream 6: Rinsing water destined for re-use is collected separately in two streams – complexing agent free and containing complexing agents. The wastewater streams pass ion exchangers before being re-used as rinsing water. The regenerate of the ion-exchanger enters wastewater stream 5.

Wastewater stream 7: Wastewater containing oils and greases, from e.g. drilling and grinding, are treated separately in a vacuum evaporator. Distillates enter wastewater stream 5. The concentrates are disposed externally by an authorized waste disposal company.

12.2Current consumption and emission levels

Specific consumption

For the production of 1 kg of bearings (final product) approximately 1.8 kg raw materials (steel, non-ferrous metals), 11.2 kWh and 3.3 m^3 water are needed (lean production). Per kg of produced bearing about 0.8 kg of waste and residues are generated.

Generated residues from electroplating or linked to electroplating activities are listed in Table 213. The quantity of residues are from 2017.

Table 213: Residues linked to electroplating 2017

Type	Category	Unit	Quantity	Origin	Treatment
Electroplating sludge (Filter cake)	hazardous	kg	131,600	Electroplating	Authorised waste disposal company
Salts, easily soluble	hazardous	kg	12,178	Electroplating – WWTP	Authorised waste disposal company
Acids, acid mixtures, inorganic	hazardous	kg	16,995	Electroplating – WWTP	Recycled in the WWTP Excess is disposed via an authorised waste disposal company
Rinsing water containing metal salts	hazardous	kg	25,320	Electroplating – WWTP (during maintenance – not annually)	
Tetrachloroethylen	hazardous	kg	25	Electroplating – degreasing	Returned to supplier
Ion exchanger resins	non-hazardous	kg	1,004*	Electroplating -WWTP	Authorised waste disposal company
Used filters and adsorbents (kieselguhr, activated carbon)	hazardous	kg	1,509	Electroplating -Rinsing, WWTP	Authorised waste disposal company
Residues from wet cleaning and maintenance of water jet cutting	non-hazardous	kg	27,217*	Electroplating Mechanical treatment	Authorised waste disposal company
Lead	non-hazardous	kg	3,527*	Electroplating Mechanical treatment	Recycling
Copper and copper containing residues	non-hazardous	kg	632,740*	Electroplating Mechanical treatment Non-ferrous metal processing Maintenance	Recycling
Non-ferrous metal scrap	non-hazardous	kg	Not reported	Not from surface treatment	Recycling
Tin anodes	Non-hazardous	kg	500	Electroplating	Recycling
Nickel and nickel containing residues	non-hazardous	kg	2,065*	Electroplating	Nickel and nickel containing residues

*Estimated amout from Electroplating- Rinsing, WWT- Processes
Source: Abfallwirtschaftskonzept 2017, Miba GmbH

Emissions to air

In 2015 emissions to air from the electroplating installation were monitored for each of the four exhaust air lines. The monitoring was conducted by an external company and served an internal assessment of the emissions to air from electroplating. In the course of the monitoring total organic carbon, sulphur dioxide (SO_2), inorganic chlorine compounds (HCl), inorganic fluoro compounds (HF), dust, heavy metals (Pb, Ni, Cu, Sn) and sodium hydroxide (NaOH) were measured in three half-hour averages per exhaust line. The measurement results refer to concentrations expressed as mass of emitted substances per volume of waste gas under the following conditions: dry gas at a temperature of 0 °C and a pressure of 1013 mbar and are expressed as mg/Nm³. Monitoring of exhaust line 1 was carried out on 22.06.2015, monitoring of exhaust line 2 – 4 on 23.06.2015. The results are presented in Table 214.

Table 214: External monitroing of emissions to air from the electroplating installation, 22. & 23.06.2015

Parameter	Unit	Exhaust line 1	Exhaust line 2	Exhaust line 3	Exhaust line 4
Q	m³/h	12600	13900	3800	4300
T	°C	20	23	23	25
Pressure	mbar	948	946	961	961
TOC	mg/Nm³	2,1	2,5	2,4	2,2
HCl	mg/Nm³	< 1	< 1	< 1	< 1
HF	mg/Nm³	< 0,6	< 0,8	< 0,7	< 0,6
HCN	mg/Nm³	< 0,1	< 0,1	< 0,1	< 0,1
SO_2	mg/Nm³	< 1	< 1	< 1	< 1
Dust	mg/Nm³	< 1	< 1	< 1	< 1
Pb	mg/Nm³	< 0,001	< 0,001	< 0,001	< 0,001
Cu	mg/Nm³	< 0,001	< 0,001	< 0,001	< 0,001
Ni	mg/Nm³	< 0,001	< 0,001	< 0,001	< 0,001
Sn	mg/Nm³	0,009	0,002	< 0,001	< 0,001

Parameter	Unit	Exhaust line 1	Exhaust line 2	Exhaust line 3	Exhaust line 4
NaOH	mg/Nm³	0,008	0,003	0,002	0,004

Source: Prüfbericht Synlab, ULI-15-0052882, 10.2015

Emissions to water

Treated process wastewater is discharged indirectly via the communal WWTP. Monitoring has to be conducted using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit (Ge30 – 57/79-2011). Minimum monitoring frequencies for self-monitoring (performed by operator) and external-monitoring are prescribed by permit (Ge30 – 57/79-2011). Emission limit values (ELV) are prescribed by permit (Ge30 – 57/79-2011).

(BF_4^-, BO_3^{3-}, NO_3^-; NO_2^-& organic components. NO_3^-; NO_2^-& organic components are treated in the communal wastewater treatment process. BF_4^- & BO_3^{3-} will be emitted with the wastewater).

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

Emissions to water from the electroplating installation of Miba Gleitlager Austria GmbH are described in the following tables. In Table 215 the minimum monitoring frequencies and ELVs prescribed by permit are presented and compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. In Table 216, Table 217 and Table 218 the self-monitoring recordings of treated process wastewater are presented. Table 219 presents the results from external-monitoring of treated process wastewater for the years 2016, 2017 & 2018.

Table 215: Emission limit values for the process wastewater from the electroplating installation in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater from the electroplating installation as prescribed by permit

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)[214]	Ordinance (indirect discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Water quantity (Q)	m^3/d	204	–	–	Continuously	–
Temperature (T)	°C	35	–	35	Continuously	Annually
pH		6.5–10.0	–	6.5–10.0	Continuously	Annually
Total suspended solids (TSS)	mg/l	150	–	150	–	Annually
Antimony (Sb)	mg/l	0.3	–	–	Monthly	Annually
Lead (Pb)	mg/l	0.5	0.05–0.5	0.5	Every operation day	Annually
Chromium – total (Cr)	mg/l	0.5	0.1–2.0	0.5	Monthly	Annually
Copper (Cu)	mg/l	0.5	0.2–2.0	0.5	Every operation day	Annually
Nickel (Ni)	mg/l	0.5	0.2–2.0	0.5	Every operation day	Annually
Zinc (Zn)	mg/l	1.0	0.2–2.0	1.0[215]	Every operation day	Annually
Tin (Sn)	mg/l	1.0	0.2–2.0	1.0	Monthly	Annually
Silver (Ag)	mg/l	0.1	0.1–0.5	0.1	–	Annually
Cyanide (CN)	mg/l	0.1	0.01–0.2	0.1	Monthly[216]	Annually

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[214] Discharge to public sewer or surface water from jig, barrel, small scale coil, automotive, PCB and other activities not large scale steel coil

[215] For wastewaters from electroplating or batch galvanising the ELV is 2.0 mg/l

[216] Spot sample, taken after oxidation unit

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)[214]	Ordinance (indirect discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Nitrite (NO_2-N)	mg/l	10	–	10	–	Annually
Ammonium (NH_4-N)	mg/l	200	–	200	–	Annually
Adsorbabale organic halides (AOX)	mg/l	1.0	–	0.1	–	Annually
Free fluoride (F)	mg/l	20	–	20	Every operation day	Annually
Sulphate (SO_4)	mg/l	2500[217] / 800[218]	–	–	Every operation day	Annually
Volatile organic halides (VOX)	mg/l	0.1	–	0.1	–	Annually
Low-volatile lipophilic substances	mg/l	100	–	100	–	Annually
Total Hydrocarbons	mg/l	15	–	15	–	Annually

Source: STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 216: Self-monitoring of treated process wastewater 2016

		Self-monitoring 2016					
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Q	m^3/d	0	88	66	25	204	366
pH		6.6[219]	8.9	8.5	8.0	6.5–10.0	364
Ni	mg/l	≤ 0.01	0.45[220]	0.148	0.04	0.5	365

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[217] Maximum value on 7 days per month

[218] ELV for the remaining days of the month

[219] One exceedance of pH, 6.1

[220] One measurement above the ELV, 0.64 mg/l. No exceedance due to “4 out of 5” rule (§4 (2) Z1, ordinance on surface treatment 2/8/6/4)

Parameter	Unit	Self-monitoring 2016 Daily min	Daily max	95 Percentile	Annual average	ELV permit	Number of samples
Pb	mg/l	≤ 0.01	0.5[221]	0.108	0.04	0.5	365
Zn	mg/l	≤ 0.01	0.27	0.02	0.01	1.0	365
Cu	mg/l	≤ 0.01	0.31	0.09	0.03	0.5	365
F	mg/l	2	20	20	13	20.0	365
SO_4	mg/l	32	1171	763.4	346	2500[222] / 800[223]	365
Sb	mg/l	≤ 0.01	0.01	0.01	0.01	0.3	12
Cr total	mg/l	≤ 0.01	0.01	0.01	0.01	0.5	12
CN	mg/l	≤ 0.01	0.04	0.035	0.02	0.1	11
Sn	mg/l	≤ 0.01	0.17	0.1205	0.04	1.0	12

