REMOVAL OF HARMFUL METALS
FROM METAL PLATING WASTE WATERS
USING SELECTIVE ION EXCHANGERS

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Academic dissertation

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Abstract

Environmental constraints have forced the metal plating industry to reduce their emissions to water systems, otherwise mass usage of metals could cause severe environmental problems. Conventional waste water cleaning technology does not meet all the new regulations for releases from surface finishing plants. There is thus a need for new, more effective methods. Selective ion exchange offers a good solution for cleaning many waste streams. The aim of this work was to study and develop selective ion exchange materials for effective and economical applications in waste water treatment in the metal finishing industry.

The research was focused on waste effluents produced in water-consuming rinsing operations, and the metals of interest were chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), and cadmium (Cd). The performance of 49 ion exchangers and sorbents was determined by studying their ion exchange equilibria. The batch method with rapid tracer technique was first used to evaluate large group of ion exchangers and sorbents in order to select the best sorbents for waste treatment. Then the batch method was used to determine the equilibrium data of the selected sorbents. Column mode experiments were used to test the selected sorbents with real waste solutions.

The best selective ion exchangers were iminodiacetate and aminophosphonate resins, and the fibrous polyfunctional exchanger with imidatsoline/carboxyl functionalities. Other exchangers of interest were oxine resin, zeolites A, X, L, and ferrierite and inorganic sodium titanate. Compared to conventional cleaning methods exchangers exhibited a more effective performance with low metal concentration solutions, in column tests exchangers removed 99.9% of the nickel and 99.5% of the zinc in solution. The main equilibrium parameters affecting the ion exchange were pH value, concentration of complexing ligands and concentration of competing counter ions. Commercially available exchangers can be used for purification of metal plating wastes, especially in applications where metal concentrations are low e.g. rinse waters or end of pipe polishing. With ion exchange technology it is possible to reach the most strict limits for the emissions and ion exchangers can be utilised as a supporting system for conventional purification technology

Preface

This work was carried out at the Laboratory of Radiochemistry between 1991-1999. Since 1978 in the Laboratory of Radiochemistry has been a working research group for solidification of liquid nuclear wastes. From the very beginning the main research area has been the separation of radionuclides with ion exchangers. Successful R&D work with inorganic ion exchangers led to industrial applications at several nuclear plants all over the world. From the beginning of 1990's, the knowledge and skills obtained in the field of nuclear waste purification were applied to new research in the area of the removal of toxic metals from metallurgical waste effluents.

I wish to express my warmest gratitude to Dr. Jukka Lehto for his guidance, support and forbearance during the past years of research. I am also grateful to Professor Timo Jaakkola for his encouragement in this study.

I would like to thank all my colleagues at the Laboratory of Radiochemistry and especially the members of the ion exchange research group for their help. I wish to thank Donald Smart for revising the language of this thesis and I owe many thanks to Jyrki Vähätalo and Kimmo Suominen for the inspiration they gave me at the very beginning of my scientific career.

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I.   Leinonen H., Lehto J. and Mäkelä A., Purification of nickel and zinc from waste waters of metal plating plants by ion exchange, *Reactive Polymers* 23(1994)221.

II.   Lehto J., Laurila T., Leinonen H. and Koivula R., Separation of Chromium with a Fibrous Ion Exchanger, *Progress in lon Exchange - Advances and Applications, Eds. A. Dyer, M.J.Hudson and P.A.Williams,* The Royal Society of Chemistry, 1997, p. 372.

III.   Lehto J., Vaaramaa K. and Leinonen H., lon Exchange of Zinc on an aminophosphonate-chelating resin, *Reactive & Functional Polymers*, 33(1997)13.

IV.   Leinonen H. and Lehto J., Ion exchange of nickel by iminodiacetic acid chelating resin Chelex 100, *Reactive & Functional Polymers*, 43(2000) in press.

V.   Leinonen H. and Lehto J., Purification of metal finishing waste waters with zeolites and activated carbons, submitted to *Waste Management & Research*.

VI.   Lehto J., Leinonen, H., Koivula R., Yli-Pentti, A. & Karppinen, T., Removal of Toxic Heavy Metals from Metallurgical Waste Effluents with Chelating Ion Exchange Resins. *In proceedings of Global Symposium on Recycling, Waste Treatment and Clean Technology- REWAS'99 , San Sebastian, Spain, 5th-9th September 1999. Eds. I.Gaballah, J.Hanger and R.Solozabal,* The Minerals, Metals & Materials Society and Fundación Inasmet, 1999, Vol III, p.2449.

In the text these will be referred to by their Roman numerals.

1. Introduction

Mankind has used metals for several millenniums and in our day the mass usage of metals is accepted as an inalienable fact. Metals do have a fundamental weakness, bulk usage of metals causes environmental damage. Thus there have been demands for the use of alternative materials. However, there is much scope to make environmental improvements to the production and use of metals (Anthony 1993/94). The hydrometallurgic industry produces many types of waste streams. Increasing costs and stricter regulations require more effective methods for cleaning these wastes. One of the most important tasks is the removal or recovery non-ferrous metals from effluents. The effective recovery of these metals is possible only if the separation process is selective enough. Selective ion exchangers can be used for reducing the amount of metal wastes; They can be used for purification of process liquids for re-use and for the treatment of final waste waters. Especially in small scale industries operating in communal areas there is the need to find easy and reliable methods for waste treatment. When waste effluents are released through a sewerage system to municipal sewage disposal plants the metal releases accumulate in the sludge which limits the profitable use of the sludge as a fertiliser or land filling material. This is important especially in countries whose populations are so dense that there are problems with the end use of sludge or ash made from sludge.

The aim of this work was to study and develop effective and economical applications for waste water treatment in the metal finishing industry. The research was focused on waste effluents produced in water consuming rinsing operations, and the metals of interest are chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), and cadmium (Cd). We will start this thesis with a short review of the literature of waste water management in the plating industry followed by a review of ion exchangers and their basic properties concerning selectivity. The thesis thus has three sections, i. e., the review section, an experimental and results section, the latter also including articles I-VI, and finally a section which contains a discussion of the significance of the results.

