

ENVIRONMENTAL EMISSIONS OF METALS IN INDUSTRIAL SURFACE TREATMENT

Background Document

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General disclaimer

SPERCs are specific environmental release categories and are meant to specify broad emission scenario information (ERCs) as suggested for the use of substances throughout their life cycles (Reihlen et al., 2016). Although specific, SPERCs still reflect emissions of a broad application area of a substance within an industry sector. For their purpose SPERCs are overly conservative and, therefore, their emission estimates are not intended to reflect all regulatory requirements that may relate to environmental emission thresholds. Please be aware that the quality of treated effluents must meet national and/or regional discharge standards before emission.

1 Statement of Purpose

To carry out an environmental exposure assessment, the quantification of the rates of substances released to the environment is key. While the ECHA Guidance R16 provides a generic set of release factors, they are less meaningful for several industry sectors, among them A.I.S.E., that have refined the Environmental Release Categories (ERCs) by detailed analysis of the sector specific typical operational conditions to build 'SPecific Environmental Release Categories' (SPERCs).

Thus, the A.I.S.E. SPERCs refine and specify emission scenario information (ERCs) for the use of substances throughout their life cycle (Reihlen et al., 2016) in the detergent and maintenance products industry.

The SPERCs described in this document are specific to environmental emissions of metals in industrial surface treatment. The surface treatment of metals and plastics increases their durability and appearance. Many factors determine the use of raw materials as well as the emission of pollutants from surface treatment leading to high absolute variations. Large scale operations predominantly form the basis for the purpose of this background document assuming worst case situations with regard to environmental emissions. This document analyses industrial surface treatment of metals and plastics with regard to its substance use rates and environmental emission of metals. It focusses to those applications where emissions of heavy metals occur that are highly hazardous to the aquatic environment, but it also looks into applications where less hazardous substances are used.

Highly hazardous heavy metals are considered as the worst case with regard to risk management measures as they typically require substance specific treatment, whereas for other environmentally hazardous chemical compounds in surface treatment pH adjustment may be sufficient (e.g. hydroxylamine (HA)). The latter and the use of e.g. nonylphenol ethoxylate (NPEO), ethylene diamine tetraacetic acid (EDTA), boron and perfluoro octanoic sulphonate compounds (PFOS) is not considered to be relevant for this SPERC and would be beyond scope.

Whereas all of the metal compounds used in surface treatment (including substrates) may have adverse effects depending on their specification, five metals were identified of most concern for the environment as they are used on a broader scale: Ni(II), Cr(III) or (VI), Cu(II), Mn(II), Zn(II).

While Cr(III) or (VI), Cu(II), Mn(II), Zn(II) were subsumed under one single SPERC Ni(II) is assessed by a separate SPERC factsheet due to its slightly different RMM efficiency. It should further be noted that since September 2017, when use of Cr(VI) compounds was restricted on the EU market by authorization, its consumption decreased significantly while appropriate alternative techniques are applied nowadays.

The factsheets covered by this document are:

AISE Code	SPERC	Type of ingredient	Application area
AISE-SPERC 5.1a v.3		Nickel-salts	Industrial use of Me-salts in surface treatment of metals and plastics
AISE-SPERC 5.1b v3		Zinc-, Chromium, Copper-, Manganese- salts	

This background document provides information on the derivation of the relevant parameters of the above-mentioned factsheets. Some details refer to tertiary references, e.g. publications listed in chapter 8 and 9.

2 Scope: Surface treatment processes using metals salts

The main purpose of metal treatment is to protect the metal surface against corrosion during its use, increase wear resistance and improve adhesion to subsequent layers (e.g. to paints). Surface treatment is usually carried out after the primary metal has been formed into workpieces or shaped substrates, such as nuts, bolts, pressed or moulded components, sheets, or coils. According to STM BREF (2006) the surface treatment is not related to a distinct vertical industry sector but involves multiple industry sectors. Among these industries are automotive & aerospace (27 %) electric and electronic equipment (14 %), industrial equipment and steel semi products (13 %), construction (9 %), food and drink containers (8 %). Metal treatment is therefore a globally widespread technology applied to almost all metal parts assembled in industry.

Modern surface treatment technologies achieve a high level of environmental protection. Best available techniques (BAT) are described in OECD and BREF documents on surface treatment for metals and plastics (OECD 2004, BREF, 2006). Most relevant processes are selected and analyzed for the purpose of this SPERC background document, with a focus to the environmental release estimation of hazardous metals.

2.1 Surface Treatment: Product Types and Relevant Metal Ingredients

The activities covered in the scope of this document use a broad range of water-based technologies, hence, the main way of metal use is as soluble salt. With regard to environmental emissions the processes differ in amount and type of ingredients.

There are two main industrial processes/product types to be distinguished in surface treatment, conversion coating and auto-catalytic coating, respectively. Whereas the conversion coating technology is based on chemical or electro-chemical interaction of a metal ion on a surface, the auto-deposition technology uses autocatalytic reactions of metal ions (or organic polymeric materials) that are chemically deposited on metal surfaces (generally ferrous iron) or plastics.

It should also be noted that due to environmental concerns industry more frequently applies alternative processes with less hazardous compounds for the same purposes. Among them are phosphate-free conversion coatings and autodeposition of non-metal coatings like chrome-free coil coating using Zirconium as a coating agent and Electro-Ceramic Coating with Titanium ("EC2 process"). Where appropriate, potential alternatives are briefly mentioned as footnotes in this document.

2.1.1 Conversion Coating

Conversion coatings are inorganic coatings for metals where the surface is converted into the coating with a chemical or electro-chemical process. Examples include phosphate conversion coatings, chromate conversion coatings, bluing, black oxide coatings on steel, and anodizing. Most relevant examples for traditional conversion coating processes are the iron-zinc phosphate conversions of car and truck bodies or the chrome-plating of light metals. Further electroplating/galvanization processes are subsumed in this chapter as well.

Iron, zinc and manganese phosphate processes¹

Phosphate coatings are the most widely used conversion coatings for industrial surface treatment. They can be applied to metal substrates such as steel, cast iron, aluminium or zinc. Phosphate coating is the treatment of ferrous metal with a dilute solution of orthophosphoric acid (H_3PO_4) and other chemicals, whereby the surface of the metal, reacting chemically with the phosphoric acid, is converted to an integral, mildly protective layer of insoluble crystalline phosphate. There is a wide variety of phosphating processes, but the most important are alkali (iron) and zinc phosphating. Iron, zinc and manganese phosphate is applied based on the required thickness of the phosphate layer (OECD 2004). Zn-Phosphating is the traditional process extensively used in car body surface pre-treatment. The system used can either be single or tricationic (Zn, Mn, Ni), depending on customer requirements. It may and may not contain toxic heavy metals such as nickel. Nickel is typically added to improve surface adhesion. Despite manganese phosphate coatings have the highest hardness in addition to their corrosion and wear resistance, there are only few applications with manganese.

Coil coating (mainly on aluminium)

In metal coil coating processes, the coating material is applied on rolled metal strips by a continuous process. Coil coating with chrome is a conversion process where a layer of Cr(III) is formed on one or two sides of a metal band. Conversion layers are either hazardous metal based (e.g. chromate, chrome-phosphate) or hazardous metal free (zirconium, manganese and titan).

Electroplating (or “electrodeposition”)

Advanced surface treatment processes include the use of electric current. Among them are electroplating, electro ceramic coatings and electro pulse anodization processes. There are three types of processes used in the galvanizing industry of which the electroplating is one: general hot dip galvanizing²; continuous hot dip galvanizing; and continuous electroplating processes (OECD 2004). Electroplating is the primary industrial metal finishing process.

Electroplating is a galvanization process applying one or more layers of a metal by passing a positively charged electrical current through an aqueous solution containing dissolved metal ions (frequently fed by a solid anode of the metal) and a negatively charged electrical current through the work piece to be plated (cathode). Electroplating processes may comprise of Cadmium, Copper, Gold, Chrome, Nickel, Silver, Platinum, Tin, Zinc, Brass, Bronze or Rhodium. An example of electroplating is the Electrolytic Chromium Coating of Steel (ECCS) with either the generation of a decorative chromium

¹ Note of heavy-metal alternative processes: phosphate-free conversion technologies can replace the traditional iron and zinc phosphate processes are free of heavy metals. Those technologies work on the basis of nano-ceramics (Zirconium-based) and thus reduce hazardous waste, also because sludge formation is marginal. Since they also reduce energy consumption these technologies are preferred today for operations for conversion coatings in large industries.

² During hot dip galvanization, the components to be coated are dipped into a bath of molten zinc and then cooled gradually, quenched in water and dried. Hot dip galvanization with Zn is very common in Europe and is sometimes seen in combination of both: first cold sealing with Ni plus subsequent hot sealing with Zn. Hot dip galvanization does not apply aqueous solutions of metals and is therefore of less environmental relevance.

layer ('bright chromium plating') or -in the case of hard chromium plating- of multiple layers to achieve a high hardness in combination with high wear resistance ('functional coating', BREF, 2006). Another example is steel strip that is electroplated with zinc. In ECCS hexavalent chromium was the most widely used. Meanwhile, trivalent chrome plating is the most common application segment that is found for decorative applications. Substitutes for hard and decorative chromium baths are e.g. electroplated Ni and/or Co compounds (BREF, 2006). In fact, electroplating is not a conversion coating process and involves the direct deposition of a thin coat of any metal on a substrate (ferrous or non-ferrous).

Anodizing³

Anodizing is an electrochemical conversion (electrolytic) process in which the surface of a metal, such as aluminium, magnesium, titanium or steel (rarely zinc and copper), in an electrolyte (chemical solution), is converted into a defined thin, extremely strong and corrosion-resistant oxide finish which has protective, decorative or functional properties. There is also a chromium anodizing process that uses chromic acid as an electrolyte to form an aluminium oxide layer to provide resistance to corrosion. The chromium anodizing process is used mainly to coat aircraft parts (e.g. wings and landing gears) as well as - less frequently - architectural structures that are subject to high stress and corrosive conditions.

Cold sealing

Anodized surfaces are usually porous and need to be "sealed" by other metal ions (e.g. with nickel). Sufficient corrosion resistance can only be achieved by blocking the existing micropores. Cold Sealing is a low-energy process at below 30°C. However, there are also two-step cold sealing processes where the second step reaches up to 70°C.

2.1.2 Autocatalytic coatings

In contrast to metal conversion and advanced surface treatment processes, autocatalytic/autophoretic coatings (autodeposition) apply functional organic polymers (e.g. epoxy/acrylic and/or urethane)⁴ or a layer of metal (e.g. nickel, copper) on metal (or plastic) surfaces without requiring a conversion of the surfaces or an electric current for deposition.