Source: Self-monitoring Miba GmbH, 2016

Table 217: Self-monitoring of treated process wastewater 2017

Parameter	Unit	Self-monitoring 2017 Daily min	Daily max	95 Percentile	Annual average	ELV permit	Number of samples
Q	m^3/d	0.14	103	58	30	204	363
pH		6.7[224]	9.0	8.3	7.8	6.5–10.0	362
Ni	mg/l	0.005	0.10	0.05	0.02	0.5	363
Pb	mg/l	0.005	0.42	0.13	0.03	0.5	363
Zn	mg/l	0.001	0.10	0.01	0.01	1.0	343
Cu	mg/l	0.004	0.42	0.07	0.03	0.5	361

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[221] 3 consecutive measurements above the ELV, each 0.79 mg/l. Exceedance as “4 out of 5” rule does not apply, i.e. measurement exceeds the ELV by more than 50 %
[222] Maximum value on 7 days per month
[223] ELV for the remaining days of the month
[224] One exceedance of pH, 5.2

Self-monitoring 2017							
Parameter	Unit	Daily min	Daily max	95 Percentile	Annual average	ELV permit	Number of samples
F	mg/l	5	20[225]	19.95	13	20.0	362
SO₄	mg/l	12	1254	893.6	470	2500[226] / 800[227]	363
Sb	mg/l	≤ 0.01	0.011	0.0105	0.01	0.3	11
Cr total	mg/l	≤ 0.01	0.01	0.01	0.01	0.5	11
CN	mg/l	≤ 0.01	0.03	0.025	0.01	0.1	11
Sn	mg/l	≤ 0.01	0.08	0.045	0.02	1.0	11

Source: Self-monitoring Miba GmbH, 2017

Table 218: Self-monitoring of treated process wastewater 2018

Self-monitoring 2018							
Parameter	Unit	Daily min	Daily max	95 Percentile	Annual average	ELV permit	Number of samples
Q	m^3/d	0.04	118	73	34.39	204	361
pH		6.70	8.90	8.4	7.97	6.5–10.0	363
Ni	mg/l	0.01	0.13	0.04	0.02	0.5	363
Pb	mg/l	0.01	0.38	0.209	0.05	0.5	363
Zn	mg/l	0.01	0.02	0.01	0.01	1.0	363
Cu	mg/l	0.01	0.31	0.12	0.03	0.5	363
F	mg/l	3	20[228]	20	14.28	20.0	363

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[225] 4 measurements above the ELV, 30 mg/l, 26, mg/l, 23 mg/l, 22 mg/l. No exceedance due to “4 out of 5” rule (§4 (2) Z1, ordinance on surface treatment 2/8/6/4)

[226] Maximum value on 7 days per month

[227] ELV for the remaining days of the month

[228] 12 measurements above ELV, 29 – 23 mg/l. 4 exceedances due to “4 out of 5” rule – “(…)out of 5 consecutive measurements 4 measurements have to be below the ELV and one is not allowed to exceed the ELV by more than 50 % (…)”(§4 (2) Z1, ordinance on surface treatment 2/8/6/4)

Self-monitoring 2018							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
SO_4	mg/l	82	1178	855.9	429.32	2500[229] / 800[230]	363
Sb	mg/l	≤0.01	0.01	0.01	0.01	0.3	12
Cr total	mg/l	0.011	0.011	0.011	0.01	0.5	12
CN	mg/l	≤0.01	0.01	0.01	0.01	0.1	12
Sn	mg/l	≤0.01	0.01	0.01	0.01	1.0	12

Source: Self-monitoring Miba GmbH, 2018

Table 219: External-monitoring of process wastewater from the electroplating installation

External-monitoring 2016, 2017 & 2018						
Parameter	**Unit**	**03.03.2016**	**21.02.2017**	**09.03.2018**	**Standard**	**ELV permit**
pH		8.2	8.1	7.2	DIN EN ISO 10523	6.5–10.0
TSS	mg/l	65.2	71.3	88.5	BN DIN 38409-9	150
Sb	mg/l	0.01	0.03	0.09	EN ISO 11885	0.3
Ni	mg/l	0.01	< 0.01	0.01	EN ISO 11885	0.5
Pb	mg/l	0.02	0.01	0.02	EN ISO 11885	0.5
Zn	mg/l	0.01	0.02	0.01	EN ISO 11885	1.0
Cu	mg/l	0.02	0.02	0.04	EN ISO 11885	0.5
F	mg/l	10.1	13.5	18.9	BN DIN 38406-4	20.0
SO_4	mg/l	191	194	762	BN DIN EN ISO 10304-2	2500[231] / 800[232]
Sb	mg/l	≤0.01	0.01	0.01	0.01	0.3

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[229] Maximum value on 7 days per month

[230] ELV for the remaining days of the month

[231] Maximum value on 7 days per month

[232] ELV for the remaining days of the month

		External-monitoring 2016, 2017 & 2018				
Parameter	**Unit**	**03.03.2016**	**21.02.2017**	**09.03.2018**	**Standard**	**ELV permit**
Cr total	mg/l	< 0.01	< 0.01	< 0.01	EN ISO 11885	0.5
CN	mg/l	≤0.01	0.01	0.01	0.01	0.1
Sn	mg/l	< 0.01	< 0.01	< 0.01	EN ISO 11885	1.0
Ag	mg/l	< 0.01	< 0.01	< 0.01	EN ISO 11885	0.1
NO_2-N	mg/l	0.1	0.08	0.11	BN DIN EN 26777	10.0
NH_4-N	mg/l	< 0.1	< 0.1	0.4	DIN EN ISO 14911	200
AOX (as Cl)	mg/l	0.08	0.1	0.12	DIN 38414-18	1.0
VOX (as Cl)	mg/l	< 0.05	< 0.05	< 0.05	SOP 209	0.1
Low-volatile lipophilic substances	mg/l	< 10	< 10	< 10	DIN 38409-17	100
Total Hydrocarbons	mg/l	< 0.1	< 0.1	< 0.1	DIN 38409-18	15

Source: Dr. Heinl ZT-GmbH, 2016–2018

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13 OTN Galvanotechnik GmbH

OTN Galvanotechnik GmbH is part of the OTN Oberflächentechnik group, which operates three surface treatment installations in Austria. On site of OTN Galvanotechnik, Elsbethen, acid zinc electroplating is carried out. At the other two company owned locations batch galvanizing and wet coating (varnish) takes place.

The acid zinc electroplating installation is an IED installation. OTN Galvanotechnik is a specialist sub-contractor (jobbing shop).

13.1Technical description

Acid zinc electroplating is carried out on the premise of OTN Galvanotechnik. Both jig and drum electroplating units are in operation.

The production process of zinc electroplating consists in general of the following:

- Pre-treatment:
  - Degreasing
  - Pre-Etching
  - Etching
  - Electrolytically assisted degreasing (anode)
  - Descaling
- Acid zinc electroplating
- Chromium conversion coating
- Drying

Pre-treatment
Pre-treatment consists of alkaline degreasing above room temperature, pre-etching with used hydrochloric acid, etching with HCl, electrolytically assisted degreasing and descaling.

Pre-etching supports the extension of the etching solution life span and helps reducing waste generation (as well as consumption of chemicals). The used etching solution form the main etching tank is used for pre-etching. Impurities accumulate predominantly in the pre-etching tank, leading to a longer life span of the main etching tank.

Electrolytically assisted degreasing removes the remains of unwanted residues from the surface, such as oil and dirt, which remain trapped in the micro-roughness of the work piece's surface. These residues are removed by the electrolytic formation of H2 gas at the surface of the cathode and of O2 gas at the surface of the anode. (STM BREF, 2006) On the premise Elsbethen the work piece is connected as the anode.

Before entering zinc electroplating the work piece passes descaling with hydrochloric acid in order to enhance metal adhesion.

Electroplating

After pre-treatment the work piece is zinc electroplated. Zinc electroplating is carried out in acid zinc electrolytes, which give bright decorative layers. For providing corrosion resistance comparable with alkaline zinc electrolytes, post-treatment is required. Metal distribution is enhanced with warm electrolytes.

Acid zinc electrolytes contain typically zinc chloride, potassium and/or sodium chloride, boric acid and wetting agents (STM BREF, 2006). The solution has a good conductivity and high cathode efficiency leading to a lower energy demand than alkaline zinc electrolytes (STM BREF, 2006).

Chromium conversion coating

After zinc electroplating the work pieces pass either trivalent or hexavalent chromium conversion (passivation). Chromium conversion coatings enhance corrosion protection, preventing the zinc surface to form white rust.

Drying

To avoid the formation of staining and corrosion after the work piece passed all these wet process steps, drying has to be applied quickly. On the premise drying with hot air (jig plant) and drying with centrifuges (drum plant) is carried out. Drying with hot air requires temperatures up to 80 °C.

Rinsing

After each process step rinsing is applied. Multiple stage counterflow rinsing units, consisting of two steps, or static rinsing units followed by final flow rinse with recirculated water are used. The latter are applied after descaling, zinc electroplating and chromium conversion coating. Rinsing water is taken from the company owned well. A fresh water buffer tank was installed to keep the water feed to the rinsing units stable, especially during dry periods. Before installing the buffer tank an accumulation of impurities and an increase in drag-outs leading to challenges for the WWTP occurred during dry periods.

Waste gas treatment

Edge exhausts are installed at the edges of the pickling baths, degreasing and the zinc electrolyte tanks. The extracted air is treated by a demister in order to reduce HCl emissions.

Bath life span

The process baths are regularly monitored and controlled. This enables an accurate dosing of the needed chemicals and avoids excess use of chemicals. Iron hydroxide sludge is removed from the zinc electrolytes by filters in order to expand the process bath's life span.

Pre-etching supports the extension of the etching solution life span and helps reducing waste generation (as well as consumption of chemicals). The used etching solution form the main etching tank is used for pre-etching. Impurities accumulate predominantly in the pre-etching tank, leading to a longer life span of the main etching tank.