2. The metal plating industry

The purpose of metal plating is to coat a metal object with a metal to protect the object from corrosion and wear, or decorate the object. A typical plated product is an iron bolt, first covered with zinc plate and the zinc surface is covered with chromium plate (Figure 1). Zinc plate prevents corrosion in two ways: mechanically and chemically, chromium plate passivates the zinc surface and prevents oxidation. In general hydrometallurgic metal plating involves one or more of the following main operations:

1. Stripping
2. Pre-treatment e. g. cleaning and pickling
3. Electrolytic or chemical deposition of metals
4. Post plating treatment e.g. chromating
5. Phosphating
6. Anodising of aluminium
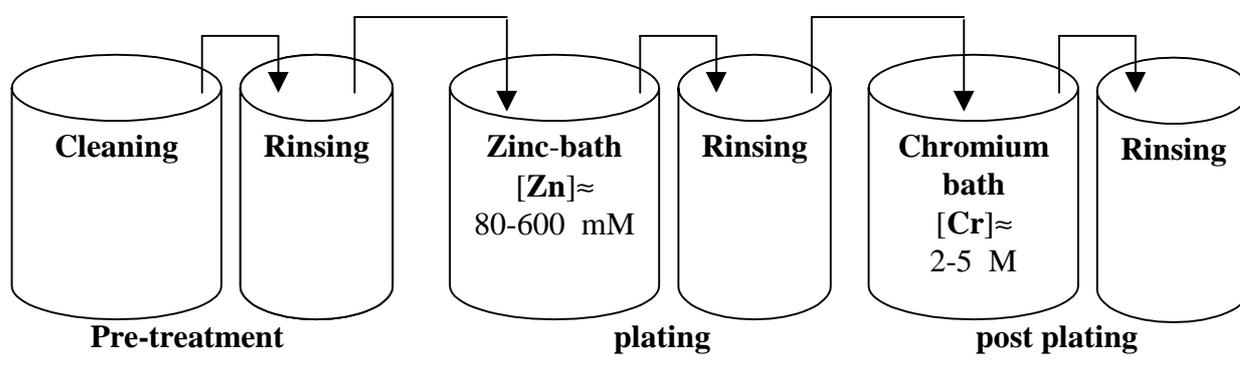
Figure 1.   Example of a typical plating process

Each of these operations consists of a treatment bath and rinsing. Waste effluents are mainly produced in rinsing from where metal containing solutions are commonly discharged into sewerage after purification. The authorities have paid increasing attention to reducing metal releases from plating plants and the new norms seem to be too tight for the smallest shops with conventional waste treatment technology.

2.1 Metal bearing waste waters

In the Uusimaa district of Finland, 24 anodizing and electroplating shops produce 110000 m^3 waste water per year, which includes variable amounts of harmful metals (Kangasmäki). The toxicity of these metals varies within a wide scale, the Paris Commission (PARCOM) and the Helsinki Commission (HELCOM) have put forward recommendations for limits for releases from surface finishing plants, (Table 1.)

Table 1.   Limits for metal releases (PARCOM 1992, HELCOM)

Metal	Concentration mg/l	
	PARCOM	HELCOM
Chromium (total)	0.5	0.7
Chromium (VI)	0.1	0.2
Copper	0.5	0.5
Nickel	0.5	1.0
Zinc	0.5	2.0
Cadmium	0.2	

Of these 24 shops, 17 occasionally or continuously exceed these limits e.g. an anodising plant, which produces 40 000 m^3 of waste per year, releases more than 40 kg nickel per year to sewerage (Kangasmäki). Effluents can be highly acidic or alkaline and they can contain high concentrations of non-toxic metals. Theoretically, it is possible to reach these limits using conventional cleaning technology e.g. precipitation but optimising the present efficiencies often demands an intensification both in the effort and training of waste management teams. Both these activities introduce new costs into the system without increasing production. Usually, there is only one kind transition metal in each separate waste stream, but very often different kinds of wastes are mixed together before metal precipitation. The precipitation of several metals together may result in some savings in labour costs, but the solubilities of different metal hydroxides vary within a wide scale, which causes the leaking either of metal cations or of soluble hydroxide complexes of metals. One of the most important reason for unsatisfactory performance of waste purification systems are the additives used in different operations during the plating process. These additives are often complex-forming ligands and the metals are bound to the soluble

complexes which are difficult to separate from the effluents. This is especially true for Ni bearing wastes where there are difficulties in reaching the demand level.

The quality of the product and effectiveness of the process give the main guidelines for the plating process and it is not economical to modify a production process only to obtain easily purified waste. Modifying the effluent can be done after the plating process but practically the only possible modification for a waste stream is the adjustment of pH values. The correct pH for the effluent is vital for a successful ion exchange operation (Hosea).

2.2 Conventional cleaning technology

Hydroxide precipitation is the standard method for removing harmful metals from metal finishing waste water. This is achieved by adjusting the pH of the waste water with an alkaline reagent to deposit the dissolved metals and settle and remove the resultant metal hydroxide precipitates. This procedure usually needs pre-treatment prior to metals precipitation, such as the oxidation of cyanide (CN^-) or reduction of Cr(VI), to deal with substances that interfere with the precipitation. Nucleation agents are also used to enhance the settling of fine precipitates. The use of nucleation enhances the performance of the cleaning procedure so that the metal concentration in effluents after purification is characteristically one order of magnitude lower than after treatment without added nucleation agents (Detrisac). Nucleation agents can be cationic polymers or a co-precipitated metals such as iron that is added as the sulphate salt to provide co-precipitation with ferric hydroxides. An excess of co-precipitation metal also masks, to some degree, complexing agents present in waste waters. While being an effective metal removal method, this process produces four times as much sludge as metal hydroxides alone (Cushinie) and metal recovery from the resulting mixed hydroxide sludge is difficult or impossible.