Autocatalytic plating

This process (also known as electroless plating) deposits an even metal-alloy layer of defined thickness to both, a conductive (e.g. steel, stainless steel, aluminium and its alloys, brass etc.) or a non-conductive (e.g. plastic) surface, without an external power source. The electroless metal solution consists of metal ions, reducing agents, and other chemicals. A limited number of metals can be deposited by chemical reduction, but in practice copper and nickel are the only two deposited on a large commercial scale (OECD, 2004). Au, Ag and Co are of minor use (OECD, 2004). Typical fields of applications are the automotive and engineering industry (corrosion inhibition), plastic industry (e.g. decorative bathroom fittings) as well as electronic industry (e.g. hole connection on circuit boards) (BSTSA, 2018).

³ Note of heavy-metal alternative processes: electro-ceramic coating, which is formed by electro deposition of titanium oxides to light metal surfaces such as aluminium, magnesium and titanium.

⁴ Note of heavy-metal alternative processes: The autophoretic coating a layer of anti-corrosive paint is applied to metal surfaces using a chemical reaction. Those processes are broadly comparable to painting but they are technically less complex and are applied by immersion baths. The organic compounds of the products coat only reactive metal surfaces and thus become self-limiting itself, resulting in the formation of uniform layers on the surfaces even in hidden and recessed areas of the work piece. Autophoretic coatings are free of heavy metals and generally have negligible emissions to the aquatic environment, because the baths are back-filled as replenished and are not subject to bath exchanges

Chromating

Chromium conversion coating⁵ is used as autocatalytic plating process to enhance corrosion protection on various metal surfaces, including electroplated zinc and cadmium, zinc die castings, tin, aluminium, magnesium and magnesium alloys, copper, brass and bronze, nickel, silver and stainless steel. Coatings are applied by chemical reaction in aqueous solutions. Chromating is often referred to as 'chrome passivation' because it is a conversion process that originally used hexavalent chromium ($\text{Cr}_2\text{O}_4^{2-}$) as the oxidant in nearly all areas of the steel processing industry. Meanwhile it has been replaced by Cr(III) alternatives. Trivalent chromium passivates have been developed producing a higher film thickness and greater corrosion resistance and performing well in comparison with iridescent Cr(VI) passivation (BREF 2016). Passivation is an essential post treatment step in zinc plating (hot dip galvanization), but can also be applied after phosphating or on Cu (incl. brass and bronze), on light metals and alloys.

2.2 Application and Process Techniques

Although industrial surface treatment using metals may lead to significant environmental emissions modern surface finishing plants have dedicated approaches to waste minimization at source, recycling, and follow integrated concepts for process plant and effluent treatment. Where conversion coating processes require the application of hazardous heavy metals, their chemical state is altered during the application process to manage both, its technical application and its removal from the wastewater, respectively. Conversion coatings where these metals are not extracted from the process by sludge and/or excess waters, require regular bath exchanges. Generally, the main impact of metals to the environment is in its ionic soluble form.

The smaller finishing shops, and especially those working with small runs of high tech electronic or aerospace parts, are for the most part manually operated. Work is transferred between each unit operation by hand or semi-automatic equipment, while large finishing shops all use automated plant (automated transporters /robots). Although the efficiency of raw material use may be less in small shops with regard to environmental emissions the large shops reveal worst case situations that are analyzed in more detail in this document.

Figure 1 illustrates the schematic flow of workpieces in a conversion coating process. Generally, there are three major process steps common to the majority of treatment processes. First the work piece is pre-treated to ensure susceptibility of the metal surface to the coating procedure. Conversion as well as auto-deposition coating require stages such as cleaning (degreasing & rinsing) and pre-treatment, i.e. activation of surface (e.g. by pickling, descaling, deoxidizing, stripping, etching, anodizing, brightening). Second, the conversion treatment creates a protective layer on the work piece, e.g. by conversion coating, passivation, sealing, autodeposition or anodizing. Lastly, the post treatment ensures durability and right appearance of the coating (e.g. sealing, passivation, rinsing). The different steps are usually subsequent processes automated in time.

The treatment of the metal parts generally occurs by immersion (bathing) or by spraying. Coatings obtained by spraying are thinner than those applied by immersion. After each stage the work pieces being processed are usually rinsed in water to avoid cross contamination between each process stage. Where applicable, roll-coating of a waterborne liquid is applied, allowing to safe subsequent rinsing steps that typically results in lower emissions.

⁵ Note: Chromium-free processes exist based on treatments with a composite organic-zirconium fluoride solution, treatments with titanium fluoride, or treatments with organic silicon derivatives (silanes) and sulphuric acid anodizing (SAA). They may require a subsequent polymer layer, such as electrophoretic lacquer, to achieve required corrosion resistance.

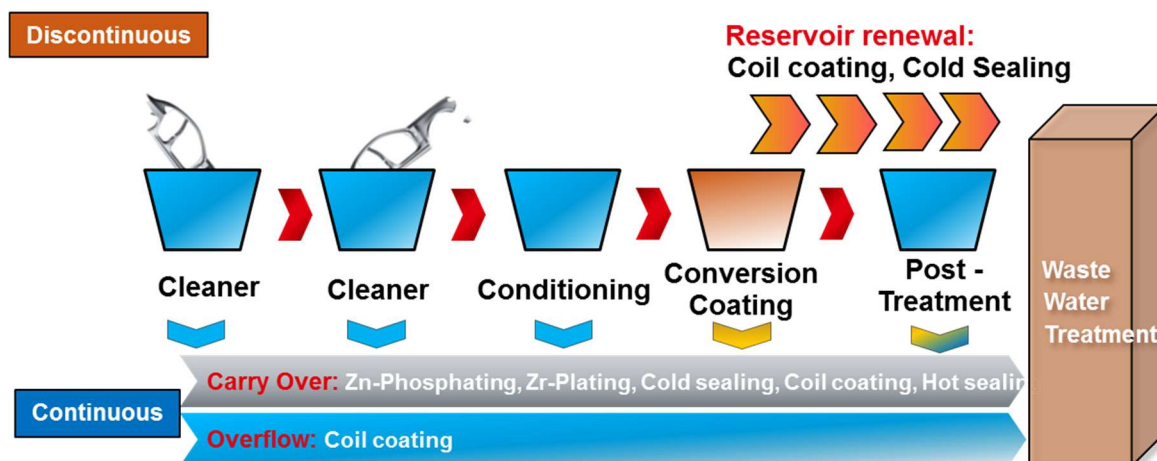


Figure 1: Schematic overview on conversion coating processes. Continuous emissions can occur during carry over (drag-out) with working pieces and overflow of access fluids. Discontinuous emissions are relevant where reservoir bath needs frequent full replenishment (e.g. coil coating).

3 Emission relevance of operational conditions

While the emissions from initial aqueous degreasing are waters containing oil and used surfactants, the intermediate rinsing steps are optimized with the purpose to minimize the cross-contamination of the process chemicals. They ensure that the finished components leave the finishing shop in a clean and safe condition. Therefore, intermediate and end rinsing are the largest potential sources of waterborne contamination as these waters carry all the process chemicals from an activity. It is good practice to consider every process discharge point whether treatment (or recycling or re-use) is better carried out on the separated stream, before mixing flows for subsequent treatment (cf also 4.1.1). For example, cleaning solutions containing complexing agents are usually separated from other waste-water streams to avoid interference with subsequent metal ion recovery (BREF 2006).

In modern surface treatment emphasis is given on waste minimization by cascade rinsing with two, three or more rinse stages in counter-current operations. On removal of the workpiece from a bath a certain amount of the process solution is lost from the bath. This is known as drag out or carry-over (Q_{dragout}). Drag-out depends on a large variety of parameters and its reduction is a key step for impacts on the environment. The quantity of material loss by drag-out from the process baths depends on the process method (continuous, rack or barrel deposition) and the shape of the workpiece (some workpieces are specifically designed with flushing holes etc.). Larger components, e.g. pressings, wirework, and prefabricated work such as computer boxes are individually jugged onto a rack, the latter being moved from tank to tank by a transporter system (conveying of racks may include tumbling, vertical position, bottom-up turn). Smaller workpieces e.g. fasteners, small pressings and coinages are processed in rotating barrels, which again are transferred from tank to tank by the transporter system. For continuous strip deposition, the strip passes through wiping rollers as it emerges from the various processing solutions, such that it is virtually dry prior to immersion in the water rinse tanks, losses are therefore minimal. Drag-out losses are reported by volume process bath to be 0.005 l/m^2 for continuous strip/wire depositions, 0.05 l/m^2 for rack deposition and up to 30 l/m^2 for barrel depositions (OECD 2004, Table 3.1). Depending on the process this may translate to a primary product loss of 5-50 %. However, drag-out ratios are dependent upon the type of plant being operated and are included in the overall efficiency considerations on a material that is used in the process.

Where a direct recirculation of process waters is inappropriate the used or exhausted baths are generally stored in equilibration tanks on-site prior to wastewater pre-treatment. It is assumed that all materials used in the cleaning and rinsing solutions end up in the waste-water and are stored on-site of both, continuous and discontinuous renewal of bath reservoirs, respectively (BREF, 2006).

By means of emission estimates, the SPERCs release factors describe all sub-processes in one.

Depending on the type of the process both, continuous and/or discontinuous emissions may be present, respectively. Table 1 summarizes the main processes with regards to their environmental relevance:

Table 1: Emission sources of individual conversion coating processes

Process	May contain heavy metals	Continuous emissions		Recovery of drag-out possible	Discontinuous emissions / Exchange of baths
		drag-out (dominant type)	over-flow		
Zn- Phosphating	Zn, Mn, Ni	+ (rack)	-	-	-
Chromatic coil coating	Cr(III + VI)	+ (continuous)	+	(+)	+
Electroplating (incl. ECCS)	Several (Cd, Cr, Ag, Au, Cu, Pt, Sn, Zn, Rh, Ni)	+ (rack, barrel)	-	+	-
Anodizing	Light metals, Cr(III + VI)	+ (rack, barrel)	-	+	+
Cold sealing	Ni	+ (rack)	-	-	+
Autocatalytic plating	Ni, Cu	+ (rack, barrel)	-	+	+
Chromating (Chrome Passivation)	Cr(III + VI)	-	-	+	-

Based on the above schematic overview it becomes evident that not all surface treatment processes have similar relevance to emissions into the aquatic environment. Therefore, the environmentally relevant processes are described in more detail below.

3.1 Short description of surface treatment processes with regard to most relevant emission paths of hazardous heavy metals

3.1.1 Zn- Phosphating (Zn, Mn, Ni)

For zinc phosphating, the dipping process is more relevant than spraying even though this generally generates higher losses. In contrast to phosphating of light metal the application to ferrous surfaces produces significant amounts of ferric-phosphate-sludges. During the conversion processes with steel only about 33 % of the product irreversibly binds to the surface of the work-piece, while another 33 % of the product creates sludges that are discarded as chemical waste. The remaining third accumulates as wastewater via carry-over and requires further treatment prior to emission. In the contrast to iron or steel, the phosphating on Zn surfaces give hardly any sludge (Henkel, pers. communication).

This type of conversion coating requires continuous replenishment of consumed material. For the continuous process, immersion baths are generally not replaced in whole (BREF, 2006). Final rinsing may be with deionized water or chemicals based on chemicals like Cr(III) (BREF, 2006, cf. also ch. 3.1.7).

