## **Effluent Polishing with Selective Ion Exchange Resins**

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Since the 1980s, finishers have relied on numerous treatment processes to meet the discharge limits imposed by regulatory agencies. Typically, these processes use alkaline precipitation and solids separation to reduce the metallic contaminants in the waste stream. In Germany, alkaline precipitation and solids separation are also the predominant processes in wastewater treatment. There, however, effluent polishing systems, incorporating selective ion exchange resins, are extremely popular. This paper describes the chemistry of selective ion exchange resins and the basic design and operation of selective polishing systems. It discusses the popularity of these systems in Germany, contrasts that with the current state of effluent polishing in the U.S., and examines the potential impact of MP&M regulations on this technology in the U.S.

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## Introduction

Since the implementation of federal pretreatment standards in the 1980's, U.S. electroplaters and metal finishers have relied on numerous treatment processes to meet the discharge limits imposed by various regulatory agencies. Typically, these processes combine precipitation and solids separation to reduce metallic contaminants. In Germany, precipitation/solids separation techniques also predominate. In contrast to the US, however, one sees significant numbers of effluent polishers, incorporating selective ion exchange resins, in Germany's surfacing finishing industry.

This paper describes the chemistry of selective ion exchange resins and the basic design/operation of selective polishing systems. It discusses the popularity of these systems in Germany, contrasts that with the current state of effluent polishing in the U.S., and examines the potential impact of MP&M regulations on this technology in the United States.

## **Effluent** polishing

Generally, an effluent polisher is a filtration device placed downstream of conventional neutralization/ solids separation equipment. Its role is to remove or "polish" metallic contaminants that pass through the primary system. In its simplest form, an effluent polisher is a mechanical filter designed to remove suspended solids entrained in clarifier overflow. The type of filter varies, depending on the volume of wastewater and the concentration of suspended solids. It can range from a simple cartridge filter to an automated microfiltration system. Well-designed systems do a good job of removing suspended matter, but typically do not reduce the concentration of soluble contaminants in the influent.

In an effort to remove both suspended solids and soluble contaminants, equipment suppliers and chemical vendors formulate "proprietary" filter media. These products generally have reasonable filtration characteristics and a measurable affinity for soluble metals. The products are often combined with various filters and sold as effluent polishing "systems". These products typically contain some type of adsorbant (activated carbon) and a filter aid (diatomaeous earth). Most have relatively low capacities for soluble metals and are usually non-regenerable.

In contrast, ion exchange resins offer relatively high capacity and can be regenerated. As a result, effluent polishing systems incorporating ion exchange resins typically provide higher throughputs and generate significantly less hazardous waste than most "proprietary" mixed media polishing filters.

## Selective ion exchange resins and their use in effluent polishing

Ion exchange resins are well known in the water treatment field. The most common are copolymers of polystyrene and divinylbenzene that have been functionalized with sulfonic acid (cationic exchangers) or substituted amines (anionic exchangers).

Although soluble metal ions are often combined with other chemicals in metal finishing streams, they typically react as cations in conjunction with ion exchangers. As a result, most ion exchange effluent polishers contain cationic resins. There are two basic types:

- 1.) Strong acid cation resins (SACs): copolymers functionalized with strongly acidic groups (sulfonic acid). These resins are relatively non-selective (see Table I). This lack of selectivity reduces the capacity of the SAC for heavy metals, particularly in pretreated high salinity waste streams.
- 2.) Weak acid cation resins (WACs): polymers or copolymers with weakly acidic functional groups. In comparison to SACs, these resins are more selective for multivalent cations. Through the years, resin

manufacturers have developed a number of WACs with different functional groups. Each functional group provides a different selectivity (see Table I).