Other possible methods for controlling the metal concentrations in waste effluents are sulphide or carbonate precipitation (Stanley), complexation-ultrafiltration (Chaufer), solvent extraction (Dalton), electrowinning, chemical metal reduction (Ulman), and also novel magnetic separation techniques (Franzreb). These methods are not very selective and they may have other disadvantages for cleaning and recovering metals from wastes. In sulphide and carbonate precipitation, the principle is the same as in

hydroxide precipitation: The metals are bound to a solid insoluble phase e.g. sulphides, in which different metals may be mixed and especially in the case of sulphides the metal recovery is laborious. The solvent extraction process can be selective but it produces liquid organic secondary waste which may cause problems. In complexation-ultrafiltration metals are bound to soluble macromolecules (0.5-20 kD) which are separated with ultrafiltration. Better selectivity can be obtained using molecules having chelating properties. However, metal retention from solution is usually less than 99%. Electrowinning and chemical metal reduction produces pure metal for recovery and Cushnie has found that electrowinning is one of the two most widely used methods of metal recovery in the plating industry in the USA, the other being atmospheric evaporation. These two leading metals recovery methods are suitable for rather concentrated liquids but uneconomical in wastewater purification. These solutions need selective concentration as a pre-treatment and therefore electrowinning is useful as a supplement process besides the other waste treatment processes.

3. Ion exchangers and their use in waste water treatment

Since the discovery of ion exchange, it has been used for water purification. However, the method is not extensively adapted to metals removal in industrial wastewater treatment. Industry has shunned ion exchange processes even if ion exchange seems to offer an ideal solution for a particular problem, such as the removal of metal ions from electroplating effluents. Bolto offers a few reasonable explanations for this anomaly i.e: Ion exchange receives little attention in technical education courses and it is not normally considered a promising research area. Ion exchange equipment more resembles a manufacturing plant than a waste water treatment facility. Finally, ion exchange has been regarded more as a method to produce pure water than as a method to purify waste (Bolto).

3.1 Ion exchange materials and their applications in waste water treatment

Ion exchange materials comprise two main groups: organic and inorganic exchangers. Both groups include synthetic and natural materials. Ion exchangers form a very heterogeneous group of materials, their only common feature is that they contain a fixed electric charge which can bind counter ions with an opposite charge. Practically all organic exchangers used in waste management have a synthetic polymer backbone, although natural polymers like cellulose, alginic acid and chitin offer an endless source of raw materials (Allan). Especially chitin and chitosan have been studied for their good metal sorption properties and found to have potential for waste management (Inoue). One probable cause for the lack of their applications is that natural polymers are commonly biodegradable. Their chemical resistance is rather good but their microbiological sensitivity restricts their use in hydrometallurgy.

3.1.1 Ion exchange resins

Organic ion exchange resins having cross linked hydrocarbon matrix and derivatized with inorganic group are the most common ion exchange materials used in industrial applications. The majority of the commercial resins are based on the styrene-divinylbenzene structure because of its good resistance against chemical and physical stress. The structure is stable at relatively high temperatures and over the whole pH range. Styrene polymer chains (Figure 2) are crosslinked with divinylbentzene (DVB) and the elasticity of resin can be adjusted by varying the amount of DVB it contains.

$-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-$

X

$-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-$

X

$-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-CH-CH_2-$

X
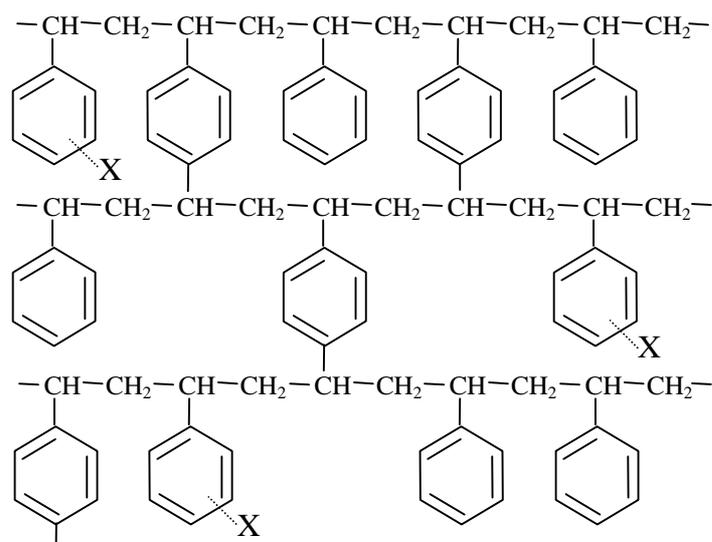
Figure 2. Styrene-divinylbentzene co-polymer X= ionogenic/functional group

The ion exchange properties of organic resins are mainly based on ionogenic groups which can be attached to practically all the styrene rings in the styrene-divinylbentzene co-polymer. Thus, resins with very low crosslinking (DVB portion 1-2%) can have the maximum theoretical concentration of the ionogenic groups of approximately 9 mmol/g. Usually, commercial resins contain ionogenic groups at a concentration in the range of 2.5-5 mmol/g. The nature of ionogenic groups can vary from strong acidic cation exchangers ($-SO_3^-$) to strong basic anion exchangers ($-N^+(CH_3)_3$) and to chelate forming exchangers. There are also active groups which have no electric charge but donor atoms attract cations by donating free electron pairs to form coordination bonds. Ionogenic, chelating, and complex forming active groups may be called functional groups.

The ion exchange systems used in the metal plating industry are mainly based on conventional technology i.e., strong acid cation or medium base anion resin in fixed bed column systems. This technology has been applied in many special applications like the two-step metal-cyanide recovery treatment of acidic copper or zinc solutions (Cushnie, Fravel) and the renovation of chromating baths (removing of cationic impurities) (Pajunen) but major waste streams are usually treated by other methods. Strong base anion resin can be used for removing anionic metal complexes from acidic waters like $ZnCl_4^{2-}$ in spent pickle solution or Cr(VI) in rinse water after chromating (Tan). Weakly acidic exchangers ($-COO^-$) have shown good separation

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performance for Zn in plating waste (Uy) and for nickel (Halle), however weakly acidic resins have no widespread applications in the plating industry. Carboxylic resins can be manufactured directly from copolymer components, so a functionalization step is unnecessary and it is easy to generate a high theoretical specific capacity for the product. The carboxylic group dissociates in a higher pH range than the sulphonic group and exchanger is easily regenerated with acid. On the other hand, the complex forming characteristics of carboxylic resins (Kononowa) are too weak for competition with complex forming agents in waste solutions.