3.1.2 Coil coating (Cr)⁶

This process is highly automatic and continuous while Cr-concentrations during the process need to be constantly maintained. This is typically reached by a continuous overflow and backfill of bath solution. Excess solution can be refilled and back-looped into the process. In addition to the continuous overflow, a carry-over of product may take place. In order to maintain the quality of the operation, the chrome baths need to be completely substituted approximately 4 times a year.

As a consequence of environmental concerns, chromium Cr(VI) is almost absent in the EU. In addition, no-rinse systems have been developed where a precise amount of pretreatment solution is applied uniformly across the strip and then dried in place. Most modern lines are using roller technology with no rinsing after application.

Due to the considerable amount of waste-water produced during traditional coil coating with chrome, there are more and more chrome-free alternatives (e.g. with Zr, Mn or Ti).

3.1.3 Electroplating (Cd, Cr, Ag, Au, Cu, Pt, Sn, Zn, Rh, Ni)

Baths are generally not replaced as a whole because electrolytes can be backfilled once deposited on the workpieces' surface. The optimum concentration of metals is maintained in the solution by frequent additions, often by dosing meters, based on an ampere/hour basis. Because of low rinsing activity, overall environmental emissions of metals by this process are considered low.

3.1.4 Anodizing (Cr, Zn, Al, Mg)

As with electroplating, anodizing baths are not replaced as a whole because electrolytes can be backfilled once deposited on the work pieces' surface. In chromium anodizing, Cr(VI) does not become part of the oxide layer and there is a significant continuous drag-out from the anodizing bath. Complete bath renewals are rare, though. Some, aluminium-rich, anodizing wastes are environmentally valuable and may be used in removing pollutants and settling solids in domestic sewage treatment processes.

3.1.5 Cold sealing of light metals (with Ni)⁷

There are processes using Ni, Co, Cu, Cr or alternatively hazardous heavy metal free solutions (see footnotes below). Cold sealing with Ni²⁺ is exemplarily described here because processes with Cr are rarely used anymore due to environmental concerns. The nickel ions contained in the product precipitate to the porous aluminium surface by a place exchange mechanism without formation of sludges. Although during the process both, continuous and discontinuous losses of the product occur, respectively, the process has the advantage that it causes substantially low environmental pollution. The working life of the product bath is virtually unlimited when run in closed loops⁸, and it therefore does not need to be discarded. Closing the loop for materials for specific process chemistries is readily achievable for processes that require the water returned to the process solution. It has been successfully applied to precious metals, cadmium, barrel nickel plating, copper, nickel and hexavalent

⁶ Note: Coil coating by phosphating of electroplated steel strips with zinc is covered under Zn phosphating conversion coating. Also, the coil coating in which an organic coating is applied on a metal strip in a continuous process (EN-10169-1:1996) is not matter of this SPERC document.

⁷ The traditional sealing processes are "hot sealing" and "steam sealing" in water. Today, these processes are much less in use due to their high energy consumption and a lower performance characteristic. There are also processes free of heavy metals (e.g. using sodium silicate, Zr-acetate, ethanolamine) which are solely controlled by pH and temperature. They are not further considered in this background document.

⁸ "Closed loop" is not zero discharge: there may be small discharges from the treatment processes applied to the process solution and process water circuits (such as from ion exchange regeneration). It may not be possible to keep the loop closed during maintenance periods. Wastes and exhaust gases/vapors will also be produced. There are also likely to be discharges from other parts of the process line, such as rinsing after degreasing or etching.

chromium for decorative rack plating, hexavalent decorative chromium, hexavalent hard chromium, etching copper from PCBs (BREF, 2006). Nevertheless, due to exhaustive usage, the working fluids may be contaminated and need to be exchanged in total on a regular basis.

3.1.6 Autocatalytic plating (Ni, Cu)

Unlike the electroplating process the finishing bath of autocatalytic plating process must be disposed after a certain number of turnovers (typically 6-8; BREF 2006). Autocatalytic coatings commonly generate more waste than other plating techniques. Residual water rinses may result in environmental exposure via the municipal waste-water treatment plants.

3.1.7 Chromating

The chromate solution circulates in closed loops. Used metals can be backfilled and no bath renewal is necessary. Rinses are re-used by counterflows. This is achieved by a combination of cascade rinsing and an evaporator to ensure that the rinsing water is in equilibrium with the evaporation. Ion exchange is used to remove accumulated impurities. Ion exchangers collect the metal cations on the rinsing before evaporation. There are no discharges of Cr(VI) or other materials from the process to waste-water. The regeneration of the ions exchangers is carried out in a hazardous waste treatment centre (BREF, 2006).

4 Application of risk reduction measures

4.1 Introduction to the reduction of heavy metal emission

The best environmental performance is usually achieved by the installation of the best technology and its operation in the most effective and efficient manner (BREF, 2006). In the EU a set of common rules for permitting and controlling industrial installations has been established in the IPPC Directive (2008/1/EC). Therefore, industrial installations generally follow Environmental Management Systems (EMS⁹), a tool that operators can use to plan, manage, control and optimize each process step incl. waste management.

Bath- and treatment solutions are optimized for most efficient use of metal ingredients. BAT is prevention, reduction, re-use, recycling and recovery. Wherever possible exhausted products are replenished, replaced, renewed or recycled on-site by avoiding surplus of waste-waters. With regard to its treatment applications there is a principle difference between electrochemical and chemical processes. In electrochemical procedures the composition of the process solution ideally remains essentially constant. That means that the service life of the process solution of electrochemical processes is theoretically infinite and these surface coating processes are principally suitable for closed loop operations. However, in practice process solutions suffer quality losses by the entry of impurities and formation of interfering substances. In chemical process solutions, on the other hand, reducing agents and other chemicals must be added in salt form constantly, so the service life of these solutions is limited in principle. Closed loop processes are impossible here and the amount of waste waters and sludges is generally higher.

Operationally, there are in principal two main categories of reduction measures for metals:

- i) the reduction of emissions due to process optimization (4.1.1) and
- ii) the reduction of emissions by technical means (4.1.2).

⁹ In the EU, EN ISO 14001 or the EU Ecomanagement and audit scheme EMAS is frequently applied

4.1.1 Process-related emission reductions of metals

The reduction of drag-out is an effective and widely applied primary measure for minimizing losses of chemicals in rinses but also reducing quality and maintenance problems with subsequent processes. Best practice for drag-out reduction is given in BREF (2006). The drag-out can be recycled back into the process by a number of ways (drag-out recovery): If a large number of baths are in use, the concentration may be high enough for the effluent to be fed directly back into the process solution replacing lost chemical. Re-dosing of rinsing solution and subsequent re-use of access overflow waters at a distinct process step may also occur. In other cases, the solution may be concentrated by evaporation before return. Typical return rates of a bath solution to the process solution tanks are dependent upon the metal being processed. Recycling rates ($F_{\text{recycle,process}}$) from process solutions for Zn, Cr, Ni are suggested to reach 1 %, 25 % and 50 %, respectively (OECD 2004, Table 3.16).

While in certain situations, single rinsing operations are necessary to maintain the integrity of the process (e.g. thick film passivation or rinsing between nickel and bright chromium), multiple stage rinsing is particularly suitable to achieve a high rinsing rate with a small amount of rinsing water. In multi-level rinsing technologies (e.g. cascade rinsing), the water flows in the opposite direction to the workpieces. Water quenching (e.g. by squeeze rolls) is another way optimizing the use of waters in coil coating or plating processes. Those waters are typically recycled until they are disposed of when there is too high a build-up of metals.

When using close-loop technologies spent rinse-water is frequently regenerated by ion exchange, reverse osmosis, electro-dialysis or evaporation techniques. In these processes the effluent from the process waters can be concentrated for direct use and/or contained metals can be regenerated (see also 4.2.4). By the introduction of multistage rinsing systems partly combined with a rinsing water recycling system and other techniques a decrease of waste-water of up to 90 % can be obtained. Likewise, achievable recovery rates, e.g. for Nickel plating, are reported by applying appropriate rinsing techniques reaching up to $F_{\text{recycle,process}} > 98 \%$ (BREF 2006).

4.1.2 Treatment techniques for emission reductions of metals

Wastewater from metal finishing industries contains contaminants such as heavy metals, organic substances, cyanides, and suspended solids, at levels which are hazardous to the environment and pose potential health risks to the public. Heavy metals, in particular, are of great concern because of their toxicity to human and other biological life. Therefore, their release must be avoided, or its concentration significantly reduced before discharging the waste-water. Obligatory risk reduction measures are therefore key elements of the SPERCs that determine the environmental release of heavy metals into the environment from industrial surface treatment.

The removal of heavy metals from waste-water occurs in several subsequent steps that may involve physico-chemical, electrochemical and/or biological techniques. The physico-chemical and electrochemical pre-treatments are usually the first steps to significantly reduce the heavy metal load of waste waters. They may consist of the following operations:

- a. chemical transformations to form solid products that are separated in a physical follow-up processes (e.g. chemical precipitation, crystallization, coagulation)
- b. physical elimination processes (e.g. filtration (UF/NF), flocculation, sedimentation, flotation, ion exchange)
- c. electrochemical treatments (e.g. electrolysis, electrocoagulation)

The above treatment techniques are effective and economic for highly concentrated waste-water streams. Each step is performed subsequently and can be combined to suit the local and regulatory requirements. According to BREF (2006) the treatment of the process water can be subdivided into

primary, secondary and tertiary stages (cf. Figure 2). They may either take place in a separate tank (e.g. precipitation and filtration), or in one tank over time (e.g. subsequent (electro-)coagulation and flocculation), respectively. The entire treatment of waste waters typically requires several adjustments of pH as well as the addition of acid, coagulant, lime or caustic, and/or polymeric flocculant. On the other end, large volumes of sludge/waste may be generated which requires disposal and is normally hazardous due to the high concentrations of heavy metals.