Process wastewater

Treated wastewater is discharged directly into the river Salzach. Process wastewater is collected in separate streams, i.e. recyclable rinsing water, non-recyclable rinsing water, acidic wastewater, alkaline wastewater and used etching concentrates.

Recyclable rinsing water is treated with ion exchangers and can be re-used in the process. The remaining wastewater streams are treated in the on-site WWTP before being discharged into the river Salzach.

The WWTP consists of:

- Chromate treatment
- Batch neutralisation
- Sludge dewatering
- Pre-neutralisation

- Sand filtration
- Ion-exchange resins
- Final neutralisation

Chromate treatment
Cr(VI) is difficult to precipitate therefore the hexavalent chromium compounds need to be reduced first by bisulphite to Cr(III). For chromate treatment the pH value is lowered below 2.5, triggering the precipitation of Cr(III) ions. For ensuring a proper precipitation, the pH value has to be stable at 2.5 for 15 minutes after addition of chemicals.

Batch neutralisation
Subsequently precipitation of heavy metals follows (neutralisation). The pH value is increased to 8.0 by adding lime milk. If the targeted pH value is exceeded HCl is added. Dosing of lime milk and HCl is automatic, depending on the monitored pH value. It is important that the pH value is stable for an appropriate time frame of ca. 20 minutes to ensure that the precipitation of metals is completed.

Sludge dewatering
After batch neutralisation, the wastewater is sent to the filter press. The dewatered sludge is disposed by external operators. The clear water is sent to the final treatment steps before being discharged.

Pre-neutralisation
In the pre-neutralisation step wastewater is collected in a tank, mixed and remains there for 20 minutes. If required HCl can be added to reach the targeted pH value of 7.0.

Sand filtration & ion exchange
For reducing remaining impurities in the treated wastewater, sand filtration is applied. Subsequently wastewater passes ion exchange resins to remove remaining metal ions from the wastewater. Regenerates from ion exchange re-enter wastewater treatment.

Final neutralisation
In the final neutralisation step the pH value can be adjusted to meet permit requirements by adding HCl or NaOH. The final neutralisation step is continuous flow. After final neutralisation the treated wastewater is discharged into the river Salzach.

13.2 Current consumption and emission levels

Specific consumption

Specific consumption parameters are recorded per kg of electroplated product.

The specific energy consumption per kg of electroplated product varies due to the requirements for the work piece and the shape of the work piece. Lowering energy consumption, whilst maintaining the required product quality, is in the interest of the operator, wherefore consumption parameters are monitored at several process steps. In general approximately 0.5 – 0.7 kWh/kg are consumed.

Process water is taken from the company owned well. Water consumption is not recorded.

Generated waste from electroplating is listed in Table 220. The quantity of wastes are from 2016.

Table 220: Waste generated from electroplating 2016

Type	Category	Unit	Quantity	Origin	Treatment
Metal hydroxide sludge	hazardous	t	200	WWTP	Authorised waste disposal company
Acids, acid mixtures	hazardous	t	30	Process baths	Authorised waste disposal company
Other sludge from wastewater treatment	hazardous	t	4	WWTP	Authorised waste disposal company

Source: OTN, own recordings

Emissions to air

Edge exhausts are installed at the edges of the process baths. The extracted air is treated in demister in order to minimise HCl emissions.

HCl emissions have to be monitored every five years by an accredited testing institute. The ELV is 10 mg/Nm^3. The monitoring frequency and the ELV are prescribed by permit. Monitoring has to be conducted via three half-hour measurements.

Table 221 presents the monitoring results from 06.03.2018. The measurements were conducted during normal operating conditions. The calculated volume flow was 21,400 m³/h.

Table 221: Monitoring results of HCl emissions to air; 0 °C, 1013 mbar, dry exhaust air

Unit	HCl	ELV	Sampling period	Standard
mg/Nm³	0.6	10	Average over 3 half hour measurement	EN 1911

Source: TÜV, 2018

Emissions to water

Treated process wastewater is discharged directly into the river Salzach. Monitoring has to be conducted using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit. Minimum monitoring frequencies for self-monitoring (performed by operator) and external-monitoring are prescribed by permit. Emission limit values (ELV) are prescribed by permit.

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

The on-site WWTP consists of:

- Chromate treatment
- Batch neutralisation
- Sludge dewatering
- Sand filtration
- Ion-exchange resins
- Final neutralisation

A detailed description of the on-site WWTP is presented in chapter 13.1.

Emissions to water from electroplating are described in the following tables. In Table 222 the minimum monitoring frequencies and ELVs prescribed by permit are presented and compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. Table 223 presents the self-monitoring recordings of treated process wastewater. Table 224 and Table 225 present the results from external-monitoring of treated process wastewater.

Table 222: Emission limit values for the process wastewater from electroplating in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)[233]	Ordinance (direct discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Water quantity (Q)	m³/d	80	–	–	Continuous	Annually
T	°C	30	–	30	Continuous	Annually
pH		6.5–9.0	–	6.5–9.0	Continuous	Annually
TSS	mg/l	50	5–30	30	–	Annually
Boron (B)	kg/d	3.8			–	Annually
Boron (B)	kg/month	31.0			–	Annually
Chromium – total (Cr)	mg/l	0.5	0.1–2.0	0.5	–	Annually
Chromium – total (Cr)	kg/d	0.04			–	Annually
Chromium – total (Cr)	kg/month	0.79			–	Annually
Cr(VI)	mg/l	0.1	0.1–0.2	0.1	–	Annually
Cr(VI)	kg/d	0.008			–	Annually
Cr(VI)	kg/month	0.16			–	Annually
Cobalt (Co)	mg/l	1.0	–	1.0	–	Annually
Cobalt (Co)	kg/d	0.08			–	Annually

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[233] Discharge to public sewer or surface water from jig, barrel, small scale coil, automotive, PCB and other activities not large scale steel coil

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)[233]	Ordinance (direct discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Cobalt (Co)	kg/month	1.6			–	Annually
Copper (Cu)	mg/l	0.5	0.2–2.0	0.5	–	Annually
Copper (Cu)	kg/d	0.04			–	Annually
Copper (Cu)	kg/month	0.79			–	Annually
Iron (Fe)	mg/l	2.0	0.1–5	2.0	–	Annually
Iron (Fe)	kg/d	0.16			–	Annually
Iron (Fe)	kg/month	3.16			–	Annually
Nickel (Ni)	mg/l	0.5	0.2–2.0	0.5	–	Annually
Nickel (Ni)	kg/d	0.04			–	Annually
Nickel (Ni)	kg/month	0.79			–	Annually
Silver (Ag)	mg/l	0.1	0.1–0.5	0.1	–	Annually
Silver (Ag)	kg/d	0.008			–	Annually
Silver (Ag)	kg/month	0.16			–	Annually
Tin (Sn)	mg/l	1.0	0.2–2.0	1.0	–	Annually
Tin (Sn)	kg/d	0.08			–	Annually
Tin (Sn)	kg/month	1.58			–	Annually
Zinc (Zn)	mg/l	2.0	0.2–2.0	1.0[234]	–	Annually
Zinc (Zn)	kg/d	0.16			–	Annually
Zinc (Zn)	kg/month	3.16			–	Annually
Chloride (Cl)	kg/d	954			–	Annually
Chloride (Cl)	kg/month	4,800			–	Annually
Fluoride (F)	mg/l	20	10–20	20	–	Annually
Fluoride (F)	kg/d	1.58			–	Annually
Fluoride (F)	kg/month	31.6			–	Annually

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[234] For wastewaters from electroplating or batch galvanising the ELV is 2.0 mg/l

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)[233]	Ordinance (direct discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Nitrate (NO_3-N)	kg/d	57			–	Annually
Nitrate (NO_3-N)	kg/month	248			–	Annually
Nitrite (NO_2-N)	kg/d	0.12			–	Annually
Nitrite (NO_2-N)	kg/month	12.6			–	Annually
Sulphate (SO_4)	kg/d	120			–	Annually
Sulphate (SO_4)	kg/month	560			–	Annually
Total phosphorus (TP)	mg/l	2.0	0.5–10.0	2.0	–	Annually
Total phosphorus (TP)	kg/d	0.16			–	Annually
Total phosphorus (TP)	kg/month	3.16			–	Annually
COD	mg/l	200	100–500	200	–	Annually
COD	kg/d	16			–	Annually
AOX	mg/l	1.0		1.0	–	Annually
AOX	kg/d	0.08			–	Annually
Low volatile lipophilic substances	mg/l	20		20	–	Annually
Low volatile lipophilic substances	kg/d	1.58			–	Annually
Low volatile lipophilic substances	kg/month	31.6			–	Annually
Hydrocarbon index	mg/l	5.0	1–5	5.0	–	Annually
Hydrocarbon index	kg/d	0.4			–	Annually
Hydrocarbon index	kg/month	7.9			–	Annually

Source: Permit 30302-152/202/94-2016; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Once per year external monitoring has to be conducted via flow-proportional daily composite samples by an accredited institute over the course of four consecutive working days.

From 2017–2019 the installation was in a start-up phase, meaning that different new units were installed. In 2018 the rack electroplating unit was installed. In 2019 the drum unit. During the start-up phase of those units, operation needed to be adjusted several times, to obtain the required end-product quality. Thus process baths needed to be exchanged more frequently. In 2019 a buffer tank for rinsing water was installed, allowing frequent renewing of the rinsing water also during dry periods which results in better rinsing of the work pieces and less drag out into the next process bath, hence extending the bath lifespan. From 2020 all major constructions were finished, wherefore emission to water measurements from 2020 are presented here.