Chelating ion exchange resins have ionogenic groups which can form coordination bonds with metals, their donor atoms are usually sulphur, nitrogen or both in the same group (Figure 3). The bonds formed in this kind of metal sorption usually have both covalent and ionic characteristics. The sorption properties of chelating resins are well known and documented (Sahni). Probably the best property of the chelating resins is their selectivity towards transition metals and the weakly acidic nature of chelating groups makes the regeneration step with mineral acid quite easy. There are also resins which do not have negatively charged ionogenic groups but which form complexes with metals. An important example of these are the picolylamine resins (Figure 3) which form rather stable complexes at low pH ranges (Grinstead). Sengupta recommends these kind of complex forming resins for removing trace amounts of metal cations from the background of very high concentrations of competing alkaline- and alkaline earth metal ions at acidic pH (Sengupta 1991).

A)   B)
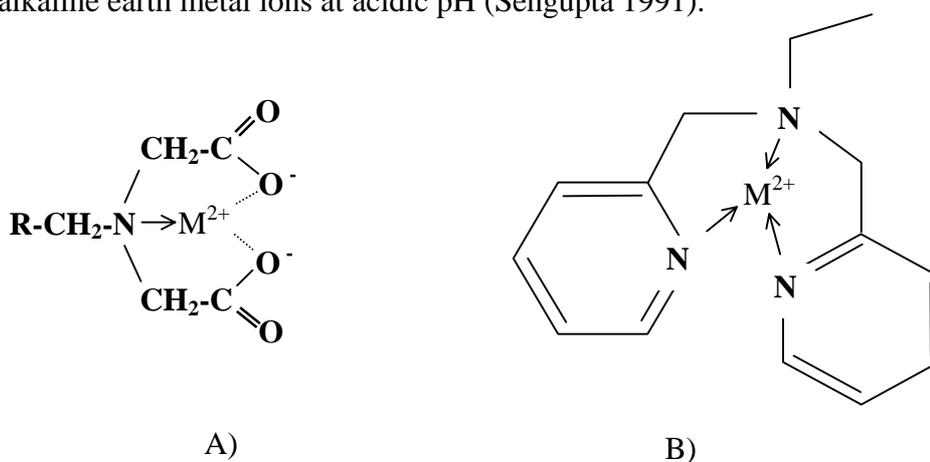
Figure 3. Divalent metal binding onto chelating exchangers A) iminodiacetic acid B) picolylamine

The applications of chelating materials for hydrometallurgic waste treatment are however few. There is an example of an elegant method for processing stable metal complexes. The method is mostly based on the ability of special resins to adsorb metals in a low pH range (Masahide). Waste solutions containing Cu as a EDTA complex are made acidic (pH≈2.5) with sulphuric acid to break the complex and the metal is separated utilising a chelating resin. Cosmen has shown that it is possible to use chelating aminophosphonate resin for continuous ion exchange in a fluidized bed and to remove metals used in the electroplating industries (Cosmen). Also resins with iminodiacetic acid or with picolylamine groups have been shown to have good properties in practice for Cu recovery (Brown).

Chelating resins seem to have several favourable properties, but there are some important reasons why these resins are not used. First, compared to conventional resins, chelating resins are expensive. Second, chelating resins are kinetically much slower in their action and consequently large volumes of the resin are required compared to conventional resins.

3.1.2 Inorganic ion exchangers

Natural inorganic exchangers can be classified into three main categories: zeolites, oxides and clay minerals. Synthetic inorganic exchangers can be classified into the following categories: zeolites, hydrous oxides, acidic salts of polyvalent metals, salts of heteropoly acids, hexacyanoferrates and other ionic compounds (Baacke, Lieser, Weiss). Inorganic exchangers have no applications for waste management in the hydrometallurgic industry, but they have interesting properties such as resistance to decomposing in the presence of ionizing radiation or at high temperatures, which have made them interesting for the treatment of nuclear waste. There are also examples of their high selectivity towards certain ions (Komarneni, Lehto1990), which indicates that they may be suitable for certain hydrometallurgic applications.

Zeolites and clay minerals are crystalline aluminosilicates. The structure of zeolites is based on tetrahedral SiO_4 and AlO_4 units, which are connected by shared oxygen atoms (Figure 4). This kind of three-dimensional structure has small pores where the exchangeable ions are located and where the ion exchange reaction takes place. Silicon is tetravalent and aluminium is trivalent, which results in negatively charged

framework structures and thus each mole of aluminium produces one equivalent of cation exchange capacity for the zeolite framework. In contrast to zeolites, clay mineral exchangers have two-dimensional layered structures.
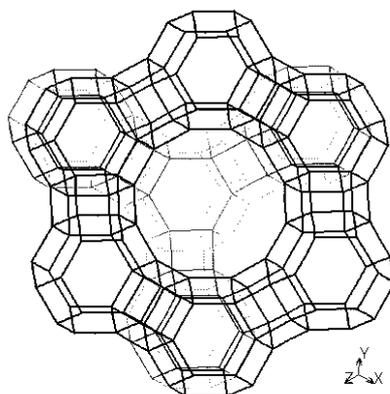
Figure 4.   The structure of the Faujasite (zeolite X and Y)

Zeolites have a rigid pore structures but the layered structures of clay minerals may have some elasticity depending on the ionic form in which the mineral exists (Scott). The ion exchange properties of zeolites and clay minerals are mainly based on the charge density and pore size of the materials.