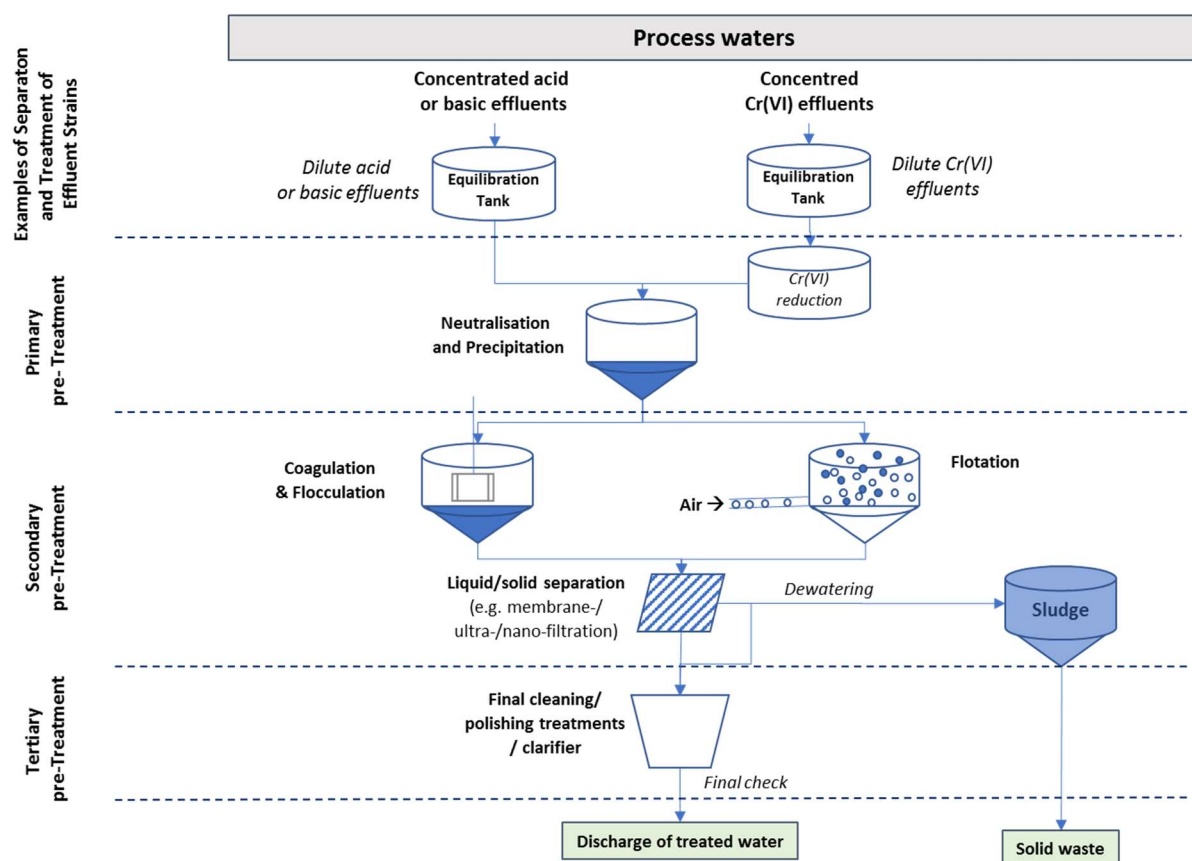


Figure 2. Schematic example of a conventional process water pre-treatment of a surface treatment process based on Cr(VI). In all process steps the pH is a critical factor to control (amended after BREF, 2006, Fig. 2.4).

Because of their ecotoxicity to activated sludge the concentration of heavy metals needs to be reduced below a certain threshold in order to maintain viability of the biological treatment. Inhibiting concentrations of heavy metals in question in an activated sludge treatment are for Cr(VI)³⁺: 10 mg/l, Cu: 1-5 mg/l, Zn: 5-20 mg/l and Ni: 2-10 mg/l (cf. Table 3.115 in Brinkmann et al, 2016).

4.2 Risk reduction measures for heavy metal during surface treatment

Due to its aqueous nature, potential emissions from surface treatment are directed to the water compartment. While some emissions are frequently reported also to air it should be noted that legal requirements generally require exposure reduction with regard to workplace safety, hence, the process tanks are normally equipped with fume extraction to remove mists and any prevent emissions of heavy metals to air. Relevant emissions are therefore only reported to the water compartment in this document.

The processes involved in the removal of heavy metals are described in more detail and their efficiencies for Cr, Ni, Zn and Mn are depicted in the following section (non-exhaustive):

4.2.1 Primary pre-treatment:

The **chemical precipitation** of metals is the most commonly used treatment in industry because it is cheap and easy to control (Fu & Wang, 2011). During the precipitation process chemical reagents react with the heavy metals to form low soluble compounds like carbonates, sulphides, and hydroxides. Multivalent metal ions are most conveniently removed by adding reagents like $\text{Ca}(\text{OH})_2$ to precipitate hydroxides or FeS for sulphide precipitation, the latter with highest removal efficiencies reached. The ultimate process control is done by precipitating metals sequentially (adjusting the pH to its optimum value for the metal). Where this is not possible and economically feasible (e.g. where there are many processes and process baths) separation of different waste-water streams is difficult and metals can be precipitated simultaneously (co-precipitation). Combining the different waste-water streams for precipitation together has the effect that metals with poor precipitation characteristics are precipitated by those metal hydroxides with good precipitation characteristic, so it is possible to reach a better result with joint precipitation.

Sulphide precipitation processes may also include the **anaerobic precipitation treatment**. This technique is especially applicable to all waste-water streams that contain considerable amounts of sulphate (Fu & Wang, 2011, BREF 2016). The process consists of the biological reaction of sulphate or other oxidized sulphur compounds to sulphide by means of sulphate-reducing bacteria; the subsequent reaction of heavy metal ions with sulphide and the precipitation of the heavy metal sulphides; and a final second biological reaction to remove excess sulphide and convert it to sulphur. The process takes advantage of the much lower solubility of metal sulphides compared to their hydroxides and achieves efficiencies of >99%.

The traditional chemical precipitation technique generates mostly hazardous waste (sludge) that requires further treatment.

Crystallization is closely related to precipitation. However, in contrast to precipitation, the precipitate is not formed by a chemical reaction in the waste-water but is produced on seed material such as sand or minerals, working in a fluidized-bed process, e.g. a pellet reactor system. The main purpose of crystallization is the abatement or recovery of heavy metals. Hence, it is a nearly waste-free process.

Reduction of Cr(VI) is relevant for process waters e.g. from chromium plating or Cr(VI) conversion coating. The step is needed because the higher oxidation state is less susceptible for secondary pre-treatment (e.g. flocculation). The reduction of Cr(VI) is chemically performed by supplementing sodium dithionite.

4.2.2 Secondary pre-treatment:

Coagulation and flocculation are used to separate suspended solids from waste-water. They occur in successive steps which are intended to overcome the forces stabilizing the suspended particles, allowing particle collision and growth of floc. Coagulation is carried out by adding coagulants with charges opposite to those of the suspended solids to the waste-water. The process is accompanied by adding coagulating agents (e.g. alum, ferric sulphate, AlCl_3 , others) and coagulation aids (e.g. polymers) to the waste-water. Mixing, pH and contact time are critical factors during this stage. A specific form of coagulation is **Electrocoagulation**, where the release of coagulant is controlled by the electrolytical dissolution of an electrode (e.g. Fe or Al). Electrocoagulation has been found to be a consistent and reliable industrial wastewater treatment process capable of removing heavy metals to levels well below pre-treatment discharge standards (Odongo & McFarland, 2014).

Flocculation is the second step in which gentle mixing aims at increasing the particle size. During flocculation solid particles (or liquid particles such as oil or grease) are combined with air bubbles producing particle/air clusters which float to the surface of a tank and are removed. This occurs in the

presence of inorganic (formed by the coagulant) or added organic polymers. The mixing velocity and energy input are usually the critical parameter of this process. Once the floc has reached the optimum size and strength, the waste-water can be brought to sedimentation, the final step of this process. During these processes rather high amounts of sludges are formed.

When sedimentation is not appropriate, e.g. when the particulates have poor settling characteristics: **Flotation** can be applied. Flotation is a process where solid or liquid particles or particulates are separated from the waste-water phase by attaching to fine gas bubbles, usually air (nitrogen or fuel gas are commonly used in the oil industry). The buoyant particles accumulate at the water surface and are collected with skimmers

Sedimentation is the separation of suspended particles and floating material by gravitational settling is traditionally applied prior to flotation. The settled solids are removed as sludge from the bottom, whereas floated material is skimmed from the water surface. The settled floc or filtrate will contain ca. 5 % solids and is further concentrated by dewatering (BREF 2006).

In wastewater treatment, **filtration** is frequently used as the final separation stage after sedimentation processes or flotation, if low emissions of particulates are wanted, such as separation of floc, heavy metal hydroxides, etc. after sedimentation, etc. However, the various coating and treatment process solutions require continuous or periodic maintenance. "In process" filtration of these solutions is an essential requirement to prolong the life of the treatment baths.

A special filtration technique of waste waters is **Membrane Filtration (MF)** and **Ultra/Nano Filtration (UF)** which is applied when a solid-free waste-water for downstream facilities, e.g. reverse osmosis or the complete removal of hazardous contaminants such as insoluble heavy metals, is desired. The choice between MF and UF depends on the particle size. While membrane filtration is used for waste-water from metal plating to remove fine particles, ultra-filtration is used in the separation of heavy metals after complexation or precipitation. Heavy metal removal efficiencies depend on the characteristics and concentrations of the metals and additives (surfactant and/or complexing agent) used for precipitation and the pH. Ni concentration after treatment by ultrafiltration can be lower than 0.1 mg/l, reaching efficiencies >99 %.

Electrolysis is a process in which an electrical current is applied to a liquid using inert electrodes and an electrical source, resulting in an effective electron transfer in the electrolyte, yielding chemical changes in the composition of the waste-water. It is mainly applied in the metal industry for the purification of rinse waters from pickling tanks or galvanic baths. The applications include recuperation of metals and used electrolytes, detoxication of nitrite and Cr(VI) and silver recuperation from fixing baths in the graphics sector. This technique is also applicable for the treatment of leachate waters containing heavy metals.

Ion exchange is the removal of undesired or hazardous ionic constituents of waste-water and their replacement by more acceptable ions from an ion exchange resin, where they are temporarily retained and afterwards released into a regeneration or backwashing liquid. Ion exchange can be applied to remove principally all unwanted ionic and ionizable species from waste-water, such as heavy metal ions, cationic or anionic, e.g. Cr^{3+} or cadmium and its compounds, with low feed concentrations, CrO_4^{2-} also with high feed concentrations. Typical effluent ion concentrations that can be achieved are in the range of 0.1–10 mg/l with influent concentrations of 10–1,000 mg/l, i.e. efficiencies of >99 % can be reached.

Evaporation techniques can be used instead of classical waste-water treatment by physico-chemical procedures. By the use of vacuum evaporators with vapour compression or infrared evaporators at atmospheric pressure zero water discharge can be achieved from an installation or from certain

process steps. This is only technically possible for small waste-water streams and by the use of a large energy input and high plant investment.

4.2.3 Tertiary pre-treatment:

Tertiary cleaning processes are mainly characterized by equilibrium processes such as settling and clarifier techniques. They therefore demand some incubation time but no specific chemical treatment. During this phase of waste treatment legislative thresholds and exposure limits are tightly controlled by municipal authorities.

4.2.4 Emerging waste water pre-treatment techniques

The above described techniques are state of the art in industrial coating of surfaces with metals. However, this list may not be exhaustive¹⁰.

4.2.5 Municipal sewage treatment

Aerobic biological treatment is the biological oxidation of dissolved organic substances with oxygen using the metabolism of microorganisms. In the presence of dissolved oxygen – injected as air or pure oxygen – the organic compounds are converted (mineralized) into carbon dioxide, water or other metabolites and biomass (i.e. the activated sludge). Metal ions are quantitatively adsorbed or complexed to organic particles to form colloidal particulate fractions that are removed via the sludge. Hence, efficiencies of heavy metal removal are highly dependent on the capacity of the waste water treatment to remove total suspended solids from the effluent (Hargreaves et al, 2017). Removal efficiencies of heavy metals during biological treatment may also be facilitated by microorganisms itself, that may act as bio-adsorbants (Carolin et al. 2017).