Table 223: Self-monitoring of treated process wastewater 01.01. – 11.12.2020

Self-monitoring 2020							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Cr – total	mg/l	0.02	0.46	0.43	0.21	0.5	47
Cr(VI)	mg/l	0.01	0.095	0.09	0.06	0.1	47
COD	mg/l	11.10	161.00	132.60	61.46	200	49
Fe	mg/l	0.10	1.30	0.83	0.41	2	45
TP	mg/l	0.16	1.12	0.84	0.37	2	34
Zn	mg/l	0.31	1.80	1.47	0.91	2	49

Source: Self-monitoring OTN, 2020

Once per year external monitoring has to be conducted via flow-proportional daily composite samples by an accredited institute over the course of four consecutive working days. In 2020 external-monitoring was carried out from Nov 9th to Nov 12th. “M1 – M4” in Table 224 and Table 225 refer to the measurement results of each day during external-monitoring.

Table 224: External-monitoring of process wastewater (concentrations)

External-monitoring 2020						Concentrations
Parameter	**Unit**	**M1**	**M2**	**M3**	**M4**	**ELV**
Wastewater discharge	m^3/d	10	24	26	16	80
Total suspended solids	mg/l	18.00	13.00	36	19.00	50
Silver	mg/l	< 0.001	< 0.001	< 0.001	< 0.001	0.1
AOX	mg/l	0.32	0.12	0.36	0.11	1
Boron	mg/l	3.50	3.50	4.60	4.10	–
Chloride	mg/l	626.00	584.00	773.00	682.00	–
Cobalt	mg/l	0.01	0.01	0.01	0.01	1
Chromium – total	mg/l	0.00	< 0.001	< 0.001	< 0.001	0.5
Chromium–VI	mg/l	< 0.03	< 0.03	< 0.03	< 0.03	0.1
COD	mg/l	82.00	77.00	98	87.00	200
Copper	mg/l	0.00	0 .01	0.01	0.01	0.5
Fluoride	mg/l	0.85	0.75	1.00	0.94	20
Iron	mg/l	0.03	0.03	0.03	0.04	2
Hydrocarbon index	mg/l	< 0.05	< 0.05	< 0.05	< 0.05	5
Nickel	mg/l	0.01	0.01	0.01	0.01	0.5
Nitrite	mg/l	0.73	0.75	0.89	0.80	–
Nitrate	mg/l	7.80	7 .40	9.30	8.50	–
TP	mg/l	0.06	0.06	0.06	0.06	2
pH		7.90	7.90	7.80	7.90	6.5–9
Low volatile lipophilic substances	mg/l	6.00	2.40	2.40	4.80	20
Tin	mg/l	< 0.001	< 0.001	< 0.001	< 0.001	1
Sulphate	mg/l	10.50	10.20	11.80	11.00	–

External-monitoring 2020						Concentrations
Parameter	**Unit**	**M1**	**M2**	**M3**	**M4**	**ELV**
Zinc	mg/l	0.16	0.15	0.20	0.20	2

Source: RHV, 2020

Table 225: External-monitoring of process wastewater (loads)

External-monitoring 2020						Loads
Parameter	**Unit**	**M1**	**M2**	**M3**	**M4**	**ELV**
Total suspended solids	g/d	180	312	936	304	-
Silver	g/d	<0.01	<0.024	<0.026	<0.016	8
AOX	g/d	3.2	2.88	9.36	1.76	80
Boron	g/d	35	84	119.6	65.6	3800
Chloride	g/d	6260	14016	20098	10912	954000
Cobalt	g/d	0.07	0.144	0.208	0.128	80
Chromium – total	g/d	0.01	<0.024	<0.026	<0.016	40
Chromium-VI	g/d	<0.3	<0 .72	<0.78	<0.48	8
COD	g/d	820	1848	2548	1392	16000
Copper	g/d	0.04	0.144	0.26	0.096	40
Fluoride	g/d	8.5	18	26	15.04	1580
Iron	g/d	0.27	0.672	0.806	0.704	160
Hydrocarbon index	g/d	<0.5	<1.2	<1.3	<0.8	400
Nickel	g/d	0.05	0.12	0.182	0.096	40
Nitrite	g/d	7.3	18	23.14	12.8	120
Nitrate	g/d	78	177.6	241.8	136	5700
TP	g/d	0.58	1.344	1.456	0.896	160

External-monitoring 2020						Loads
Parameter	**Unit**	**M1**	**M2**	**M3**	**M4**	**ELV**
Low volatile lipophilic substances	g/d	60	57.6	62.4	76.8	1600
Tin	g/d	<0.01	<0.024	<0.026	<0.016	80
Sulphate	g/d	105	244.8	306.8	176	120000
Zinc	g/d	1.6	3.6	5.2	3.2	160

Source: RHV, 2020

Table 226: Measurement standards external-monitoring emissions to water

Parameter	Standard
Total suspended solids	DIN 38409-2 {1987-03)
Silver	EN ISO 11885
AOX	DIN EN 1485
Boron	EN ISO 11885
Chloride	analog EPA 325.1
Cobalt	EN ISO 11885
Chromium – total	EN ISO 11885
Chromium-VI	ÖNORM M 6288
COD	ÖNORM ISO 15705 (2003-06)
Copper	EN ISO 11885
Fluoride	EN ISO 10304-3
Iron	EN ISO 11885
Hydrocarbon index	ÖNORM EN ISO 9377-2 (2001-06)
Nickel	EN ISO 11885
Nitrite	DIN EN 26777 {1993-05)
Nitrate	DIN EN 26777
TP	ÖNORM EN ISO 6878 (2004-09)

Parameter	Standard
pH	DIN EN ISO 10523 (2012-04)
Low volatile lipophilic substances	DIN ISO 11349
Tin	EN ISO 11885
Sulphate	analog EPA 375.4
Zinc	EN ISO 11885

Source: RHV, 2020

13.3 References

AEV Oberflächenbehandlung, BGBl. II Nr. 44/2002: Verordnung des Bundesministers für Land- und Forstwirtschaft, Umwelt und Wasserwirtschaft über die Begrenzung von Abwasseremissionen aus der Behandlung von metallischen Oberflächen (AEV Oberflächenbehandlung), BGBl. II Nr. 44/2002

Permit 30302-152/202/94-2016: Wasserrechtliche Bewilligung, 30302-152/202/94-2016, BH Salzburg-Umgebung, 2016

RHV (2020): Fremdüberwachung OTN Galvanotechnik, Reinhalteverband Grossraum Salzburg, 2020

STM BREF (2006): Integrated Pollution Prevention and Control Reference Document on Best Available Techniques for the Surface Treatment of Metals and Plastics, European Commission, 2006

TÜV (2018): Bericht der akkreditierten Prüfstelle über die am 03.06.2018 durchgeführte Messung, TÜV Austria, 2018

14 Stiefler GmbH

Stiefler GmbH is a specialist sub-contractor (jobbing shop) offering zinc electroplating and anodizing (of aluminum).

Both the electrolytic zinc coating and the anodizing plant are IED plants.

Environmental Management System

Stiefler GmbH implemented several environmental management and resource saving measures, i.e.:

- material flow management to reduce water use
- aluminum sulphate (AlSO4) and sodium aluminate (NaAlO2) are recycled and reused, e.g. in the fertilizing industry
- retardation regeneration of sulphuric acid from anodizing
- stabilization of the current density as a part of the energy management
- heat recovery for hall preheating
- heat retention system for heated baths
- separation of waste streams to enable recycling or targeted treatment

Quality Management System

Stiefler GmbH has an according to ISO 9001 and EURAS QUALANOD certified quality management system implemented.

14.1Technical description

In the following, the zinc electroplating and anodising processes are described separately.

Zinc electroplating

Both acid and alkaline zinc electroplating is carried out at Stiefler GmbH. Alkaline zinc electroplating is done without using cyanide. Work pieces are transported either by drums or racks.

The process consists of the following parts:

- Pre-treatment
  - Degreasing
  - Pickling
  - Electrolytically assisted degreasing
- Zinc electroplating
- Chromium conversion coating

The work pieces pass the individual treatment steps on frames or in drums.

Pre-treatment
Pre-treatment consists of alkaline degreasing, pickling and electrolytically assisted degreasing. Alkaline degreasing is done above room temperature. Electrolytically assisted degreasing removes the remains of unwanted residues from the surface, which remain trapped in the micro-roughness of the work piece’s surface.

These residues are removed by the electrolytic formation of $H2$ gas at the surface of the cathode and of $O2$ gas at the surface of the anode. (STM BREF, 2006) The work piece can be connected as anode or cathode.

Zinc electroplating
After pre-treatment the work piece is zinc electroplated. Zinc electroplating is carried out in acid zinc electrolytes or in alkaline cyanide-free zinc electrolytes.

Acid zinc electrolytes contain typically zinc chloride, potassium chloride, boric acid and organic brighteners and wetting agents (STM BREF, 2006). The solution has a good conductivity and high cathode efficiency leading to a lower energy demand than alkaline zinc electrolytes (STM BREF, 2006).

Alkaline cyanide-free zinc electrolytes contain usually zinc oxide and sodium hydroxide or potassium hydroxide (STM BREF, 2006). The solution has a low conductivity thus a higher voltage and a higher energy demand is needed (STM BREF, 2006).

Chromium conversion coating
After zinc electroplating the work pieces pass chromium conversion solution (passivation). Chromium conversion coatings enhance corrosion protection, preventing the zinc surface

to form white rust. At Stiefler GmbH both hexavalent and trivalent chromium conversion coatings are applied.

Rinsing
After each process step the work piece is rinsed. Multiple stage counterflow rinsing units consisting of two or three steps are used in order to minimise water use. Excess water from the rinsing unit is fed back into the process baths.

Waste gas treatment
The process baths are equipped with edge exhaust air extraction. Extracted air gets treated in wet scrubbers to reduce the emissions of HCl to air. The scrubbing liquid is therefore alkaline (NaOH). The scrubbing liquid is reused until the required conditions (measured by conductivity) cannot be reached anymore. Used scrubbing liquid is treated in the on-site WWTP.

Bath life span
The process baths are regularly monitored and controlled in the in-house laboratory. This enables an accurate dosing of the needed chemicals and avoids excess use of chemicals. Iron hydroxide sludge is removed from the zinc electrolytes by filters in order to expand the process bath's life span.