Some studies of natural zeolites and some hydrous oxides have been made for their profitable use in waste treatment. Clinoptilolite and chabazite have been investigated for the separation of transition metals from mixed metal contaminated effluents (Ouki), also phlogopite mica and mordenite have been studied for Cs and Sr sorption (Liang, Komarneni). Clinoptilolite has been rather extensively used in radioactive waste decontamination (Hutson).

Synthetic inorganic exchangers form heterogeneous groups but there are a few selective hydrous oxides, hexacyanoferrates and zeolites which play an essentially part in nuclear waste management. Investigations of modified titanates (Anthony, R.G.1993, Bortun, Yamazaki), synthetic hydroxyapatite (Lazic) and hexacyanoferrates (Lehto 1990, Lehto 1991) have been targeted to find a method for the selective separation of Sr, Cs and Ag from nuclear wastes. Nuclear waste management is very expensive compared to waste management in the hydrometallurgic industry, so, very

expensive synthetic exchangers can be used if the over-all process is still cost-effective. On the other hand, there are some studies to find inexpensive selective inorganic materials, which can compete with chelating exchangers: Modified titanates (Anthony, R.G.1993, Davis) and composite of iron oxyhydroxides and gypsum (Sengupta, 1995). Granular hexacyanoferrate has been utilised in several industrial scale applications for Cs separation (Harjula,1998)

3.1.3 Activated carbons

Activated carbons are chemically stable materials and they are known to take up metal complexes from solutions and thus they could be utilised for waste purification in certain chemical environments for the removal of metal complexes, which are commonly used in plating baths (Bansal et. al.). Especially, anionic complexes cannot be removed with ordinary cation exchange resins and metal complexation in the solution phase reduces the performance of chelating resins in metal removal processes. Besides surface area and pore structure, the sorption behaviour of activated carbon is characterised also by the raw material, preparation and activation methods. There are only a few special applications for activated carbon in the waste management of hydrometallurgy e.g., gold extraction from cyanide solution (Dean) is advantageous compared to ion exchange. Activated carbon has been shown to have very effective sorption properties for Cd, Cr, Zn and Cu in sewerage waters (Argo) which can be considered to be as difficult a matrix as wastewater from the plating industry.

3.1.4 Industrial ion exchange processes

Although ion exchangers are used mainly in packed bed columns, a variety of different techniques can be utilised in the ion exchange with industrial processes. Continuous operation and integration with the production process are important for effective production in plating shops. There are numerous variations of semi continuous moving-bed systems in which the resin is periodically transferred from a loading column to a regeneration column, Cosmen has successfully used this kind of technique for the separation of metals used in the plating industry (Cosmen). A step forward is the truly continuous moving-bed system, in which the resin is continuously moving from loading column to regeneration column. These continuous systems need

rather large amounts of resin compared to reciprocating flow systems, in which the resin is in a packed bed column and the column height is very short but the bed has a large diameter (Brown), the reaction zone in the column covers a larger portion of the resin than in conventional packed bed column or in moving bed systems. The ion exchanger is always loaded to a low level and that results in kinetic improvements. Both the reduction in resin volume and kinetic enhancement are advantageous for the use of chelating resins. Klein has reported the successful application of a short-bed ion exchange system. In the zinc plating process, which produces effluents at 3.5-4.5m^3/h, the Recoflo$^®$ system can recover Zn and sulphuric acid cost-effectively (Klein).

3.2 Ion exchange equilibrium

An ion exchanger is an insoluble material (R) that has ionogenic groups to which counter ions (A) can be bound (IUPAC). In the ion exchange reaction (1), liquid is contacted with the ion exchanger, and ions C and A are exchanged:

$$z_c \, RA^{Z_a} + z_a \, C^{Z_c} \rightleftharpoons z_a \, RC^{Z_c} + z_c \, A^{Z_a} \qquad (1)$$

Thermodynamic formulation and prediction of binary A/C ion exchange equilibrium is rather simple compared to the handling of a multicomponent equilibrium which becomes progressively more complicated as the number of exchanging components is increased (Towsend). Every exchanger has a maximum amount of charged sites per gram of exchanger; this value is called the theoretical specific capacity (Q) [meq/g]. The capacity is identical to the charge density due to ionogenic groups.

3.2.1 Selectivity

Selectivity is a characteristic of an ion exchanger, which makes the exchanger prefer one counterion to another; thus selectivity drives the reaction either to the left hand or right hand side. The selectivity coefficient for A/C ion exchange in reaction 1 can be written as follows.

$$K_{C/A} = \frac{[RC]^{Z_A} [A]^{Z_C}}{[C]^{Z_A} [RA]^{Z_C}} \qquad (2)$$

Equation (2) is obtained when the mass-action law is applied to the ion exchange without activity corrections. The selectivity coefficient depends on experimental conditions (Helfferich), and the value of the coefficient can vary in the range of a few orders of magnitude.

Helfferich lists several properties of an exchanger on which selectivity depends; the most important factors for selectivity towards metal cations are: electric interactions between ion and exchanger, pore structure and elasticity of the exchanger and other interactions between exchanger and ion. Most often selectivity is a result of a combination of two or more factors.

Electric interactions between metal cation and exchanger involve two main interactions, they are electroselectivity and electrostatic attractions.

Electroselectivity is due to the Donnan potential, which is the electric field between the exchanger and the electrolyte solution. The concentration of counter ions (cations) is larger in the exchanger and the concentration of co ions (anions) is larger in the solution. The migration of the ions from one phase to another causes the electric potential difference between the two phases. The Donnan potential increases with increasing exchange capacity, and with dilution of the solution the potential pulls counter ions to the exchanger and excludes the co ions from the solution. The force that interacts with the ions is proportional to the valence of the ions and this causes a preference for ions with higher valences.

Electrostatic attraction is interaction between counterion and ionogenic groups in situations where the character of the interaction is only weakly chemical. The force is proportional to the ion exchange capacity, which produces a higher charge density in the exchanger. Electrostatic attraction prefers ions with higher valence, smaller ions and ions with stronger polarisation.