4.3 Efficiencies of risk management measures (RMM) for the reduction of metals

The most frequent combinations of the concerned heavy metals of this background document is summarized in the below table 2. The efficiencies of metal surface treatment waste management are generally achieved on-site in a waste water treatment sequence of processes and F_{RMM} is the effective efficiency typically reached by a combination of single RMMs as tabulated in table 2. In addition, RMMs must always be set in place so that they fulfill local regulatory requirements - typically at concentration level - and effluent levels are generally controlled tightly by authorities.

¹⁰ **Collection of other emerging RMMs: Ultrasonic Reactors** can be used for sulphate-rich waste waters are treated using ultrasonic waves to produce almost colloidal precipitate, that initiated effective flocculations by supplementing anionic polyacrylamide to build heavy metal carbamides. With the subsequent clarification step sludge is removed and treated in a filter press and can then be disposed of or reused/recycled. Efficiencies for heavy metals are reported up to 99.7%. **Reverse osmosis** is used in the surface finishing industry for purifying rinse-water and for recovery of chemicals from rinse-waters. It produces water that can be returned in a closed circuit ("closed loop") through a washing process. Reverse osmosis can be utilized in processes such as brass, copper plating, silver, zinc, etc.. Many multi-charged ions can be rejected by reverse osmosis at rates exceeding 99 %. Single charged ions typically have rejection rates in the range of 90 - 96 %. This technique is applicable with diluted water from the majority of processes, with the exception of very oxidized baths (BREF, 2006). **Further techniques** are i.e. supercritical water oxidation, application of new adsorbants, electrodialysis and photocatalysis (Barakat, 2011).

Table 2. Efficiencies of pre-treatment processes (F_{RMM}) for different metals as reported in literature (cf. 4.2.1; 4.2.2; n.r. = not reported). ¹¹

	Cr^a	Cu	Zn^b	Ni	Mn	Ref
Chemical precipitation	87-99.7%	99-100%	99-100%	95%	n.r.	Fu & Wang, 2011 BREF 2016 Carolin et al 2017
Crystallization	n.r.	n.r.	98-99.6%	98-99.6%	n.r.	BREF 2016
Flotation	95%	82%	98%	88-93%	n.r.	Carolin et al 2017
Electrolysis	80-90%	n.r.	n.r.	n.r.	n.r.	BREF 2016
Electrochemical treatment, e.g. Electro-coagulation	100%	98-100%	96-100%	98-100%	78.2%	Fu & Wang, 2011 Akbal & Camcı 2012 Carolin et al 2017
Ion exchange	80-99%	80-99%	80-99%	80-99%	n.r.	Fu & Wang, 2011 BREF 2016 Carolin et al 2017
Ultrafiltration / Nanofiltration	82-100%	97-100%	98-99%	95.1-99.2%	99.6	Fu & Wang, 2011 BREF 2016 Carolin et al 2017
Typical total achievable on-site efficiency (F_{RMM})^c	99%	99%	99%	95%	99%	SPERC relevance

^a Cr(VI) is of higher ecotoxicity than Cr(III). Hexavalent chromium compounds (chromates or dichromate) are difficult to precipitate and are normally reduced to trivalent (chromium (III) ions), which are subsequently precipitated as chromium (III) hydroxide on neutralization. The reduction is made at pH values under 2.5.

^b Note that the formation of sludges, e.g. phosphate sludge during the phosphating process is leading to precipitation and is therefore subsumed in F_{RMM}

^c F_{RMM} is considered as the typical overall efficiency factor reached on-site for a respective metal.

Municipal sewage treatment

This para sets some general considerations on the removal of metals in municipal STPs although not part of the SPERC (i.e. not included in release factors): Total-Cr is effectively abated by biological treatment. No Cr(VI) is expected at the outlet of a biological WWTP as it will readily react and reduced to Cr(III). Cu can often be effectively abated by biological treatment. Zinc and Nickel is to some extent abated by biological treatment, albeit less than copper or chromium. Manganese is of less environmental relevance because it is -comparably to Fe- not very ecotoxic to the environment. Removal efficiencies are therefore difficult to assess in literature.

¹¹ Note: this summary is not exhaustive and may be amended or replaced by other appropriate techniques as introduced in ch. 4.2.

Typical efficiencies of the removal of some heavy metals during biological treatment in municipal STPs are noted in table 3:

Table 3: Typical off-site (e.g. municipal) RMM efficiencies for selected metals, reported for aerobic activated sludge systems (n.r. = not reported).

	Cr	Cu	Zn	Ni	Mn	Ref
Aerobic biological treatment (activated sludge)	>90%	82-90%	50-90%	30-80%	n.r.	BREF 2016, Hargreaves et al 2018*

* mean values

5 SPERC Information sources and justification

The variety of metal surface coating makes it difficult to reduce information to just two SPERC processes. The most important factors influencing variations of use and emission rates are the input substrate (e.g. steel or non-ferrous metal), the form of the workpiece, transport technology during the treatment, cleaning and rinsing technology, coating programs and waste-water pre-treatment technologies (BREF 2006). A good starting point for the determination of use rates and emission factors is the measure per workpiece unit of surface area treated. The justification of information analysis acknowledges the high variation in surface coatings by focusing the release and emission rates on large-scale operations, assuming for the highest absolute emissions and therefore worst-case estimations.

5.1 Justification of use rates

BREF (2006) reported use rates for some metal treatment processes. However, the use amounts are reported heterogeneously across the different techniques and by units. Most commonly the product use relates to the surface area that is treated; others report concentrations of products in use or mass units per tons of treated metal. In order to unify the use amounts for the purpose of the SPERCs they are all converted to realistic use amounts in kg/d, indicative for the respective process (M_{SPERC}).

5.1.1 Considerations of discontinuous bath exchanges on the use rate and RF

As outlined in the chapter 3 and 4 of this background document waste waters may evolve from continuous as well as from discontinuous processes during surface coating (cf. table 1). The overall process efficiency (F_{eff}) considers the amount of applied substances relative to its losses, e.g. via carry-over, sludge formation and/or bath exchanges. Overall, substance efficiencies of several processes are reported in literature for phosphating, Zn-, Ni-, Cu- and Cr-Plating, anodizing, cold sealing and electroplating (BREF, 2006, Table 3.8 and 3.9). In some processes, larger bath volumes are exchanged during a short period and released batch-wise together with continuously generated waste-water. However, because biological WWTP are sensitive to larger hydraulic changes and/or concentration peaks of metals the production of waste-water is typically buffered against short-term (e.g. daily) and long-term (e.g. weekly) variations. For this purpose, equalization tanks are generally put in place, either decentralized at the various production sites or centrally in or near the final WWTP to allow waste-water from batches to be released over a longer time period (equalization). The buffering and retention volumes also allow operators to check the compatibility of the waste-water influent with the subsequent treatment.

Typical bath sizes and release pattern are summarized in table 4:

Table 4: Summary of one-time releases and estimation of correlated additional annual bath volumes released to on-site pre-treatment

Process	Bath size [m ³]	One-time releases per year	Additional bath volume released [m ³ /a]
Phosphating (Zn, Mn, Ni)	<250-75	none	none
Coil coating (Cr(III),Cr(VI))	<5-2	4-12	<60
Electroplating (Cd, Cr, Ag, Au, Pt, Cu, Sn, Zn, Rh, Ni)	<5	none	none
Anodizing (Cr(III), Cr(VI), Zn, Al, Mg)	<20	0.5	<10
Cold sealing (Ni)	<50-20	1	<50
Autocatalytic plating (Ni, Cu) (except closed loop chromating)	<6-1	150*	900

* baths typically last for 2-3 d (large scale) to 2-3weeks (small scale). Conservative assumption at large scale is exchange every second day for 300 working days (OECD 2004).

According to BREF (2006, ch. 3.3.1.1), the retention and/or removal efficiency is independent of the proportion of metal used. Hence, where bath exchanges occur infrequently and/or more than one surface coating processes run in parallel, an average percentage of removal efficiency (not the achievable maximum) will be reached.

From the above there are two important considerations in bath exchanges from metal surface treatment:

- As a typical on-site treatment capacity an additional release of 1-10 m³ wastewater per day can be assumed. This may, however, fluctuate by mass emission. As bath releases represent material losses, they are accounted for in the indicative use rate - M_{SPERC} (cf. 5.1.2 ff).
- Concentrations of released metals in waste-water streams remain stable during bath releases! The releases of discontinuous reservoirs do not lead to significant emission increases by matter of concentrations as baths are typically stored on-site and treated according to local capacities. This fluctuation is therefore irrelevant for considerations of the RF (cf. 5.3).

The daily fraction of metal to waste-water and waste can be derived from the use amount (100 %) via the efficiency of the on-site RMM (F_{RMM}):

5.1.2 Indicative use rates in phosphating

Phosphate coatings typically consist of phosphates of the metal used in the product while partly the corresponding surface metal can be incorporated. The surface weight of layers is typically 0.3 – 5 g/m². They fall into three main types, that form different thicknesses of phosphate layers (OECD, 2004):

- Iron phosphate requires an amorphous coating suitable to a coating film in the order of 300-700 mg/m².
- Zinc phosphate is either lightweight (1.0-4.5 g/m²), medium weight (4.5-10 g/m²) or heavy weight (10-30 g/m²), and
- Manganese phosphate for coatings of 10-30 g/m² (OECD 2004).