Process wastewater
Treated wastewater is discharged indirectly. Wastewater from zinc electroplating is treated in a dedicated WWTP and not together with wastewater from anodising.

Wastewaters from the electroplating unit are collected in separate streams, i.e. concentrates and used rinsing water.

The WWTP consists of:

- Chromate treatment
- Batch neutralisation
- Sludge dewatering
- Sand filtration

Chromate treatment
Cr(VI) has to be reduced to Cr(III) as Cr(VI) is difficult to precipitate.

Cr(VI) reduction is done by using sodium bisulphite. For chromate treatment the pH value is lowered below 2.5, triggering the precipitation of Cr(III) ions. For ensuring a proper precipitation, the pH value has to be stable at 2.5 for 15 minutes after addition of chemicals.

Batch neutralisation

Subsequently precipitation of heavy metals follows. The pH value is increased to 8.5 – 9.0 by adding lime milk or NaOH.

If the targeted pH value is exceeded HCl is added. Dosing of NaOH and HCl is automatic, depending on the monitored pH value. It is important that the pH value is stable for an appropriate time frame of ca. 20 minutes to ensure that the precipitation of metals is completed. Flocculation agents can be added.

Sludge dewatering

After neutralisation, the wastewater is sent to a sedimentation tank. The settled sludge is sent to a chamber filter press. The dewatered sludge is disposed by external operators.

Sand filtration

As a final treatment step the treated wastewater is sent through sand filters before being discharged into the sewer.

Anodising of aluminium

Anodising of metals is an electrolytic surface oxidation process resulting in an oxide layer, which is firmly attached to the work piece, providing corrosion protection. In anodising, the work piece is (as the name indicates) connected as the anode. During the anodising process, the negatively charged anion migrates to the anode where it is discharged with a loss of one or more electrons. The metal reacts with the oxygen of the anion and a layer of oxide forms on the surface. (STM BREF, 2006)

Aluminium is predominantly anodised, with alumina (Al2O3) formed at the surface. (STM BREF, 2006). Magnesium, titanium, tantalum and niobium can be also anodised. At Stiefler GmbH only aluminium is anodised.

Aluminium is typically anodised in sulphuric acid electrolytes (STM BREF, 2006).

Oxide layers from anodising are mainly transparent wherefore the work piece remains its metallic look. Pre-treatment determines the final look of the anodised work piece.

The work piece can be coloured in different ways, e.g. immersion colouring, electrolytic colouring, interference colouring or integral colouring. At Stiefler GmbH electrolytic colouring is used.

Commonly the anodised aluminium is placed in an acid solution containing metal salts and an alternating current (AC) is applied. This deposits oxide of the other metal which penetrates into the pore of the alumina, with the residual oxide layer remaining on top. The film obtains a colour characteristic of the metal salts used. The metal salt most commonly used in Europe is tin. For special applications, nickel, cobalt and copper can be used. Tin sulphate gives shades from light bronze to black, depending on the process time. (STM BREF, 2006)

To increase corrosion resistance and to retain surface colouring, sealing is applied to the anodised work piece. Sealing can be carried out in hot or cold processes. At Stiefler GmbH hot water sealing is applied.

With hot sealing, the pores in the oxide layer are closed by hydrating the aluminium oxide to bohemite (AlO(OH)): the pores are closed by the increased volume of the bohemite structure. The sealing process is carried out by dipping the anodised parts in hot or boiling deionised water. (STM BREF, 2006)

Work pieces are moved by a crane system. The anodising unit is fully automatized.

The production process of anodising at Stiefler GmbH consists of:

- Chemical pre-treatment
  - Degreasing
  - Pickling
  - Descaling
- Anodising
- Electrolytic colouring
- Hot water sealing

Pre-treatment

Degreasing and pickling is done in alkaline baths. Descaling in acidic baths.

Anodizing

Anodising of aluminium is done in sulphuric acid electrolytes, which is the most common technique for anodising of aluminium. The temperature of the electrolyte is typically between 15 and 30 °C.

Electrolytic colouring

Electrolytic colouring of the anodised work pieces is carried out at Stiefler GmbH. Colouring is optional.

Hot water sealing

As a final step hot sealing is carried out, to increase corrosion resistance. The sealing process is carried out by dipping the anodised parts in hot or boiling deionised water (STM BREF, 2006).

Rinsing

After each process step, the work piece is rinsed. Multiple stage counterflow rinsing units consisting of two or three steps are used in order to minimise water use. Excess water from the rinsing unit is fed back into the process baths. Rinsing water containing nickel, cobalt or fluoride (from sealing) is treated with ion-exchange resins and reused in the anodizing process subsequently.

Bath life span

The process baths are regularly monitored and controlled in the in-house laboratory. This enables an accurate dosing of the needed chemicals and avoids excess use of chemicals. For increasing the life span of the anodising bath a retardation unit for the regeneration of sulphuric acid anodising solution is operated. A retardation unit consists basically of anion ion exchange resins through which the anodizing solution is sent to reduce the concentration of aluminium in the process solution (which accrues during the anodizing process). To increase the life span of the hot sealing bath, additional rinsing is applied.

Waste gas treatment

Process baths are equipped with lids to reduce inter alia diffuse emissions to air. The baths are equipped with edge exhaust air extraction. When work pieces enter a process bath (either in a drum or on a rack) the bath lids need to be opened. During that time the transporting crane functions as a lid. The crane is also equipped with an exhaust air extraction system.

The extracted air is treated in a wet scrubber to reduce sodium hydroxide (from pre-treatment baths), sulphuric acid (anodizing) and mists from hot sealing. The scrubbing liquid is collected and reused. After several applications the scrubbing liquid is sent to the WWTP. The extraction capacity of the waste gas treatment system is 75,000 m^3/h.

Wastewater treatment
Treated wastewater is discharged indirectly. Wastewater from anodising is treated in a dedicated WWTP and not together with wastewater from zinc electroplating. Wastewater from anodizing is treated in separate streams, i.e. acidic/alkaline wastewater and wastewater containing heavy metals.

The WWTP consists of:

- Batch neutralisation
- Sludge dewatering
- Ion exchange
- Sand filtration

Acidic/alkaline wastewater
In the batch neutralisation unit acidic/alkaline wastewater is neutralised by adding hydrochloric acid or sodium hydroxide. After settling, the precipitated metal salts enter sludge dewatering (chamber filter press). The clear water is sent through the sand filtration unit before being indirectly discharged.

Wastewater containing heavy metals
Wastewater containing heavy metals is treated analogous to acidic/alkaline wastewater. In the batch neutralisation unit the precipitation of heavy metals is triggered by increasing the pH value to 8.5 – 9.0. To enhance flocculation (especially of tin) iron(III)chloride is added. After settling, the accruing sludge is dewatered in a chamber filter press. The clear water is sent through cation exchange resins to remove remaining heavy metals. As the final step sand filtration is applied before indirect discharge.

14.2 Current consumption and emission levels

Due to the big variety of electroplated products (regarding size, shape, quality requirements, etc.) representative specific consumption parameters cannot be derived.

Waste generation

Generated residues linked to electroplating and anodizing activities are presented in Table 227. The quantities of residues are from 2015.

Table 227: Residues linked to electroplating and anodizing processes from 2015

Type	Category	Unit	Quantity	Origin	Treatment
Iron & steel waste (contaminated)	hazardous	t	33.77	Entire process	Authorised waste disposal company
Copper Cu	hazardous	t	1.7	Entire process	Authorised waste disposal company
Zinc sludge	hazardous	t	1.14	Zinc electroplating	Authorised waste disposal company
Other metal hydroxide sludge	hazardous	t	432.8	WWTP	Authorised waste disposal company
Aluminium hydroxide	hazardous	t	534.3	Anodizing	Authorised waste disposal company
Other aqueous concentrates	hazardous	t	3.0	Pre-treatment	Authorised waste disposal company
Sludge from tank cleaning	hazardous	t	45.5	Pre-treatment	Authorised waste disposal company

Source: Stiefler GmbH, own recordings, 2015

Emissions to air

Process baths are equipped with edge exhaust air extraction. Anodizing process baths are additionally equipped with lids to reduce diffuse emissions to air. The extracted air is treated in a wet scrubber to reduce sodium hydroxide (zinc electroplating), sulphuric acid (anodizing) and mists from hot sealing. The scrubbing liquid is collected and reused. After several applications the scrubbing liquid is sent to the WWTP.

HCl emissions from the electroplating unit have to be monitored all three years by an accredited testing institute. The ELV is 30 mg/Nm³.

Sodium oxide (Na_2O) and sulfuric acid (H_2SO_4) emissions from anodizing have to be monitored all five years by an accredited testing institute. The ELVs are 100 mg/Nm³ Na2O and 60 mg/Nm³ H_2SO_4.

Table 228 presents the monitoring results from 07.11.2015. For each parameter the average of three half hour measurements was calculated and is presented below. The measurements were conducted during normal operating conditions.

Table 228: Monitoring results of Chloride emissions to air from electroplating, 1013 mbar, dry exhaust air

Parameter	Unit	Average of 3 half hour measurements	ELV	Sampling period	Standard
HCl	mg/Nm³	0,11	30	half hour measurement	EN 1911
Na_2O	mg/Nm³	<0,3	100	half hour measurement	EN 1911
H_2SO_4	mg/Nm³	0,11	60	half hour measurement	EN 1911

Source: FTU GmbH, Prot. Nr. 2014/16

Emissions to water

Treated process wastewater is discharged indirectly. Monitoring has to be conducted using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit. Minimum monitoring frequencies for self-monitoring (performed by operator) and external-monitoring are prescribed by permit. Emission limit values (ELV) are prescribed by permit.

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

The WWTPs consist of:

- Chromate treatment
- Neutralisation

- Sludge dewatering
- Sand filtration

A detailed description of the on-site WWTPs is presented in chapter 14.1.