The structural elasticity of exchanger causes selectivity partly on the basis of the hydrated ion diameter and partly on the basis of the stability of the hydration shell. Every metal cation dissolved in water has a hydrate layer, which has a characteristic thickness and stability. The model presented by Marcus describes these factors (Marcus 1987). Whenever fully hydrated large counter ions are in an elastic exchanger they produce a pressure that tends to make the solid matrix swell, the phenomenon is

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known as the swelling pressure. If a small counter ion replaces the large one, the swelling pressure becomes lower and this causes a preference for ions with small hydrated diameters. The effect of the swelling pressure gets stronger in parallel with increasing crosslinking of resins. Some inorganic ion exchanger materials have a similar character. The swelling of clay minerals is affected by the hydration properties of the counter ion and parallel selectivity depends on the degree of swelling (Laudelout).

Zeolites have a practically rigid structure with a regular pore size; characteristically in the range of 4-7Å, and in the case of a large cation, small pores can totally exclude the ion, because the swelling pressure can be considered to be an infinite factor. Thus, exchangers with rigid lattices work as molecular sieves. On the other hand, zeolites with high exchange capacities (high charge density) can strip the hydration shell from the metal cation. Most metals have cationic diameters less than 4 Å. In the case of the zeolites the character of selectivity changes as a function of ion exchange capacity. With a low capacity zeolite, a sieve-like action is dominant and the increasing exchange capacity emphasises the role of the hydration shell. Zeolites with pore diameters less than the fully hydrated metal prefer cations with a hydrate layer which has the lowest possible stability. Finally, the significance of the hydration shell is at its minimum with zeolites with very high capacities; High charge density can strip the hydration shell regardless of hydration energy and the selectivity depends on the association of cation to zeolite (Baacke).

Other interactions between cation and ionogenic groups are mainly the formation of chemical bonds, which may have a character in the range from a pure ionic bond to a more covalent bond, called a coordination bond in the case of transition metals. The character of the bond is due to the ability of the exchanger and of the cation to donate and to accept electrons. Inorganic exchangers form ion bonds with all metals, there are only few exceptions, like organic complexing agents, which are immobilised in inorganic substructure (Motojima, Sugawara). Immobilised ligands form sparingly soluble compounds or stable complexes with sorbed metal. Organic ion exchangers form a wide variety of bonds from ion bonds to coordination bonds. The ionic character of the bond is stressed when an exchanger has only an oxygen donor in an ionogenic group. A more covalent character appears when the exchanger has chelate

forming groups or donor atoms without an electric charge such as sulphur or nitrogen. The main rule is that ion exchangers prefer ions which form stronger bonds with the solid phase.

3.2.2 The distribution coefficient and practical capacity

The distribution of metals between solution and solid depends of the selectivity of the ion exchanger, in certain experimental conditions. For trace ion exchange a useful measure for metal distribution is the distribution coefficient (K_D), which is defined by:

$$ \mathbf{K_D} = \frac{[\mathbf{RC}]}{[\mathbf{C}]} \qquad [\text{ml/g}] \qquad (3) $$

Under the special condition that ion C is present at trace level([C] ≪ [A] , [RC] ≪ [RA], [RA]≈Q) selectivity coefficient $K_{C/A}$ is practically constant and

$$ \mathbf{K_D} = \frac{(\mathbf{K_{C/A}} \mathbf{Q}^{\mathbf{Z_C}})^{\frac{1}{\mathbf{Z_A}}}}{[\mathbf{A}]^{\frac{\mathbf{Z_C}}{\mathbf{Z_A}}}} \qquad (4) $$

The K_D values are thus independent of the trace ion concentration [C] and inversely proportional to $[A]^{Z_c/Z_a}$. Although in general the experimental conditions, such as metal concentration and pH, have a strong effect on the distribution coefficient, the K_D value can be used as a comparative measure of the efficiencies of various exchangers and sorbents.

The capacity that can be loaded with the metal involved, in certain experimental conditions, is called the practical specific capacity Q_A [meq/g], which is usually experimentally determined. From this practical capacity it is possible to calculate the maximum processing capacity Q_P [ml/g] of the column operation, in terms of solution volume that that can be purified from ion C with a given mass of exchanger.

$$ \mathbf{Q_p} = \frac{\mathbf{Q_A}}{[\mathbf{C}]_{\mathbf{i}}} \qquad [\text{ml/g}] \qquad (5) $$

where $[C]_i$ = initial feed concentration of solution [eq/l].

The K_D value can be used for estimation of the solution volume passed through the column at 50% breakthrough, V_{50}. A volume V_S of solution is eluted through a column, which has a mass m_e of exchanger R. The feed solution has a concentration $[C_i]$ and eluate has a concentration $[C]$ for a metal C.

The amount of substance, metal ion C, in exchanger (R) is N_R after volume V_S of solution has been eluted through the column. The amount of substance in the eluate is N_L. The total amount of substance originally in solution volume V_S is N_{TOT}, i.e.

$N_R = m_e [RC]$

$N_L = V_S [C]$

$N_{TOT} = V_S [C_i]$

Because practically all the metal is exchanged $N_L \ll N_R$; $N_{TOT} = N_R$ and the capacity is totally used $Q_A \approx [RC]$. One obtains from equation (3)

$$K_D = \frac{1}{[C]} [C_i] \frac{V_S}{m_e} \qquad (6)$$

At equilibrium the exchanger in the column does not absorb the metal any more so $[C] = [C_i]$ and

$$\frac{V_{50}}{m_e} = K_D \qquad (7)$$

in case of symmetrical breakthrough curve.

3.2.3 Other chemical and physical phenomena involved in ion exchange

In the waste effluents, beside exchangeable harmful metals, there are species which interfere and compete for the ion exchange reaction. Metal separation from complex waste solution by selective ion exchange is chemically rather complicated. In addition to basic ion exchange equilibria one must consider several chemical equilibria.