1 4010	1. Selectivity of 10th Excitatinge Results	
Functional Group	Selectivity Sequence	Lewatit Type
<ol> <li>Cation Exchanger</li> <li>Strongly acidic R-SO<sub>3</sub>H</li> </ol>	$\begin{array}{l} Ba^{2+} > Pb^{2+} > Sr^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Co^{2+} \\ > Zn^{2+} > Fe^{2+} > Mg^{2+} > Mn^{2+} > Alkalis \end{array}$	SP 112, S 100
1.2 Weakly acidic R-COOH	$\begin{array}{l} Cu^{2+}\!>\!Pb^{2+}\!>\!Fe^{2+}\!>\!Zn^{2+}\!>Ni^{2+}\!>Cd^{2+}\!>Ca^{2+}\!>\\ Mg^{2+}\!>\!Sr^{2+}\!>Ba^{2+}\!>Alkalis \end{array}$	CNP 80
<ul> <li>2. Chelating Resins CH<sub>2</sub>COONa</li> <li>2.1 R-CH<sub>2</sub>-N CH<sub>2</sub>COOH Iminodiacatic acid O</li> </ul>	$\begin{array}{l} Cu^{2+} > Hg^{2+} > Pb^{2+} > Ni^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+} > Fe^{2+} \\ > Mn^{2+} > Ca^{2+} > Mg^{2+} > Sr^{2+} > Ba^{2+} > Alkalis \end{array}$	TP 207, TP 208
ONa 2.2 R-CH <sub>2</sub> -NH-CH <sub>2</sub> -P ONa Amino methylphosphonic	$\begin{array}{l} Pb^{2+}\!\!>\!Cu^{2+}\!>\!Zn^{2+}\!>Ni^{2+}\!>Cd^{2+}\!>Co^{2+}\!>Ca^{2+}\!>Mg^{2+}\\ >Sr^{2+}\!>Ba^{2+}\!>Alkalis \end{array}$	VP OC 1060
S 2.3 R-CH <sub>2</sub> -NH-C NH <sub>2</sub> Thiourea	$Hg^{2+} > Au^{1+/3+} > Pd^{2+} > Pt^{2+/4+} > Ir^{3+} > Os^{4+} > Rh^{3+}$ (noble metals are fixed both as cation and anion complexes)	TP 214
3. Anion exchanger Weakly basic H		MP 62, MP 64
+ $CH_3$ K-CH <sub>2</sub> -N CH <sub>3</sub> Strongly basic + CH <sub>3</sub> R-CH <sub>2</sub> -NCH <sub>3</sub> CH <sub>3</sub>	$\begin{array}{l} ClO_4^- > Me(CN) > PGM^* > Chlorocomplexes > \Gamma > \\ CrO_4^{2^-} > NO_3^- > Br^- > HSO_4^- > C\Gamma > H_2PO_4^- > F^- > \\ CN^- > H_2BO_3^- > HCO_3^- > HSiO_3^- \end{array}$ $\begin{array}{l} The weak anions CN^-, H_2BO_3^-, HCO_3^-, HSiO_3^- \\ are only fixed by strongly basic anion exchange resins \end{array}$	M 500, MP 500
	*Platinum group metals	

Table I: Selectivity of Ion Exchange Resins

In addition to selectivity, some WAC's, unlike SACs, have strong chelating character. As a result, many can exchange metallic cations in the presence of strong complexing agents. Many ion exchange technicians place "special WACs" in an entirely different category and call them "chelating resins".

The iminodiacetate (IDA) functional 'chelating resin" has found a niche in effluent polishing. It is without question the most popular selective resin type for this application. The IDA type resin demonstrates a high degree of selectivity and strong chelating functionality. Unlike other 'chelating resins'', however, it offers efficient regeneration characteristics. This combination of high selectivity, strong chelating character, and true regenerability results in a polishing media with very desirable characteristics: high throughput, low effluent metal residuals, and minimal hazardous waste generation.

### **Selective Polishing in Germany**

Geographically, Germany is relatively small, but highly industrialized and densely populated. As a result, it has limited natural resources, public water supplies and space. In response to these limitations, the application of ion exchange resins developed rapidly in Germany in the 1930's and 40's, particularly in the field of resource recovery.<sup>\*</sup> In the 1960's, the technology broadened to include the recovery of metals and rinse waters with conventional, strongly dissociated resins. With the advent of IDA resins in the late 60's, "end-of-pipe" selective polishers were successfully introduced to the German metal finishing industry in 1972.<sup>\*\*</sup>

The ion exchange applications department at Bayer AG in Leverkusen, Germany has over thirty years of experience in the application of Lewatit TP-207, an IDA-type resin. Much of this work has focused on effluent polishing and the effect of common complexing agents on heavy metal exchange (see Table 2). This work, combined with that of qualified equipment manufacturers/consultants, led to the installation of IDA resin-based selective polishing systems in the majority of metal finishing facilities in Germany.