Emissions to water from electroplating and anodizing are described in the following tables. In Table 229 and Table 230 the minimum monitoring frequencies and ELVs prescribed by permit are presented and compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. Table 231, Table 232 and Table 233 present the self-monitoring recordings of treated process wastewater from electroplating. Table 234, Table 235 and Table 236 present the self-monitoring recordings of treated process wastewater from anodizing. Table 237 and Table 238 present the external-monitoring results from zinc electroplating and anodizing.

Table 229: Emission limit values for the process wastewater from zinc electroplating in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Zinc electroplating						
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)[235]**	**Ordinance (indirect discharge)**	**Min. monitoring frequency self-monitoring**	**Min. monitoring frequency external-monitoring**
Q	m³/h	30	–	–	Weekly	Annually
T	°C	30	–	35	Weekly	Annually
pH		6.5–9.5	–	6.5–10.0	Weekly	Annually
TSS	mg/l	150	–	150	–	Annually
Chromium – total	mg/l	0.5	0.1–2.0	0.5	Weekly	Annually
Cr(VI)	mg/l	0.1	0.1–0.2	0.1	Weekly	Annually

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[235] Discharge to public sewer or surface water from jig, barrel, small scale coil, automotive, PCB and other activities not large scale steel coil

Zinc electroplating Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)[235]	Ordinance (indirect discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Cobalt (Co)	mg/l	1.0	–	1.0	–	Annually
Iron (Fe)	mg/l	2.0	–	–	Weekly	Annually
Zinc (Zn)	mg/l	2.0	0.2–2.0	2.0	–	Annually
Copper (Cu)	mg/l	0.5	0.2–2.0	0.5	–	Annually
Nickel (Ni)	mg/l	0.5	0.2–2.0	0.5	Weekly	Annually
Cyanide (CN)	mg/l	0.1	0.01–0.2	0.1	–	Annually
Fluoride (F)	mg/l	20	–	20	–	Annually
Sulphide (S)	mg/l	1.0	–	1.0	Weekly	Annually
COD	mg/l	200	–	–	Weekly	Annually

Source: Permit 1/1-An-4053/22/108-2007; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 230: Emission limit values for the process wastewater from anodizing in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Anodizing Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)[236]	Ordinance (indirect discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
T	°C	30	–	35	Weekly	Annually
pH		6.5–9.5	–	6.5–10.0	Weekly	Annually

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[236] Discharge to public sewer or surface water from jig, barrel, small scale coil, automotive, PCB and other activities not large scale steel coil

Anodizing						
Parameter	**Unit**	**ELV Permit**	**BAT-AEL (BREF 2006)[236]**	**Ordinance (indirect discharge)**	**Min. monitoring frequency self-monitoring**	**Min. monitoring frequency external-monitoring**
TSS	mg/l	150	–	150	–	Annually
Cobalt (Co)	mg/l	1.0	–	1.0	Weekly	Annually
Iron (Fe)	mg/l	2.0	–	–	Weekly	Annually
Tin (Sn)	mg/l	1.0	0.2–2.0	1.0	Weekly	Annually
Nickel (Ni)	mg/l	0.5	0.2–2.0	0.5	Weekly	Annually
Fluoride (F)	mg/l	20	–	20	Weekly	Annually
COD	mg/l	200	–	–	Weekly	Annually

Source: Permit KS-AN-4053/42/141 -2011; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

Table 231: Self-monitoring of treated wastewater from electroplating 2017

Self-monitoring 2017							**Electroplating**
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Cr total	mg/l	0.002	0.492	0.233	0.075	0.50	245
Cr(VI)	mg/l	0.059	<0.1	<0.1	0.1	0.10	241
Ni	mg/l	0.05	0.499	0.32	0.169	0.50	245
pH		6.6	8.5	8.11	7.633	6.5–9.0	51
Zn	mg/l	0.167	2.0	1.597	0.764	2.00	245
Fe	mg/l	0.023	1.93	0.89	0.29	2.00	245
S	mg/l	<0.1	<0.1	<0.1	<0.1	0.1	245
COD	mg/l	56.7	199.0	188.85	168.82	200	51

Source: Self-monitoring Stiefler, 2017

Table 232: Self-monitoring of treated wastewater from electroplating 2018

Self-monitoring 2018							**Electroplating**
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Cr total	mg/l	0.0023	0.471	0.157	0.07	0.50	244
Cr(VI)	mg/l	0.015	<0.1	<0.1	0.096	0.10	228
Ni	mg/l	0.03	0.492	0.402	0.21	0.50	245
pH		6.6	8.9	8.2	7.4	6.5–9.0	49
Zn	mg/l	0.02	1.9	1.69	0.67	2.00	245
Fe	mg/l	0.017	1.57	0.63	0.27	2.00	245
S	mg/l	<0.1	<0.1	<0.1	<0.1	0.1	245
COD	mg/l	65.8	197	195	171	200	61

Source: Self-monitoring Stiefler, 2018

Table 233: Self-monitoring of treated wastewater from electroplating 2019

Self-monitoring 2019							**Electroplating**
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Cr total	mg/l	0.00	0.455	0.14	0.68	0.50	196
Cr(VI)	mg/l	0.011	<0.1	<0.1	0.095	0.10	178
Ni	mg/l	0.0013	0.493	0.4	0.2	0.50	196
pH		6.6	8.3	8.1	7.4	6.5–9.0	41
Zn	mg/l	0.096	1.97	1.79	0.8	2.00	196
Fe	mg/l	0.05	0.6	0.35	0.19	2.00	190
S	mg/l	<0.1	<0.1	<0.1	<0.1	0.1	196
COD	mg/l	70	195	192	172	200	41

Source: Self-monitoring Stiefler, 2019

Table 234: Self-monitoring of treated wastewater from anodizing 2017

Self-monitoring 2017							Anodizing
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
pH		6.8	8.2	8.0	7.7	6.5–9.0	51
Sn	mg/l	0.091	0.94	0.86	0.46	1.0	51
Fe	mg/l	0.068	1.81	0.45	0.26	2.0	51
COD	mg/l	0.00	180	141.5	76.71	200	51

Source: Self-monitoring Stiefler, 2017

Table 235: Self-monitoring of treated wastewater from anodizing 2018

Self-monitoring 2018							Anodizing
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
pH		6.7	8.3	8.2	7.5	6.5–9.0	50
Sn	mg/l	0.022	0.97	0.83	0.52	1.0	37
Fe	mg/l	0.178	1.302	0.85	0.48	2.0	49
COD	mg/l	30.3	159	102.9	63	200	47

Source: Self-monitoring Stiefler, 2018

Table 236: Self-monitoring of treated wastewater from anodizing 2019

Self-monitoring 2019							Anodizing
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
pH		6.9	8.3	8.1	7.5	6.5–9.0	41
Sn	mg/l	0.022	0.87	0.66	0.27	1.0	29
Fe	mg/l	0.022	0.628	0.53	0.23	2.0	40

Self-monitoring 2019							Anodizing
Parameter	Unit	Daily min	Daily max	95 Percentile	Annual average	ELV permit	Number of samples
TSS	mg/l	5	144	140	53	150	31
COD	mg/l	30.4	125	95.3	61.9	200	40

Source: Self-monitoring Stiefler, 2019

Table 237: External-monitoring of process wastewater from zinc electroplating

Zinc electroplating – External-monitoring						
Parameter	Unit	17.02.2017	14.02.2018	14.02.2019	ELV	Standard
T	°C	19,1	17,9	15,9	30	ONORM M 66 16
pH		7,8	7,5	7,6	6,5–9,0	EN ISO 10523
TSS	mg/l	<10	37	<10	30	DIN 38409-2
COD	mg/l	70	136	173	200	ÖNORM ISO 15705
CN	mg/l	< 0,0088	<0.0088	<0,0088	0,1	ISO 6703
F	mg/l	1,8	1,3	3,2	20	EN ISO 10304-1
Cr(VI)	mg/l	0,023	<0,0036	<0,0036	0,1	ISO 11083
Cr – total	mg/l	0,04	0,0071	<0,003	0,5	EN ISO 11885
Fe	mg/l	<0,026	0,13	0,069	2	EN ISO 11885
Ag	mg/l	0,01	<0,01	0,025	0,1	EN ISO 11885
Zn	mg/l	0,57	0,63	0,53	2	EN ISO 11885

Source: WSB, 2017–2019

Table 238: External-monitoring of process wastewater from anodizing

Anodizing – External-monitoring						
Parameter	**Unit**	**17.02.2017**	**14.02.2018**	**18.02.2019**	**ELV**	**Standard**
Q	m^3	72	76	69		–
T	°C	17,8	17,2	18,2	30	ÖNORM M 6616
pH		7,8	7,5	7,4	6,5–9 ,5	ÖNORM EN ISO 10523
Settleable substances	ml/l	<0,1	<0,1	<0,1		ÖNORM M 6271
COD	mg/l	27	20	52	200	ISO 15705
F	mg/l	0,078	0,053	<0,1	20	EN ISO 10304-1
Fe	mg/l	0 ,035	0,096	0,16	2	EN ISO 11885
Co	mg/l	<0,004	<0,004	<0,02	1	EN ISO 11885
Ni	mg/l	<0,004	<0,004	<0,02	0,5	EN ISO 11885
Sn	mg/l	0,049	0,18	0,053	1	EN ISO 11885
Settleable substances – load	l/d	<7,2	<7,6	<6,9		Calculated
COD – load	g/d	1940	1520	3590		Calculated
F – load	g/d	5,62	4,03	<6,9		Calculated
Fe – load	g/d	2,52	7,3	11		Calculated
Co – load	g/d	<0,288	<0,304	<1,38		Calculated
Ni – load	g/d	<0,288	<0,304	<1,38		Calculated
Sn – load	g/d	3,53	13,7	3,66		Calculated

Source: WSB, 2017–2019

14.3 References

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15 Voestalpine Stahl GmbH

The voestalpine group focuses on product and system solutions based on steel and other metals. The group consists of four divisions: Steel Division, High Performance Metals Division, Metal Engineering Division and Metal Forming Division. The headquarter is based in Linz. (voestalpine, 2020)

On the premise of the headquarter continuous steel coil electroplating (zinc) is carried out. The electroplated steel coils are destined for the automotive industry.