Hydrolysis of the exchanger (8) takes place when hydronium ion produced in the autoprotolysis of water exchanges to counter-ions loaded in the resin. This is a

common phenomenon with weakly acidic resins and with inorganic exchangers. Dilution of the electrolyte drives the reaction to the right and the equilibrium pH value in batch exchange may rise even to 10-11 in dilute solution with a chelating resin (Lehto 1994). Considerable conversion to the H^+-form may take place which will suppress the uptake of metal ions. A high pH value in solution does not directly affect the cation exchange reaction but changes in metal speciation in a solution may interfere with ion exchange equilibria.

$$R\text{-Na} + (H^+ + OH^-) \rightleftharpoons R\text{-H} + Na^+ + OH^- \tag{8}$$

$$R\text{-A} + C^+ + M^+ \rightleftharpoons R\text{-M} + C^+ + A^+ \tag{9}$$

$$R\text{-A} + C^+ + L^- \rightleftharpoons R\text{-A} + C\text{-L} \tag{10}$$

$$R\text{-A} + C^+ + (H^+ + OH^-) \rightleftharpoons R\text{-A} + COH + H^+ \tag{11}$$

The effect of competing cations M in equation (9) transports the equilibrium to the right and depresses the K_D value of metal C. This negative effect can be avoided by using an exchanger that is highly selective towards metal C.

The complexing agents L in solution suppress the ion exchange and move the equilibrium in equation (10) to the right. The ligand may have originated from the production process or it may be diluted atmospheric carbon dioxide. Hydrolysis of cations (11) has a similar effect. Complex formation has a negative effect on the distribution coefficient. If analytical methods are used to determine the total concentration of metal species (e.g. atomic absorption spectrophotometry) it is observed that the distribution $K_{D/obs}$ (12) of metal C is lower than the distribution of ionic C (Lehto 1995).

$$K_{D/obs} = \frac{[RC]}{[C] + [CL] + [COH]} < \frac{[RC]}{[C]} \tag{12}$$

One possible interfering factor is also the peptization of exchanger which produces colloidal exchanger particles in the solution. Colloids act like ion exchangers, they bind ions and keep small portions of metal in solution (Harjula 1993). Peptization mostly concerns inorganic ion exchangers.

4. Experimental

This study contained three main stages:

1.   The first stage was selecting the best sorbents and ion exchangers with a possible potential for waste treatment.
2.   The second stage was column testing of the selected sorbents and ion exchangers in real waste solutions
3.   The third stage was the studying of the sorption equilibria of these selected materials in chemical media that corresponded to the actual waste purification as closely as possible.

Numerous sorbents and ion exchangers were evaluated by the batch ion exchange method and the best materials were selected and selection was based on the K_D values. Column tests were carried out on a considerably smaller group of selected materials with waste effluents. Ion exchange equilibria studies were done by the batch method for the most promising exchangers. The radio-tracer technique was utilised for all metal ions that had suitable radio-isotope and atomic absorptions spectrophotometry (AAS) was used in parallel to check the absolute metal concentrations during the test procedures.

4.1. Exchangers

A wide variety of exchangers and sorbents were tested by the batch mode test (Tables 2 and 3). For practical reasons the tested exchangers were handled in two sets, which were studied with different groups of solutions. Exchangers in the set from article (I) were tested with the waste solutions (Table 1 in (I)). The studied materials included 15 organic resins, mostly chelating cation exchangers, but also strong and weak cation exchangers and chelating anion exchangers. In this group there were also synthetic inorganic exchangers, natural and modified minerals, fibres, pure and modified active carbons, and deacetylated chitin polymers (I). This set of exchangers and sorbents were used as supplied, chelating exchangers were mostly in the sodium form.

The other set of ion exchangers was studied with waste simulants and with pure metal chloride solutions (Table 1 in (V)). This set had 15 zeolites with eight different structures and the silicon/aluminium ratio varied from 1 to 22. The set also contained five active carbons made from different raw materials. Zeolites were in the Na form after pretreatment with 1 M NaCl solution and they were tested with liquids in the pH range of 4-9. The solubility of aluminium (low and high pH range) and silicon (high

pH values) restricts the use of zeolites for waste effluents in the neutral pH range. Active carbons were used as supplied. Carbons were tested for their ability to sorb anionic complexes.

Table 2   Organic ion exchangers evaluated in the study

AMBERLITE IRC 718	Rohm and Haas	IMINODIACETIC ACID (Na^+)
CHELITE C	Serva	IMINODIACETIC ACID
DIAION CR 20	Mitsubishi	POLYAMINE (OH)
DUOLITE ES 467	Rohm and Haas	AMINOPHOSPHONATE (Na^+)
IMAC GT 73	Rohm and Haas	UNKNOWN
LEWATIT TP 214	Bayer	INCLUDING S AND N
SPHERON OXIN	Lachema	8-HYDROXYQUINOLINE
SPHERON SALICYL	Lachema	SALICYLIC ACID
SPHERON THIOL	Lachema	3-MERCAPTO-2-HYDROXYPROPYL
VARION BSM	Nike	MERCAPTILE (Na^+)
VARION BTAM	Nike	INCLUDING S AND N (Na^+)
VARION BTKM	Nike	TIOCARBAMATE (Na^+)
CHELEX 20	Bio-Rad	IMINODIACETIC ACID (Na^+)
AMBERLITE IRC 50	Rohm and Haas	CARBOXYL ACID (H^+)
AG 50W x8	Bio-Rad	SULPHONIC ACID (H^+)
FIBAN AK-22	(4)	IMIDATSOLINE AND CARBOXYL GROUPS
FIBAN K-4	(4)	CARBOXYL ACID
CHITOSAN STANDARD	Novasso	CHITOSAN
CHITOSAN ACID RESISTANT	Novasso	CHITOSAN

Table 3   Inorganic ion exchangers and activated carbons evaluated in the study
                *) material is prepared in the Laboratory of Radiochemistry