As noted in 3.1.1, for the automotive industry the most important processes are: single or tricationic (with the use of Zn, Mn, and/or Ni). All phosphate preparations are usually applied as a liquid concentration between 2-10 % product/l. The calculation of the indicative use amount (M_{SPERC}) is based on steel coatings with reasonable product bath concentrations of up to 5 % (50 g/l). The product

typically consists of about 8 % Zn, 2.5 % Ni and 2 % Mn, respectively. The quantification of M_{SPERC} follows a large-scale production based on a fictitious automotive site serving as a worst-case assumption with regard to use quantities. Data are derived by expert judgement (Henkel, pers. communication):

A large-scale automotive company processes up to 1,000 car bodies by dip coating per day. The surface of one body is conservatively estimated to be 100 m² per default leading to 100,000 m²/d of treated surface. The car bodies are cleaned and conditioned in several treatment steps until they enter the conversion bath that may reach volumes of up to 250 m³. In automotive industries usually a high-quality light phosphate coat is applied. The process consumes up to roughly 6 g product/m². Correspondingly, a use of 0, 6 kg product per body or 600 kg per day on-site can be calculated. Hence, the M_{SPERC} of the metals in this process calculates for Zn: 48 kg/d, Ni: 15 kg/d and Mn: 12 kg/d, respectively. These use rates are indicative and can serve as a realistic worst-case estimation of these metals in an industrial phosphating process (M_{SPERC}). According to BREF (2006, Table 3.8, 3.9) there are different process efficiencies for each metal, 40 % for Zn, 8-16 % for Ni and 21 % for Mn. In practice about a similar part is lost via drag-out and formation of sludges. Therefore, the mass balance for the process leading to M_{SPERC} can be depicted as follows (table 5):

Table 5: Use amounts of metal during large-scale coil phosphating process of car bodies (explanations see text)

	Metal	Surface coating	Drag-out	Sludge	M_{SPERC}
Phosphating	Zn	19.2 kg/d	14.4 kg/d	14.4 kg/d	48 kg/d
	Ni	1.2-2.4 kg/d	6.3-6.9 kg/d	6.3-6.9 kg/d	15 kg/d
	Mn	2.6 kg/d	4.7 kg/d	4.7 kg/d	12 kg/d

5.1.3 Indicative use rates in coil coating

A large industrial coil coating process has been analyzed to determine M_{SPERC} . In this setting, up to 480 m²/min metal bands (double sided) are coated adding up to approximately 500,000 m² of coated metal surface daily (two shifts allowing for maintenance). The process bath (typically 2-5 m³) requires a constant concentration of ca. 0.3 % Cr(VI) to maintain equal quality of the plating. This is achieved by a continuous overflow and backfilling of lost material. While the instant surface coating consumes Cr(VI) the subsequent coating process typically consumes only Cr(III). In total, the coating consumes approximately 50 mg Cr per m². The bath works by continuous overflow allowing a backfill of chromium. In addition, the process can be run in closed loops (CL) that allow for drag-out recovery. In addition to the closed loop process, also no-rinse applications are frequent ("dry-in-place"). In this case the bath is completely used up and no bath renewals are necessary. While typical Cr-concentrations of products are at 10 %, the use of Cr calculates to 230 kg product per day or 25 kg Cr/d at a large-scale operation (500,000 m²/d x 0.05 g/m²).

Being a conversion coating process, the lifetime of the bath is limited especially when process water is backfilled due to accumulation of by-products. According to BREF (2006, Table 8.41), a renewal of the bath is foreseen regularly every 2-8 weeks depending on the chromate type (black, yellow or blue finishing). Taking four weeks as a reasonable worst-case assumption (i.e. 12 exchanges/a), a typical large-scale operation may produce an additional amount of 180 kg Cr per anno (12 x 5 m³ x 0.3 % [Cr]). The depleted bath solution is directed to reservoirs and subsequent water treatment. Typically, up to 1-10 m³ wastewater per day can be treated and released on-site. However, due to the maximum bath size of 5 m³, an additional amount of 3-15 kg [Cr]/d may be added to the indicative daily use amount. Hence, an additional maximum use of 15 kg/d is prognosed resulting in an indicative use rate of M_{SPERC} = 40 kg/d in total for closed loop processes (i.e. coating + bath renewal).

Where closed loops are not possible (n-CL) the drag-out accounts for about 5 ml/m² for continuous strip/wire (OECD, 2004) leading to an additional 2.5 m³/d of process waters at large scale operations (at 500,000 m²/d). According to OECD (2004, Table 3.16), a small degree of recovery of metal occurs also at n-CL processes using techniques such as electrowinning and/or ion exchange, which is reported to be at 25 % for Cr. Due to the lack of continuous back-loop, the bath does not need such a frequent change as for processes with closed loops. The exchange cycles are therefore prolonged to a quarterly basis (i.e. 4 times per year). The M_{SPERC} at n-CL process therefore calculates to an additional chromium consumption of 5.6 kg [Cr]/d for the drag-out and 15 kg/d for the bath exchanges (5 m³ x 0.3 % [Cr]) adding to a M_{SPERC,n-CL} of approx. 31 kg Cr/d (table 6).

Table 6: Use amounts of Cr during large-scale coil coating process (explanations see text)

	Surface coating (25kg Cr/d)		Drag-out	Bath renewal	M _{SPERC}
	Cr(III)	Cr(VI)			
Coil coating (Cl)	25 kg/d	0 kg/d	-	<15 kg/d	<40 kg/d ^a
Coil coating (n-Cl)	23.75 kg/d	1.25 kg/d	5.6 kg/d (mostly CrVI)	<15 kg/d (mostly CrVI)	<45.6 kg/d ^b

^a mostly Cr(III), ^b 21,85 kg/d Cr(VI) + 23,75 kg/d Cr(III)

In contrast, small/medium size industries process up to 100,000 m² per day with a Cr consumption of 5 kg/d (M_{SPERC,CL}) and 6.1 kg Cr/d for processes without closed loops (M_{SPERC,n-CL}). Assuming smaller bath sizes of <2 m³, the M_{SPERC} calculates to 11.1 kg [Cr]/d with closed loop processes and to 12.1 kg [Cr]/d without.

5.1.4 Indicative use rates in electroplating

For electroplating, there were no useful statistics available on metal uses with regard to the corresponding amount of treated surface area. However, BREF (2006) provide an individual analysis of some industrial reference plants in Germany that perform electroplating activities with Zn, Ni, Cu and Cr. Their daily use rates are derived from yearly use amounts divided by the number of working days (300d) and are depicted in table 7. They vary significantly with technology and size of the facility. In addition, the use amount also not always correlate to the treated surface area. Therefore, the 75th percentile of these data has been used to determine an indicative use rate (M_{SPERC}) for this industrial electroplating activities:

Table 7: Reported use values from individual industrial plating plants ("German reference plants" acc. BREF 2006, Annex 8.5).

	Treated Surface [m ²]	Zn [kg/d]	Cr [kg/d]	Ni [kg/d]	Cu [kg/d]
Plant A	54,000	-	-	3.4 ^a	3.6
Plant C	40,000-50,000	-	4.2	36.5 ^a	2.5 ^a
Plant E	63,000	13.7 ^a	7.9	-	-
Plant F	660,000	33.3	2.2	-	-
Plant G	158,000	34.3 ^a	-	-	-
Plant H	200,000	76.9 ^a	29 ^b	0.7 ^b	-
Plant K	n.r.	177 ^a	35 ^b	-	-
Plant L	468,000	173 ^a	0.52	-	-
M _{SPERC} (75 %tile)	200,000	150	18.4	20	3.3

^a anode material, ^b estimated from product use

5.1.5 Indicative use rates in anodizing

The equipment and chemicals used for anodizing are very similar to those used in electroplating. In the anodizing process the metal, usually aluminium, is made the anode in an electrolytic cell, the cathodes are made of lead or aluminium. The applied current oxidizes the metal to its oxide, thus producing an insulating layer. The most frequently applied “sulphuric acid anodizing” (e.g. for decorative, architectural and hard engineering purposes) use generally little¹² or no additional heavy metals. On the contrary, the chromic acid anodizing¹³ use bath concentrations containing typically 45-50 g/l CrO₃ corresponding to approximately 25 g Cr[VI]/l (Chemetall/BASF pers. comm). The thickness of the oxide layer (no Cr[VI]) reached depends on the electrical charge and duration of the workpiece in the bath and range between 4-15 µm for chromic acid anodizing. In the aerospace industry, typical bath sizes reach 1-20 m³ (Chemetall/BASF, pers. communication). There is significant drag-out from the bath to the rinse. The total drag-out is estimated to reach 200 g/m² workpiece. In addition, about 1/3 of the bath volume is replaced about two times a year by fresh bath solutions containing Cr(VI). Depending on the quality of the bath solution a total replacement of the bath is rarely needed and conservatively estimated to occur every second year only.

The estimation of a reasonable M_{SPERC} is based on the above specifications on a large-scale use in the aerospace industry, that treat about 100,000 m² metal surface per year. Hence, about 20 m³ of bath solution will be lost due to drag-out, that corresponds to 500 kg [CrVI]/a. In addition, bath renewal adds to the consumption as follows: assuming a large bath size of 20 m³ and a replacement of 1/3 twice a year (ca.12 m³/a) plus a bi-annual complete bath renewal (i.e. 10m³/a) adds to 22 m³ bath solution or 550 kg [CrVI]/l. In total 1050 kg [CrVI]/a or 3 kg Cr[VI]/d will be used at a large scale facility using chromium for anodizing.

Table 8: Use amounts of Cr(VI) during a large-scale anodizing process (explanations see text)

	Metal	Surface coating	Drag-out	Bath renewal	M _{SPERC}
Anodizing	Cr(VI)	-	<1.4 kg/d	<1.6 kg/d	<3 kg/d

5.1.6 Indicative use rates in cold sealing

For the quantification of M_{SPERC}, a large-scale application of cold sealing has been analyzed based on expert input (pers. communication): A large factory continuously coats up to 800,000 m² metal surface each year, which calculates to ca. 2700 m²/d at 300 working days. Per m² typically 3 g product (i.e. 1 g Ni) is used, which results in a use rate of ca. 8 kg product/d or 2.7 kg [Ni]/d.

Cold sealing is applied in bath sizes ranging from 1m³ (small scale) to 50 m³ (large scale). Medium bath sizes are at 20 m³. According to BREF (2006, Table 8.41) the lifetime of the bath solution of sealing processes can be infinite with a bi-weekly refill cycle. However, due to bath contamination and maintenance and depending on the process a regular exchange of the entire bath may be required once per year (Chemetal/BASF, pers comm). Actual concentrations of nickel used vary, but product concentrations of Ni-salts (e.g. as acetate or fluoride) are typically about 0.5 % of which approximately 1/3 is Ni²⁺ (Hao and Cheng, 2000). Therefore, a complete bath exchange in a large-scale facility (50 m³ x 0.5 % x 1/3) would amount to another 330 kg [Ni] per year for a large-scale operation. Assuming an

¹² A special case is electrocolour anodizing, where the colour is applied using an electrolyte that deposits metal ions like tin, in some cases copper, nickel, cobalt, iron or lead into the pores. A similar technique with nickel, cobalt and copper is used for sealing the pores at low temperature. For the anodizing of bright trim (aluminium chemical brightening), small additions of copper or nickel salts as metal nitrates (1-5 g/l) are used as reaction inhibitors (OECD, 2004). These special processes are considered of low overall relevance for the SPERC document.

¹³ Acc. OECD (2004) phosphoric acid is being investigated as a replacement for chromic acid

additional release of 1-10 m³/d another 1.65-16.5 kg [Ni]/d can be added to an indicative use rate in correlation to a maximum daily emission.

As with all metal treatment processes the drag-out of bath solutions depends on size and shape of the work piece (ch. 3). Typically, there are static drag-out tanks (static water rinses). Together with the waters from a subsequent rinsing steps, which contain low concentrations of those metals in use they are returned to the process tank continuously or periodically and stocked with product (closed loop process). However, taking the generic nature of this SPERC on emission situations to account -for the purpose of this assessment- about 25% of the product is assumed to be lost by drag-out and rinsing of the workpiece leading to emissions. When taking the daily use amount of Ni as a starting point this will result in a continuous loss of approx. 0.7 kg Ni/d (2.7 kg/d / 4). This product loss is accounted for in the M_{SPERC} and, therefore, the indicative (worst case) use amount of Ni in cold sealing on large-scale amounts to 19.9 kg [Ni]/d (table 9).