Environmental Management System
In the headquarter Linz the following environmental management systems are implemented: ISO 14001, ISO 9001, OHSAS 18001 and EMAS.

15.1Technical description

The operation of the continuous coil electroplating plant started in 1985. In the electroplating plant large steel coils are electroplated with zinc. Finished cold-rolled steel coils are the feed material for the continuous coil electroplating plant.

In general the electroplating process consists of the following steps:

- Coil reception
- Degreasing
- Pickling
- Electroplating
- Phosphating layer conversion coating
- Cr-free passivation
- Drying
- Oiling
- Unloading

Coil reception
At coil reception, the finished cold-rolled steel coils are uncoiled and welded together with

the next coil, to allow a continuous process. Coil reception is equipped with a looper that guarantees that the strip can go on moving at a constant speed in the processing section (even during welding, when the strip end is held still).

Degreasing

Pre-treatment

Alkaline spray degreasing consisting of phosphates, silicates, sodium hydroxide or sodium carbonate together with brushing cleans the strip surface from oils and greases. Subsequently electrolytic degreasing is applied.

Pickling

In order to remove oxide layers from the steel strip surface pickling with sulphuric acid is applied.

Electroplating

The steel strip is electroplated in a pure zinc electrolyte consisting of zinc and sulphuric acid. The electrolyte is heated to above room temperature (approx. 60 °C) to improve metal distribution. The electroplating reaction in continuous steel coil electroplating does not differ from common discontinuous electroplating (using jigs or drums). Nevertheless, the design of the electrolytic cell differs significantly.

Electrolytic cells for continuous coil electroplating

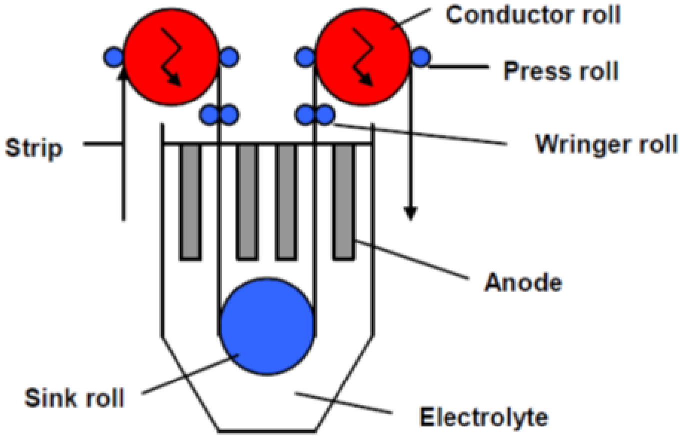
The cleaned and pickled strip is fed through electrolytic cells, which are the heart of an electrolytic line. The main components of a continuous coil electrolytic cell are:

- Conductor roll: this gives the steel strip a negative electrical charge. The voltage is transformed into current by means of a rectifier. The negative pole of the rectifier is connected to the carbon brushes of the conductor roll
- Press roll: provides good contact and high electric conductivity between conductor roll and steel strip
- Anode: repels the positive ions towards the steel strip (cathode). The positive pole of the rectifier is connected to the anode
- Sink roll: turns the steel strip by 180°
- Squeeze rolls (wringer rolls): minimise the drag-over (drag-in) into the next cell

- Conductor roll cleaning device: cleans the surface of the conductor roll to avoid surface defects on the steel strip (STM BREF, 2006)

There are three main types of cell geometry – vertical cell, horizontal cell, radial cell. The continuous steel coil electroplating plant in Linz is designed in vertical cells. Figure 2 illustrates a typical vertical cell. Multiple cells of this kind are in use in the continuous coil electroplating plant of voestalpine GmbH. The steel strip can be coated on both sides, or only on one side (by simply moving one anode away).

Figure 2: Vertical cell for continuous coil electroplating – Alternativtext: Figure 1 presents a typical configuration for continuous coil electroplating in a vertical cell. The strip of the to be coated coil passes over a conductor roll. Press rolls press the strip towards the conductor rolls. Wringer rolls keep the strip in line. The strip passes through the electrolyte vertically. Via the sink role the direction of the strip is redirected (U-turn) upwards, where the strip passes again the wringers and a conductor roll. The anodes are in the electrolyte.



Source: STM BREF, 2006

Phosphating layer conversion coating

Post-treatment

A phosphating solution is sprayed on the electroplated steel strip. Phosphating layer conversion is a chemical deposition of zinc phosphate crystals on the surface of the work piece triggered by a pickling reaction.

Cr-free Passivation

Passivation prevents the electroplated steel from surface damages, e.g. white rust caused by water condensation (where there is insufficient air access) (STM BREF, 2006).

Passivation is carried out by spraying a Cr-free solution on the electroplated steel strip.

Oiling

A wet film of oil is applied to the surface by an electrostatic oiler. This provides an improved protection against white rust corrosion (STEM BREF, 2006).

In a final step the strip is dryed by means of hot air drying devices before passing quality control and a final electrostatic oiling step.

Process & cooling water

Process water is used for the process baths and for rinsing. For the process baths deionised water from reverse osmosis is used.

Cooling water is needed for cooling of the electrolyte, the rectifier and the conductor rolls. Cooling water is reused via a closed loop system which itself is indirectly cooled by once through cooling with surface water.

Rinsing

After each process step the work piece is rinsed. Multiple stage counterflow rinsing units consisting of two or three steps are used in order to minimise water use. Excess water from the rinsing unit is fed back into the electroplating baths or into the degreasing baths.

Process wastewater

Treated wastewater is discharged indirectly. Wastewater from continuous coil electroplating is treated together with wastewater from batch galvanising.

The WWTP consists in general of:

- Continuous neutralisation for rinsing water with low acidic or alkaline concentration
- Discontinuous neutralisation for acidic and alkaline concentrates
- Sand filtration

Wastewater is collected and treated separately, depending on whether it is alkaline or acidic. Alkaline wastewater (mainly from degreasing) is passing an oil separator before entering neutralisation.

In the neutralisation unit the pH value is lowered to 2.5 using HCl or excess pickling solution (if required). By adding sodium hydroxide and/or lime milk the pH value is subsequently increased to 9 – 10. This triggers the precipitation of the metals contained in the wastewater. It is important that the pH value is held stable for an appropriate time frame of ca. 20 minutes to ensure that the precipitation of metals is completed. Wastewater with low concentration (e.g. rinsing water from pre-treatment) is treated in continuous neutralisation. Wastewater with high concentrates is treated in batch neutralisation.

After neutralisation, the wastewater is sent to the filter press. Dewatered sludge from alkaline wastewater is disposed by external operators. Dewatered sludge from acidic wastewater is disposed internally. Sludge from acidic wastewater contains mainly zinc.

In a final step the wastewater is treated in a sand filter before passing end control and being discharged into the public sewer.

Waste gas treatment
Waste gas from degreasing is collected and treated in a demister before being emitted. Generated wastewater from the demister is sent to the on-site WWTP.

Waste gas from pickling, electroplating and post-treatment is collected and treated in an air-washer and subsequently in a demister. Accruing wastewater is sent to the on-site WWTP.

Waste gas from the zinc dissolving station can contain dust and is treated in a demister before being emitted.

Bath life-span
The process baths are regularly monitored and controlled in the in-house laboratory. This enables an accurate dosing of the needed chemicals and avoids excess use of chemicals.

The degreasing solution is reused. The quality is maintained by treating the degreasing solution with magnet filters. Therefore only a small fraction of the degreasing solution needs to be discarded.

15.2 Current emission levels

Waste generation

Generated waste from electroplating or linked to electroplating activities is listed in Table 239.

Table 239: Waste linked to electroplating 2018

Type	Category	Unit	2016	2017	2018	Origin	Treatment
Sludge from neutralisation – alkaline wastewater	hazardous	t	879.8	1089.2	565.2	WWTP	Authorised waste disposal company
Sludge from neutralisation – acidic wastewater	Non-hazardous	t	2027.4	2406.5	3024.1	WWTP	Authorised waste disposal company
Acids, acid mixtures	hazardous	t	No data	No data	6.4	Pickling	Authorised waste disposal company
Bases	hazardous	t	12.8	No data	No data	Degreasing	Authorised waste disposal company
Waste oil	hazardous	t	No data	4.5	5.2	Post-treatment	Internal thermal reuse

Source: VOEST, own recordings

Due to a change in the electroplating process, sludge generated from alkaline wastewater treatment decreased from 2017 to 2018, whilst sludge from acidic wastewater treatment increased by approximately the same amount from 2017 to 2018. Thus, the process change triggered a shift in sludge generation.

Emissions to air

Waste gas from degreasing is collected and treated in a demister. Waste gas from pickling, electroplating and post-treatment is collected and treated in an air-washer and subsequently in a demister. Waste gas from the zinc dissolving station can contain dust and is treated in a demister before being emitted.

Emissions to air have to be monitored every five years by an accredited testing institute. The monitoring frequency and the ELVs are prescribed in permit (UR-200820303/146-Wb/Rs).

Table 240 – Table 243 present the monitoring results from continuous coil electroplating, post-treatment and zinc dissolving. The monitoring was conducted on 19.01.2015, during normal operating conditions. The waste gas volume flows are presented in Table 244.