		1	<b>J</b>	2	
	Cu	Ni	Zn	Cd	Pb
Cyanides	/	/	/	+	+
Multivalent carboxylic acids					
-oxalic acid	+	+	+	+	+
-tartaric acid	+	+	+	+	+
-citric acid	+	+	+	+	+
-gluconic acid	+	+	+	+	+
-glucoronic acid	+	+	+	+	+
Amino carboxyalic acids					
-glycine	+	+	+	+	+
-NTA	(+)	/	(+)	(+)	(+)
-EDTA	/	/	/	/	/
Ammonia	+	+	+	+	
Aliphatic amines					
-ethylene diamine	+	+	+	+	+
-diethylene triamine	+	+	+	+	+
-triethanolamine	+	+	+	+	+
Hydroxyalkyl amines <sup>1</sup>	+	+	+	+	
Alkyl phosphonic acids <sup>2</sup>	(+)	+	+	+	
Organosulphides <sup>3</sup>	/	/	/	/	/

# Table 2:Lewatit TP 207Effect of Chelating Agents on Adsorption of Heavy Metals

+ Adsorption of metal ion in presence of the chelating agent

(+) Limited adsorption

/ No adsorption

-- Not tested

1. Known e.g. under the trademark "Quadrol" and "Pluriol"

2. Known e.g. under the trademark "Turbinal"

3. Known e.g. under the trademark "TMT 15" (Trimercaptotriazine) and "Plexon 1105" (Diethyldithiocarbamate)

<sup>&</sup>lt;sup>\*</sup>Dorfner. Konrad (Editor), Ion Exchangers, Walter de Gruyter Berlin. New York, NY 1991 pg. 13 -15

<sup>\*\*</sup> Applications Bulletin, "Lewatit Selective Ion Exchangers", Bayer AG. Leverkusen, Germany.

The current acceptance level of polishers in metal finishing waste treatment facilities is quite high. It is estimated that over 60% of the metal finishing facilities incorporate "end-of-pipe" selective polishers in their treatment trains.<sup>\*</sup> The driving force behind this high percentage is regulatory pressure.

Table 3 summarizes the current pretreatment discharge levels and those in place prior to 1990 in Germany. There is little doubt that the revised requirements drove a number of facilities to upgrade their conventional precipitation system. With most of the individual values between 0.1 and 0.5 ppm, it is easy to see why selective polishers were added at the end of the pipe.

Most recently, the Rhenish-Westphalian Institute for Water Research found Lewatit TP-207 suitable for removing trace residuals of Ni from the drinking water supplies in Germany. Residual concentrations of < 20 ppb are required.<sup>\*\*</sup>

	Germany Current Values <sup>1</sup> ppm	Germany Previous Values <sup>2</sup> ppm	US Current Values <sup>3</sup> ppm	US Proposed Values ppm
Copper	0.5	2	3.38	0.57
Nickel	0.5	3	3.98	0.64
Zinc	2	5	2.61	0.17
Cadmium	0.2	0.5	0.11	0.09
Lead	0.5	2	0.69	0.09
Chromium	0.6	3.5	2.77	0.55
Silver	0.1	2	0.43	0.06
Cyanide	0.2	1	1.2	0.13

Table 3:Regulations for Metal Finishing EffluentsMinimum requirements on the discharge of toxic substances into surface and municipal waters

1 Values valid for the Federal Republic of Germany 1990 onwards

2 Values valid for the Federal Republic of Germany up to January 1, 1990

3 Source: 40 CFR 433 (48 FR 32485; July 15, 1983).

4 Source: Federal Register, Vol. 66, No.2, January 3, 2001

#### Selective polisher design and operation

A typical effluent polisher installed at the end of a conventional waste treatment system is shown in Figure 1.

The pH of the overflow from the clarifier is typically reduced. A pH of <7 minimizes the precipitation of CaCO<sub>3</sub> in line neutralized influents and reduces the presence of colloidal metal hydroxides. Adsorption of heavy metals in the presence of complexing agents is also improved. At lower pH's, most stability constant (pK stab) values are reduced. As a result, these complexes are adsorbed more easily on the resin.

Although ion exchangers are excellent filters, the resins are expensive and difficult to backwash in comparison to conventional sand/gravel media. Therefore, a prefilter is recommended to remove the

<sup>&</sup>lt;sup>\*</sup> Technical Discussion, H. Heiko Hoffmann, Applications Specialist, Bayer AG (retired). Leverkusen. Germany.

<sup>&</sup>lt;sup>\*\*</sup>Aquatech 2000. Stetter, Dieter, *Pilot-scale Studies on the Removal of Trace Metal Contaminants in Drinking Water*.

majority of the suspended solids carried over from the clarifier. The type of prefilter is dependent on the size of the system.

The design of the ion exchange vessels also varies with the size of the system. Often, the units are wound fiberglass pressure vessels with plastic internals. Rubber-lined steel vessels are also common. Two columns, placed in series, are recommended. The first column provides primary service and does most of the polishing. The second column polishes the effluent from the first unit and acts as the sole exchanger when the primary vessel is regenerated. The freshly regenerated unit is then placed in service at the end of the train. Single column systems are not recommended. Inconsistent effluent quality and expensive on-line monitoring limit their use. Three column systems ("merry-go-round's") offer superior performance. This configuration is also operated serially. Two columns are always on-line in this configuration, a significant advantage.