Table 9: Use amounts of Ni during large-scale coil coating process (explanations see text)

	Metal	Surface coating	Drag-out	Bath renewal	M _{SPERC}
Cold Sealing	Ni	2.7 kg/d	0.7 kg/d	<16.5 kg/d	<19.9 kg/d

5.1.7 Indicative use rates in autocatalytic plating

While a number of metals can be deposited by electroless plating, only Cu and Ni are commercially relevant. Autocatalytic nickel electrolytes are based on sulphates or chlorides with metal contents of approximately 12 g [Ni]/l or 6 g [Cu]/l in the product (OECD 2004, ch. 2.8). While some increase of efficiency and a reduction in waste is reported by the use of electrodialysis the solution lifetime in this process is limited by the build-up of reaction products (BSTSA, 2018). Autocatalytic plating (incl. chromating) requires regular exchange of baths. Because the degree of electrodialysis application remains small, typical use amounts can be derived from reported disposal figures. OECD (2004; Table 3.8) reports typical size of an electroless nickel tank is 200-1000 litres, though tanks up to 6000 litres are in use. The time interval between solution changes varies depending upon the size of the facility. For large scale users, bath renewals may be required at 2-3 day intervals while for smaller scale users changes at intervals of 1-2 weeks may be sufficient. Under the assumption of a static process (i.e. use of max. 3000 l bath/d) a use amount at large-scale operations of <18 kg [Cu]/d or <36 kg [Ni]/d can be calculated as a reasonable worst case M_{SPERC}.

5.1.8 Summary of indicative use rates (M_{SPERC}) of ch. 5.1.1-5.1.7

Table 10: M_{SPERC} of single metals as a result of highest use amounts of different processes in industrial surface coating (worst case M_{SPERC} used is indicated in bold letter)

Process	Metal				
	M _{SPERC} [kg/d] – large-scale				
	Zn	Ni	Cu	Cr(III or VI)	Mn
Phosphating	48	15	-	-	12
Coil coating, closed loop (CL)	-	-	-	<40	-
Coil coating, no closed loop (n-CL)	-	-	-	<45.6	-
Electroplating	150	20	3.3	18.4	-
Anodizing	-	-	-	3	-
Cold sealing	-	19.9	-	-	-
Autocatalytic plating	-	<36	<18	-	-
Effective M_{SPERC}	150	36	18	46	12

5.2 Justification of days emitting

The justification of the emission days is a reasonable worse case assumption of a large industrial site, operating at >300 days a year. The 300 days per year excludes holidays (Sundays) and days for maintenance where operations are stopped or limited.

5.3 Justification of release factors

The justification method applied for deriving the release factors is literature and expert judgement (Reihlen et al., 2016). In this background document best available techniques (BREF 2006) and emission scenario documents (OECD 2004) were analyzed and amended by further literature data and industry expert knowledge from product suppliers. All considerations are based on good management and working practice as well as state of the art process and site design.

General considerations on the derivation of release factors to water, air, soil and wastewater is outlined below (5.3.1.), while process specific considerations are depicted in the respecting subsequent sections (5.3.2).

5.3.1 General considerations on RF in metal surface coating

Release factors to the environment and waste are generally derived from a mass balance of the process where the amount of metal used in a process is 100 % ($F_{use} = 1$; e.g. M_{SPERC}). Equation 1 indicates that the substance use is distributed to the workpiece as a coating material and a fraction emitted:

$$F_{use} = F_{eff} + F_{emm} \quad (\text{eq.1})$$

where:

F_{use}	=	The total metal used in the process (e.g. M_{SPERC}) is set to 1	[-]
F_{eff}	=	Process efficiency factor: metal fraction used in the process for coating	[-]
F_{emm}	=	Emission factor: The metal fraction emitted during the process	

The emitted fraction (F_{emm}) is distributed to different environmental compartments and can be described by individual release factors (RF) to water, air, soil and waste. As outlined in the following chapters (cf. 5.3.1.2 and 5.3.1.3) the releases to air and soil during metal surface treatment can be neglected. Therefore, eq 1 simplifies to:

$$F_{use} = F_{eff} + (RF_{water} + RF_{waste}) \quad (\text{eq.2})$$

The overall efficiencies of the installed RMMs (F_{RMM}) determine the distribution of a metal to water ($1 - F_{RMM}$) and waste (F_{RMM} , cf. table 2), respectively. They can be described as follows:

$$RF_{water} = (F_{use} - F_{eff}) \times (1 - F_{RMM}) \quad (\text{eq. 3})$$

$$RF_{waste} = (F_{use} - F_{eff}) \times F_{RMM} \quad (\text{eq. 4})$$

5.3.1.1 RF_{Water}

In order to calculate releases from metal finishing process it is necessary to know certain characteristics about the metal finishing technologies employed (ch. 3), specific efficiency values (where reported) and/or monitoring data (where available). For some surface coating processes, release factors to water can be found in literature (e.g. for electroplating). In other cases, the release factors to water and waste can be derived from the overall substance efficiency during the process. Where the process efficiency values are available, the release factor to water can be derived acc. to eq 3.

Detailed justifications for the release factors are given in 5.3.5.1-5.3.5.6. A summary of RF_{water} is depicted in table 11:

Table 11: Release factors to water from different surface coating processes after on-site treatment (indicative RF_{water} for metal surface treatment in bold):

		Cr	Cu	Ni	Zn	Mn
Process		%	%	%	%	%
Zn-Phosphating	to waste water	-	-	2.75	0.07	0.25
Coil coating		0.2	-	-	-	-
Electroplating		0.5	0.4	0.05	0.037	-
Anodizing		1	-	-	-	-
Cold sealing		-	-	2	-	-
Autocatalytic plating		-	0.2	0.25	-	-
Highest RF_{water}		1	0.4	2.75	0.07	0.25

5.3.1.2 RF_{Soil}

There is no direct release to soil from surface coating. Solid wastes are disposed of as chemical waste (see below). Therefore, RF_{soil} is set to zero.

5.3.1.3 RF_{Air}

According to BREF (2006) the emissions of metals to air are negligible. Fume extraction for the process tanks may be necessary to remove gases (formaldehyde and others) of which metal ions are not affected. Fumes are collected by an extraction unit and typically scrubbed prior to discharge. Potential emissions to air may also contain acids and therefore be subject to health and safety legislation for the protection of the worker. Their releases may require treatment in order to meet environmental regional and local regulations. As air emissions are considered to be negligible, they are assumed to be zero per default.

5.3.1.4 RF_{Waste}

Generally, the solutions and effluents are discharged into an internal effluent system leading to reservoirs. Some waste process solutions may be stored and disposed of as liquid waste, sent for specialist recycling or recovery or disposed of as hazardous wastes. However, during the treatment of the effluent streams containing metal the dissolved metal ions essentially precipitate as insoluble compounds. Sludge from surface coating is usually classified as hazardous chemical waste. Therefore, heavy metal free alternatives become more and more abundant in surface coating. Where heavy metals are used, the sludge is usually a mixture of metal hydroxides, oxides, phosphates, sulphates, and/or sulphides depending on the precipitating agent used. Wastes that cannot be recovered internally may be valorized externally by third parties. To assist with this, it may be good practice to keep these waste streams separate to maintain a concentration of components that makes recovery

viable or to prevent contamination. Metals in the sludge may be recovered off-site. For any further detail on waste management refer to the respective BREF (2018).

The amount of sludge depends on various processing factors like contamination of the input material, the amount of metal oxides dissolved or eroded from the workpiece/substrate surfaces, discharge of process solution dragged-out by the workpieces/substrate, or the service lifetime of the process solutions. That means that the generation of sludge without internal recycling measures is directly proportional to the drag out and the service lives of the process solutions. Generally, the metal losses by drag out related to the metal input material lies between 5 and 30 % (BREF, 2006). However, there are some chemical conversion processes like Zn-Phosphating, where the fraction of the metals uses reaches roughly 50 % in the sludges (cf. Tab 5). The primary sludge produced has a water content of usually over 95 % and is drained by means of filter presses to about 60 % water content and is disposed of in this form as sludge.

Further to literature reports of on release factors for waste, RF_{waste} can be calculated according to eq. 4 (see above).

A summary of RF_{waste} is depicted in table 12:

Table 12: Release factors to waste from different surface coating processes (indicative RF_{waste} in bold):

		Cr	Cu	Ni	Zn	Mn
Process		%	%	%	%	%
Zn-Phosphating	to waste	-	-	90	60	79
Coil coating		19.8	-	-	-	-
Electroplating		4.5-48.5	4.5-19.5	5-19	5-30	-
Anodizing		99	-	-	-	-
Cold sealing		-	-	38	-	-
Autocatalytic plating		-	5	4.8	-	-
Waste ranges		4.5-99	4.5-19.5	5-90	5-60	79

5.3.2 RF related to individual surface coating processes

Generic in-process efficiencies of surface coating processes are reported by BREF (2006). They range from 8-40% for metal uptake in phosphate corrosion layer via phosphating processes to 95% for coil coating and chromium plating. However, there was a lack of quantitative data and therefore the release factors reported for the purpose of these SPERCs were based on industry expert judgement in addition. Available data of several processes and -in addition to the process efficiencies- include state of the art (good practice) RMMs as outlined in ch. 4 have been summarized per process in the following sections.

5.3.2.1 Phosphating (Zn, Mn, Ni)

According to expert judgement, industrial large-scale phosphating processes such as in the automotive industry consumes a total amount of approximately 180 t product per year that calculates to 600 kg/d (cf. 5.1.1.). During this process the efficiency of metal uptake in the phosphate corrosion layer of the working piece is 40 % for Zn, 8-16 % for Ni and 21 % for Mn, respectively (BREF, 2006; Table 3.8; 3.9). By applying appropriate RMM with corresponding F_{RMM} of 0.99 (Zn), 0.95 (Ni) and 0.99 (Mn) the resulting release amounts to wastewater are 0.6 %, 4.6 % (worst case) and 0.8 % for Zn, Ni and Mn respectively. Correspondingly, the RF_{waste} can be based on the metal distribution in the phosphating process provided by BREF (2006, Table 3.8). Accordingly, the amount of metal leading to sludge production is 53 %, 37 % and 54 % for Zn, Ni and Mn, respectively. Adding the amount of metal that is

retrieved via RMM, RF_{waste} is calculated to ca. 60 %, 90 % and 79 % for Zn, Ni and Mn, respectively. The release factors for wastewater and waste are depicted in tables 11 and 12.