Table 240: Monitoring results of emissions to air from continuous coil electroplating; 0 °C, 1013 mbar, dry exhaust air

Continuous coil electroplating					
Parameter	**Unit**	**Half-hour measurement**			**ELV**
		1	**2**	**3**	
Zn	mg/Nm³	0.509	0.393	0.506	–
Ni	mg/Nm³	0.009	0.006	0.009	0.5
Cr	mg/Nm³	0.002	0.002	0.002	1

Source: Umwelt- und Betriebsanalytik voestalpine Stahl GmbH, 2015

Table 241: Monitoring results of emissions to air from post-treatment; 0 °C, 1013 mbar, dry exhaust air

Post-treatment					
Parameter	**Unit**	**Half-hour measurement**			**ELV**
		1	**2**	**3**	
Zn	mg/Nm³	0.121	0.191	0.341	–
Ni	mg/Nm³	0.002	0.002	0.006	0.5

Post-treatment					
Parameter	**Unit**	**Half-hour measurement**			**ELV**
		1	**2**	**3**	
Cr	mg/Nm³	0.002	0.002	0.002	1

Source: Umwelt- und Betriebsanalytik voestalpine Stahl GmbH, 2015

Table 242: Monitoring results of emissions to air from zinc dissolving station 1; 0 °C, 1013 mbar, dry exhaust air

Zinc dissolving station 1					
Parameter	**Unit**	**Half-hour measurement**			**ELV**
		1	**2**	**3**	
Zn	mg/Nm³	0.414	0.404	0.330	–
Ni	mg/Nm³	0.007	0.007	0.007	0.5
Cr	mg/Nm³	0.002	0.002	0.002	1

Source: Umwelt- und Betriebsanalytik voestalpine Stahl GmbH, 2015

Table 243: Monitoring results of emissions to air from zinc dissolving station 2; 0 °C, 1013 mbar, dry exhaust air

Zinc dissolving station 2					
Parameter	**Unit**	**Half-hour measurement**			**ELV**
		1	**2**	**3**	
Zn	mg/Nm³	0.434	0.596	1.083	–
Ni	mg/Nm³	0.008	0.011	0.022	0.5
Cr	mg/Nm³	0.002	0.002	0.002	1

Source: Umwelt- und Betriebsanalytik voestalpine Stahl GmbH, 2015

Table 244: Treated waste gas volume flow from continuous coil electroplating, post-treatment, zinc dissolving station 1 & zinc dissolving station 2

Volume flow	Unit	Continuous coil electroplating	Post-treatment	Zinc dissolving station 1	Zinc dissolving station 2
Operating conditions	m^3/h	6004.5	10584.3	15571.1	10281.6
Standard conditions (wet)	m^3/h	5178	9135	13873	9069
Standard conditions (dry)	m^3/h	4904	8663	13442	8870

Source: Umwelt- und Betriebsanalytik voestalpine Stahl GmbH, 2015

Emissions to water

Treated process wastewater is discharged indirectly. Monitoring has to be done using 24-hour flow-proportional composite samples (fpcs) unless prescribed differently by permit. Minimum monitoring frequencies for self-monitoring (performed by operator) and external-assessment are prescribed by permit (UR-200820303/146-Wb/Rs). Emission limit values (ELV) are prescribed by permit (UR-200820303/146-Wb/Rs).

In the STM BREF (2006) BAT-AELs for emissions to water are expressed as daily composite samples.

Wastewater from continuous coil electroplating is treated together with wastewater from batch galvanising.

On-site wastewater treatment consists of:

- Continuous neutralisation for rinsing water with low acidic or alkaline concentration
- Discontinuous neutralisation for acidic and alkaline concentrates
- Sand filtration

A detailed description of the on-site WWTP is presented in chapter 15.1.

Emissions to water from electroplating and batch galvanising are described in the following tables. In Table 245 the minimum monitoring frequencies and ELVs prescribed by permit are presented and compared to the BAT-AELs for emissions to water from the STM BREF (2006) and the Ordinance on wastewater emissions from surface treatment of metals. In Table 246, Table 247 & Table 248 the self-monitoring recordings of treated process wastewater from 2016, 2017 and 2018 are presented.

Table 245: Emission limit values for the process wastewater from electroplating and batch galvanising in comparison with BAT-AELs (BREF 2006) and the Ordinance on wastewater emissions from surface treatment of metals. Minimum monitoring frequencies for treated wastewater as prescribed by permit

Parameter	Unit	ELV Permit	BAT-AEL (BREF 2006)[237]	Ordinance (indirect discharge)	Min. monitoring frequency self-monitoring	Min. monitoring frequency external-monitoring
Water quantity (Q)	m³/d	800	–	–	–	5 years
Temperature (T)	°C	35	–	35	15 days	5 years
pH		6.5–9.5	–	6.5–10.0	15 days	5 years
Total suspended solids (TSS)	mg/l	30	–	150	15 days	5 years
Chromium – total (Cr)	mg/l	0.5	0.1–2.0	0.5	15 days	5 years
Cr(VI)	mg/l	0.1	0.1–0.2	0.1	15 days	5 years
Nickel (Ni)	mg/l	0.5	0.2–2.0	0.5	15 days	5 years
Zinc (Zn)	mg/l	2.0	0.2–2.0	1.0[238]	15 days	5 years
Sum of hydrocarbons	mg/l	5.0	–	15	15 days	5 years
Sulphate (SO_4)	mg/l	3000	–	–	15 days	5 years

Source: Permit UR-200820303/146-Wb/Rs; STM BREF 2006; AEV Oberflächenbehandlung BGBl. II Nr. 44/2002

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[237] Discharge to public sewer or surface water from jig, barrel, small scale coil, automotive, PCB and other activities not large scale steel coil

[238] For wastewaters from electroplating or batch galvanising the ELV is 2.0 mg/l

External-assessment has to be conducted all 5 years. In the course of external-assessment, compliance with all relevant permit conditions has to be checked. This includes an assessment of the measured emission values regarding their ELVs. The resulting report has to be transmitted to the competent authority. A measurement in the course of the external-assessment is not required.

Table 246: Self-monitoring of treated process wastewater 2016

Self-monitoring 2016							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Q	m³/d	79.00	612.20	594.01	398.38	800	39
T	°C	15.8	30.3	29	25.5	35	366
pH		1.4	9.4	8.6	8.0	6.5–9.5	366
TSS	mg/l	2.00	24.00[239]	21.60	15.14	30	28
Cr total	mg/l	0.00	0.34	0.12	0.04	0.5	28
Cr (VI)	mg/l	0.00	0.09[240]	0.07	0.02	0.1	28
Sum of hydrocarbons	mg/l	0.00	1.10	0.57	0.20	5.0	23
Ni	mg/l	0.00	0.08	0.04	0.02	0.5	23
SO_4	mg/l	187.00	3000.00[241]	2760.00	2091.10	3000	31
Zn	mg/l	0.02	0.79	0.27	0.14	2.0	23

Source: Self-monitoring VOEST, 2016

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[239] 3 consecutive measurements above the ELV (33 mg/l; 35 mg/l; 37 mg/l)

[240] One measurement above the ELV (0.24 mg/l)

[241] 2 consecutive and 3 single measurements above the ELV (between 3050 mg/l – 3840 mg/l)

Table 247: Self-monitoring of treated process wastewater 2017

Self-monitoring 2017							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Q	m³/d	62.30	623.00	601.15	431.06	800	27
T	°C	15.4	32.3	29.6	26.3	35	360
pH		0.2	9.3[242]	8.6	7.8	6.5–9.5	360
TSS	mg/l	1.00	28.00[243]	28.00	14.08	30	25
Cr total	mg/l	0.01	0.09	0.03	0.02	0.5	23
Cr (VI)	mg/l	0.00	0.02	0.01	0.00	0.1	23
Sum of hydrocarbons	mg/l	0.00	2.60	1.74	0.26	5	23
Ni	mg/l	0.00	0.07	0.06	0.02	0.5	23
SO_4	mg/l	945.00	2580.00[244]	2479.50	2197.79	3000	28
Zn	mg/l	0.05	0.66	0.33	0.14	2	23

Source: Self-monitoring VOEST, 2017

Table 248: Self-monitoring of treated process wastewater 2018

Self-monitoring 2018							
Parameter	**Unit**	**Daily min**	**Daily max**	**95 Percentile**	**Annual average**	**ELV permit**	**Number of samples**
Q	m³/d	95.20	562.90	517.08	416.30	800	22
T	°C	16.8	37.6	30.6	26.9	35	344
pH		2.0	11.9[245]	9.1	8.1	6.5–9.5	344

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[242] One measurement above the ELV (9.8)
[243] One measurement above ELV (42 mg/l)
[244] 3 consecutive measurements above the ELV (3530 mg/l, 3880 mg/l, 4420 mg/l) and one single measurement above the ELV (4190 mg/l)
[245] One measurement above the ELV (11.9)

Self-monitoring 2018							
Parameter	Unit	Daily min	Daily max	95 Percentile	Annual average	ELV permit	Number of samples
TSS	mg/l	4.00	24.00	20.40	10.38	30	24
Cr total	mg/l	0.01	0.03	0.03	0.01	0.5	24
Cr VI	mg/l	0.00	0.02	0.02	0.00	0.1	24
Sum of hydrocarbons	mg/l	0.00	2.10	1.49	0.27	5	24
Ni	mg/l	0.00	0.04	0.03	0.01	0.5	24
SO_4	mg/l	566.00	2970.00	2578.00	1910.25	3000	24
Zn	mg/l	0.04	0.55	0.26	0.12	2	24

Source: Self-monitoring VOEST, 2018

Measurements below the limit of detection are represented by the value 0.00 mg/l in the self-monitoring records.

15.3 References

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Table of Tables

Abbrevations

CDC	Cathodic dip paint coating
RTO	Recuperative thermal oxidatio
WWTP	Wastewater treatment plant
ELV	Emission limit value
PCB	Printed circuit board
HDI	High density interconnect (board)
MLB	Multilayer board
ECCS	electro-chemical chromium plating
CML	Continuous motion line
VAV	Austrian Ordinance for VOC emitting plants

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