Downflow service and cocurrent regeneration are recommended. Vessels should be only half-filled to permit vigorous backwashing. "Packed bed" systems incorporating counter-current regeneration are more efficient. Their use is encouraged in recovery and demineralizing applications. In effluent polishing applications, however, the variability of most waste streams is such that "ruggedness" is more important than efficient regenerant consumption. In reality, the actual loading is minimal. As a result, the inherent inefficiency of a conventional co-current system is not a significant factor.

Selective resins have relatively poor kinetic characteristics in comparison to conventional ion exchange resins. Service flow rates from 10-20 bed volumes (BV) / hour (1.25-2.5 gpm/ft<sup>3</sup>) are recommended with 4 foot minimum bed depths. In most ion exchange applications, regeneration frequency is dependent on the influent concentration and hydraulic load. Polishers, however, are typically regenerated prior to breakthrough on a timed basis. It is recommended that "working" units be regenerated at least twice per month. Routine regeneration is necessary to maintain optimal flow characteristics and to minimize bacterial and/or chemical fouling.





The resins are regenerated with a dilute solution of hydrochloric or sulfuric acid. To minimize calcium sulfate precipitation, hydrochloric acid is preferred. After acid regeneration and rinsing, selective resins often must be partially or completely converted to a salt form; typically the sodium form. The resin is converted to the sodium form by passing a dilute solution of sodium hydroxide through the resin bed. Since selective resins swell dramatically from the acid to sodium form, it is recommended that conversion take place in an upflow direction. This significantly reduces resin attrition by permitting the resin to swell freely. The degree of conversion can be varied from 50-100% of the theoretical capacity, depending on the characteristics of the influent and the desired effluent pH. If 50% conversion is indicated, the entire resin bed must be thoroughly mixed prior to service. The ability to air mix the resin bed is desirable even if the resin is completely converted. Air mixing can be very useful if the bed requires rigorous cleaning.

Regeneration/conversion schedules vary significantly from manufacturer to manufacturer and from application to application. For example, conversion to the calcium form with dilute lime slurry may provide significant advantages in comparison to sodium hydroxide. Reputable equipment manufacturers can determine which schedule is appropriate for a particular application and should be consulted. Additional information on regeneration and conversion is also available in the literature.

## **Performance limitations**

Selective resin effluent polishers have distinct advantages in comparison to other systems. The application of IDA resins in these systems, however, has its limitations.

- 1. High concentrations of fats and oils, such as those found in alkaline cleaning solutions, coat the resin beads and impair performance.
- 2. Some anionic complexes cannot be broken with IDA resins (see Table 2). EDTA and most cyanide complexes are notable. These complexes pass directly through the resin bed.
- 3. Lead and trivalent chromium are not efficiently removed from IDA resins with conventional regeneration schedules.Modified regeneration schemes must be used periodically to extract these cations.
- 4. Strong oxidizing agents (like  $S_2O_8$ ,  $H_2O_2$ ), particularly in the presence of heavy metals, adversely affect the functionality of IDA resins.
- 5. Sulfide-based pretreatment chemistries are not compatible with selective effluent polishing systems. Colloidal precipitatescommonly associated with these chemistries are not removed and the residual precipitating compounds affect effluent quality.

Residual metal concentrations of <0.1 ppm are obtainable with dual column polishers, but the listed limitations and other factors significantly influence performance. Equipment manufacturers with extensive wastewater treatment experience can identify potential problems, optimize pretreatment chemistries, and reasonably predict performance for a given application. Treatability evaluation is recommended.

## Selective polishing in North America

It is clear that selective effluent polishing has made its mark in Germany. In the U.S., these systems barely penetrate the wastewater treatment market. Clearly the most significant difference relates to regulatory requirements. Table 3 lists Federal pretreatment standards for metal finishers. In comparison to German standards, the U.S. requirements are significantly less stringent. As a result, many facilities find that local POTW limits can be met with existing equipment, at least periodically. A second reason relates to historical differences in the two countries' technology approaches for trace level treatment.

In the 1970's, a number of US studies looked at sulfide precipitation as an alternative to conventional neutralization and clarification. As a result, a number of inorganic and organic sulfide-based systems gained reasonable commercial success. These systems were installed in both stand-alone and polishing applications and promised superior effluent quality and sludge reduction. In most cases, these systems did provide better effluent quality. In Germany, however, these systems never found broad acceptance. These systems usually require an excess of chemical to insure complete precipitation. This excess is typically toxic to aquatic organisms. As a result, these residuals must be eliminated prior to discharge, at least in Germany. Proportional chemical feed requires expensive monitoring and metering equipment to work effectively. Selective ion exchange systems provided an inexpensive alternative to meet discharge limits and to handle the variability of the incoming metal load. Given the current differences in discharge regulations and treatment technology histories, can selective effluent polishers find a place in the US water treatment market?