5.3.2.2 Coil coating (Cr)

There is no process efficiency reported in literature for the coil coating. Although emission levels are reported from monitoring for some plants using large-scale coil coating with Cr (BREF, 2006) -at 0.03-1 mg/l for total Cr and 0.001-0.02 mg/l for Cr(VI)- they are useless for the determination of the release factor. Therefore, the information on the coil coating process provided in 5.1.3 was analyzed, taking the open loop process as a worst-case assumption. Therein, of the 31 kg [Cr]/d (M_{SPERC}) that is applied in the process, 25 kg [Cr]/d are used for the coating of the metal surface, resulting in an efficiency of >81 %. Applying equation 3 and 4, the RF_{water} and RF_{waste} for the coil coating process is calculated to be at 0.2 % and 18.8 %, respectively. The data are summarized in tables 11 and 12.

5.3.2.3 Electroplating (Cr, Cu, Zn, Ni)

As outlined in chapter 3.1.4 loss of metals during electroplating is generally small, which is due to rare bath replacements. Rinses are generally re-used by counterflows in such a way that process waters are returned via electrolyte circulation tanks that can be connected to an evaporator. Here, the diluted electrolyte is concentrated, or it is directed to ultrafiltration where the filtrate is returned. In this manner ca 90-99 % of the bath solution is returned the process tank (OECD, 2004; BREF, 2006). Bath sizes are reported to be around 5m³ (OECD 2004). The process can therefore be considered near to a close loop. In this manner, high process efficiencies with respect to input materials are reported by BREF (2006, Table 3.5 and 3.9) and reach max values of 95 % for Zn-, Cu- and Ni-plating, and 96 % for Cr-plating. However, depending on the shape of the work piece reported emission ratios (waste plus wastewater) from electrolytic plating, including electrolytic chromium coating (ECCS) of steel, frequently lead to conservative efficiencies of 80 % for Cu, 81 % for Ni, 70 % for Zn and 52 % for Cr. The thinner the plated chromium layer, the more difficult it is to reach a very good metal efficiency. Therefore, metal efficiency for decorative hexavalent chromium plating are only at ca. 50 %. In small plants without a concentrator and closed loops a drop down to only 20 – 30 % efficiency is reported (BREF, 2006). However, for the purpose of this SPERC background paper large-scale processes are seen with higher environmental relevance.

The release factors of electroplating processes as reported by BREF from the German reference plants are in total at 0.05 % (metals discharged as % of input). The reported factors for individual metals were used as representative release factors to water. They are depicted in table 13. From the reported overall process efficiencies, RF_{water} and RF_{waste} were derived and summarized in tables 11 and 12.

Table 13: Release factors to waste water of German reference plants as of BREF (2006, Table 3.15)

Release factors for single metals in German reference plants		Zn [%]	Cr [%]	Ni [%]	Cu [%]	Overall metals discharged as % of input
	Process Efficiencies [%] (large-scale)	70-95	52-96	81-95	80-95	
Plant A	18-34			0.05	0.05	0.05
Plant C	73-96		0.032	0.008	0.14	0.02
Plant E	80	0.07				0.007
Plant F	83	0.008	0.05			0.01

Plant G	77	0.037				0.037
Plant H	64	0.015				0.015
Plant K	90	zero discharge				
Plant L	72	0.002				0.002
Ranges		0.002-0.037	0.32-0.48	0.008-0.05	0.05-0.14	0.002-0.05
Worst-case RF_{water} [%]		0.037	0.48	0.05	0.4	0.05
Worst-case RF_{waste} [%]^a		5-30	4.5-48.5	5-19	4.5-19.5	4.5-48.5

$$^a \text{RF}_{\text{waste}} = (1 - \text{F}_{\text{eff}}) \times \text{F}_{\text{RMM}}$$

5.3.2.4 Anodizing (Cr)

The major discharges from the anodizing industry are sodium sulphate and aluminium. There will be very minor discharges of other metals from a variety of low concentration sources which are mainly due to drag-out and cleaning processes (OECD, 2004). According to BREF (2006, Table 3.9) an anodizing process efficiency has been reported to be at 90 %. However, as chromium acid is used as an electrolyte only and is not incorporated into the surface layer of the treated workpiece, 100 % of the used chromium is relevant for emission. Therefore, according to equation 3 and 4 the release fraction of the process to water is at 1 % and to waste at ca 99 % (cf. Table 11 and 12).

5.3.2.5 Cold sealing (Ni)

There is no process efficiency reported in literature for the cold sealing. During the cold sealing process on anodized light metals (like aluminium) Ni ions precipitate on the surface forming a layer of different Ni compounds typically at a thickness between 10-25 µm. As outlined in 5.1.3, 2.7 kg/d are used for the sealing process while another 1.8 kg/d are lost due to drag-out and bath refills. Hence, the efficiency of the cold sealing process is calculated to be 60 %.

No sludges are generated during the cold sealing process. The release of process waters to the waste water treatment comprise therefore 40 % of the process waters in total. Therefore, according to equation 3 and 4, the RF_{water} and RF_{waste} can be calculated to be at 2 % and 38 %, respectively. The data are summarized in tables 11 and 12.

5.3.2.6 Autocatalytic plating (Cu, Ni)

The losses due to drag-out in normal use will be small and in many cases so small as to require little or no treatment (OECD, 2004). Waste disposal may occur at the end of the working life of the solution when the solution has to be discarded. Due to its chemical complexity (e.g. use of complexing agents) the degree of process solutions recovery is typically small. Instead, they are stored and disposed of as liquid waste by sending to a specialist for recycling. Where this is not the case the used process baths are treated on-site by state-of-the-art RMMs (cf. ch. 4).

According to BREFF (2006) the efficiency of the use of Ni is at 95 % leading to 5 % of Ni remaining in the used baths, i.e. prior to waste water treatment. Correspondingly the process efficiency for Cu is assumed to be at a similar level. With typical process bath concentrations of 6 g Cu/l or 12 g Ni/l, the used bath may thus still contain up to 1.2 g Cu and/or 0.6 g Ni. When considering state-of-the-art RMM (cf. Table 2), emissions of a large-scale operation lead to an overall release factor to water of 0.2 % for Cu and 0.25 % for Ni. Correspondingly, the RF_{waste} is at <5 % for Cu and Ni (cf. Table 11 and 12).

5.3.3 Derivation of release factors for SPERC

The release factors for the two effective SPERCs on industrial use of Me-salts in surface treatment of metals and plastics have been justified in the above sections and were finally selected as worst-case values from tables 11 and 12. The resulting release factors are tabulated in table 14.

Table 14. Summary of release factors for the SPERCs for industrial use of me-salts in surface coating.

	AISE SPERC 5.1a v.3	AISE SPERC 5.1b v.3
	Industrial use of Me-salts in surface treatment of metals and plastics – Nickel	Industrial use of Me-salts in surface treatment of metals and plastics – Zinc, Chromium, Copper, Manganese
Processes	Phosphating, Electroplating, Cold sealing, Autocatalytic plating	Phosphating, Coil coating, Electroplating, Anodizing, Autocatalytic plating
Release factors	% of amount applied	
To air	0%	0%
To water	5%	1%
To soil	0%	0%
To waste	5 - 90%	5 - 99%

6 Conservatism

The conservatism in the emission estimation of the SPERCs for the industrial use of metals in coating applications is warranted by assuming worst cases in both, the release factors and the use rates. Their conservatism is detailed in section 5.1. and 5.3. Monitoring data on heavy metals (usually composite samples, BREF, 2006) indicate that the amount of single metals discharged as a percentage of the input metals varies between 0.002 and 0.1 % and are therefore well below the conservative assumptions of this SPERC background document.

The conservatism in the release rates is rooted in two causes. First, the worst-case values of the release factors have been selected throughout the process. Second, the analysis uses historic data from literature (BREF, OECD and others) on surface coating applications. Sophisticated process and treatment techniques play an important part in achieving improved environmental performance and with regard to the use of heavy metal minimization of releases. All, energy and raw material savings as well as environmental factors become more and more important driving the development of process efficiency or searching for alternatives. Hence, the M_{SPERC} and release factors used in the SPERCs for the industrial use of metals in surface coating applications reflect technologies that is more than ten years old and are most likely improved with regard to environmental burden today.

Further details of conservatism are:

- Consideration of large-scale operations reveal M_{SPERC} at high level
- Estimations of treated surface at high end
- M_{SPERC} in cold sealing and coil coating assumes open-loop processes, although in many cases this process is run in closed loops.
- For the derivation of RF's worst-case assumptions are followed (e.g. open loop process for coil coating process, lowest reported process efficiencies were taken, in autocatalytic plating the RF is based on 100 % metal used)

Given the need for continuous efficiency gains in industrial processes and the concurrent technological advancement it is fair to assume that surface coating processes and corresponding RMM have become more efficient. This implies that the fractions of heavy metals, that are released to air, water, and waste, have decreased. In conclusion, this also contributes to the conservatism of the emission estimation of the SPERCs for the industrial use of adhesives and sealants.

7 Applicability of SPERCs

7.1 Tiered assessment

Due to the characteristics described above we consider the SPERCs to be suitable for use in standardized, lower tier REACH assessments of the vast majority of their industrial surface coating processes also in lower scales. Their envisaged use is for risk assessors to distinguish trivial substances and emission situations from problematic ones based on standardized emission estimates. Based on this distinction, efforts can be focused on further (higher tier) assessments and refinement of problematic issues.

7.2 Regional assessment

In view that there is very limited regional variation in the industrial use processes of industrial use of metals for surface coating applications, SPERCs may be applicable for emission estimation of similar industrial uses not only in the EU but also in other regions as long as they are associated with similar state-of-the-art RMM as outlined in ch. 4.

8 References

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9 Annexes

Table 15 Indicative emission ratios and efficiencies for some heavy metals from surface coating (F_{eff} = efficiency of metal utilization in the process; F_{RMM} = efficiency of risk management as depicted in ch. 4, n.k. = not known)

Process	Product use at large scale [kg/d]	Metal	Conc in Product ^a	Bath sizes [m ³]	One-time releases per year	M_{SPERC} [kg/d]	F_{eff} [%]	F_{RMM} [%]	RF_{water} [%]	RF_{waste} [%]
Phosphating	600	Zn	8%	75-250	none	48	40	99	0.07 ^b	60
		Ni	2.5%			15	8-16	95	2.75 ^b	90
		Mn	2.5%			15	21	99	0.25 ^b	79
Coil coating	310	Cr	10%	2-5	4-12	31	80	99	0.2	19.8
Electroplating	>80	Cr	<23%	<5	<150	18.4	52	99	0.5	4.5-48.5
	>66	Cu	<5%			3.3	80	99	0.4	4.5-19.5
	>134	Ni	<15%			20	81	95	0.05	5-19
	5000	Zn	<3%			150	70	99	0.037	5-30
Anodizing	>60	Cr	<4%	<20	0.5	3	0	99	1	99
Cold sealing	>13	Ni	<33%	20-50	1	4.5	60	95	2	38
Autocatalytic plating	1500	Cu	1.2%	1-6	none	18	95 ^c	99	0.2	19.8
	6000	Ni	0.6%			36	95 ^c	95	0.25	5

^a where range of metal-concentration is given, the highest concentration has been used as a worst case

^b RF calculation based on mass balance from BREF (2006, Table 3.8)

^c excluding spent baths