Metal finishers with direct discharges can add "end-of-pipe" polishers if they cannot consistently meet their more stringent permit requirements. Indirect dischargers with conventional systems can also improve regulatory performance if consistency has been a historical problem. In some areas of the country, indirect

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discharge limits have already exceeded the performance capabilities of conventional neutralization equipment. In California's Bay Area, IDA systems are installed to help meet local pretreatment discharge limits for nickel that exceed those of the German government. Copper limits in this area are also quite low. For these applications, German installations are a model for effluent compliance.

In addition to effluent compliance, many U.S. manufacturers are interested in recycling water. Conventional ion exchange can certainly be used. For "end-of-pipe" recycling, however, reverse osmosis is more applicable due to the high TDS. Recovery rates are usually <80%. This > 20% reject stream can often be processed through a selective exchanger and discharged. Another compelling argument for selective polishing is not related to effluent quality.

Many large and small metal finishing facilities use aluminum and iron salts, with two-stage pH adjustment, to co-precipitate complexed metals. Typically, these salts are added in large excess to remove residual concentrations of a few ppm not precipitated during pH adjustment. Often, co-precipitant concentrations are an order of magnitude higher than the targeted residual metals. Selective polishing systems offer the potential to significantly reduce the required dose of co-precipitants in conventional systems. Reduction is obviously realized in co-precipitant chemical feed, but that is insignificant in comparison to reduction in hazardous waste generation.

In this application, the residual complexed metals are not co-precipitated. They pass through the primary system and are removed by the selective polisher. The exchanged metals are eluted with acid and the regenerated resin is converted with alkali. The used acid and alkali are stored and slowly metered to the front of the system. This bleed of spent regenerant can improve the performance of the primary system.

Many wastewater treatment systems experience swings in influent composition. Often, a controlled bleed of spent acid equalizes the metal load and provides a seed for precipitation. The spent regenerant acts similarly and provides a reasonably constant source of metal ions. Any excess caustic from the conversion is used for pH adjustment. If on-site regeneration is not practical, alternatives are available. The centralized treatment market is growing in the U.S. A number of companies provide centralized treatment services similar to service deionizing operations. Simple cartridges are charged with selective resin and placed in-service. They are essentially selective polishers regenerated off-site.

It is clear that numerous selective polishing applications exist in the US, even with most discharge limits in the 1-5 ppm range. Applications experience and knowledge of the waste stream are required to obtain acceptable results. Reputable engineering / equipment manufacturers have this experience and knowledge. Treatability is recommended to gain additional knowledge of the stream and to optimize the usefulness of the polishing system.

## Selective Polishing and MP&M

Proposed M P & M effluent limitations were published in January 2001. Table 3 lists average daily limits for various M P & M subgroups for selected parameters. Figure 2 compares these values with existing U.S. and German pretreatment standards. The proposed values are quite similar to those currently enforced in Germany and are significantly lower than the existing U.S. standards, particularly for copper, nickel, and chromium. Given the history of selective ion exchange polishing in Germany and the similarities in the current German and proposed MP&M limits, it is reasonable to suggest that the selective polisher will be an effective tool at facilities subject to these limits in the future.

Since their publication, significant debate on the feasibility and impact of the proposed rules has passed and will continue. Regardless of the final rule and/or the definition of best available or best practical technology, it is simply important to recognize that selective polishers typically improve the quality and consistency of the treated effluent.



## Summary

It is estimated that over 60% of the metal finishing operations in Germany use selective ion exchange polishing. The German government reduced heavy metal discharge limits to sub-ppm levels and drove the installation of these systems. Less regulatory pressure and other factors have limited the historical use of these systems in the US. Given the proposed sub-ppm MP&M limits, selective ion exchange polishing provides a proven treatment technology for U.S. manufacturers looking to meet these requirements.

Regardless of the final form of the proposed regulations, other opportunities exist for selective polishers, ranging from RO reject treatment systems to sludge reduction projects in conventional co-precipitation systems. Selective polishers offer significant advantages, but also have limitations. Applications should be evaluated with the help of experienced engineering/equipment and/or service suppliers. Treatability testing is often recommended to better understand the limitations of the waste stream and to optimize the advantages of the selective polisher.