ZEOLITE A	Alltach Assoc.	ALUMINIUM SILICATE Si/Al=1
A-4	Tosoh/Japan	ALUMINIUM SILICATE Si/Al=1
X (F-9)	Tosoh Japan	ALUMINIUM SILICATE Si/Al=1.23
SK-40	Linde USA	ALUMINIUM SILICATE Si/Al=2.43
AW 500	Linde USA	ALUMINIUM SILICATE Si/Al=1.6 - 3
TSZ 330 HUD (US-Y)	Tosoh Japan	ALUMINIUM SILICATE Si/Al=2.75 - 3.25
TSZ 500 KOD	Tosoh Japan	ALUMINIUM SILICATE Si/Al=3.1
TSZ 410 KOA	Tosoh Japan	ALUMINIUM SILICATE Si/Al=3.7
ZEOLON 900 Na	US	ALUMINIUM SILICATE Si/Al=5
Clinoptilolite	Natural	ALUMINIUM SILICATE Si/Al=5
TSZ 350 HUA (US-Y)	Tosoh Japan	ALUMINIUM SILICATE Si/Al=4.5 - 6
HSZ- 700 KOD	Tosoh Japan	ALUMINIUM SILICATE Si/Al=6.1
TSZ 640 NAA	Tosoh Japan	ALUMINIUM SILICATE Si/Al=8
HSZ 710 KOA	Tosoh Japan	ALUMINIUM SILICATE Si/Al=8.5
TSZ 360 HUD (HS-USY)	Tosoh Japan	ALUMINIUM SILICATE Si/Al=6.5 - 10
TSZ - 720 KOA	Tosoh Japan	ALUMINIUM SILICATE Si/Al=10.25
ZSM 5	Degussa	ALUMINIUM SILICATE Si/Al=22.5
Filtrasorb 400	Chemviron carbon	ACTIVATED CARBON
Eurocarb PHO	Eurocarb products Ltd	ACTIVATED CARBON
NORIT SA 2	Norit	ACTIVATED CARBON
NORIT PK 0,21-1	Norit	ACTIVATED CARBON
Norit Row Supra	Norit N.V.	ACTIVATED CARBON
Hydrodarco 3000	Norit N.V.	ACTIVATED CARBON
Norit C Gran	Norit N.V.	ACTIVATED CARBON
		ACTIVATED CARBON
NORIT PK + MnO$_2$	*) (1)	ACTIVATED CARBON IMPREGNATED WITH MnO$_2$
NORIT PK + 8HQ	*) (2)	ACTIVATED CARBON IMPREGNATED WITH 8-HYDROXYQUINOLINE
SERPENTINE		MAGNESIUM SILICATE MINERAL
MODIFIED PHLOGOPITE	*)	MICA MINERAL
SODIUM TITANATE	*) (3)	TITANIUM OXIDE
VISIL AP	Kemira Fibres	POLYSILICIC ACID

4.2. Waste waters and test solutions

The waste waters used in the experiments contained nickel from mixed pretreatment
and plating bath (Ni concentration 0.034-0.51 mmol/l, pH 3-7) , zinc from rinsing
after a basic zinc cyanide bath (0.31/4.6 mmol/l, pH 10/12.1 respectively) and
chromium from rinsing after a chromating bath (1.0/28 mmol/l, pH 6.1/1.3
respectively). The composition of the industrial effluents can vary within a wide

range, therefore it was necessary to make a set of waste simulants, (Table 4). The simulants represented common non-mixed effluents produced in plating shops; the metals, complexing agents, and additives were typical for common processes used in the plating industry.

Table 4   Test solutions

metal	publication	code	liquid composition and purpose	PH_i
Cr	V	Cr I	1 mM $Cr_2(SO_4)_3 \bullet 15H_2O$, 0.01 mM H_2SO_4	1.8
	V	Cr II	1 mM CrO_3, 0.01 mM H_2SO_4	3.0
	V	Cr III	0.025 mM $Cr_2(SO_4)_3 \bullet 15H_2O$	1.8
			0.95 mM CrO_3, 0.01 mMH_2SO_4	
			2500-fold dilution of chromium plating bath, simulating rinsing water	
	II		0.1 mM Cr in citrate buffer (Lurie)	1-5
Co	V	Co I	1 mM $CoCl_2$ reference solution	7.9
Ni	I, IV, V	Ni I	10^{-5}-0.1 M $NiCl_2$ or $Ni(NO_3)_2$ reference solution	7.0
	V	Ni II	0.8 mM $NiSO_4 \bullet 7H_2O$, 0.2 mM $NiCl_2 \bullet 6H_2O$	
			0.5 mM H_3BO_3	
			1000-fold dilution of Watt's nickel plating bath, simulating rinsing water	6.1
	V	Ni III	1 mM $Ni(SO_3 NH_2)_2 \bullet 4H_2O$	
			0.5 mM H_3BO_3	6.3
			1000-fold dilution of sulphamate nickel plating bath, simulating rinsing water	
	I		0.03-0.5 mM nickel waste	3-7
Cu	V	Cu I	1 mM $CuSO_4 \bullet 5H_2O$ reference solution	5.5
	V	Cu II	1 mM $CuSO_4 \bullet 5H_2O$, 0.65 mM H_2SO_4	3.0
			800-fold dilution of acidic copper bath, simulating rinsing water	
	V	Cu III	1 mM CuCN, 2 mM NaCN	10.5
			0.4 mM NaOH, 3 mM $NaKC_4H_4O_6 \bullet 4H_2O$	
			500-fold dilution of copper cyanide bath, simulating rinsing water	
Zn	V	Zn I	1 mM $ZnCl_2$ reference solution	4.1
	III		0.00001-0.1 M NaCN , Zn tracer $5x10^{-7}$M	
	III		0.0001-2 mM EDTA , Zn tracer $5x10^{-7}$M	
	III		0.001 –0.3 M $C_6H_5Na_3O_7x2H_2O$, Zn tracer $5x10^{-7}$M	
	III		0.01-0.3 M $C_6H_{11}NaO_7$, Zn tracer $5x10^{-7}$M	
	III		0.001-5 M NaCl , Zn tracer $5x10^{-7}$M	
	V	Zn II	1 mM $ZnCl_2$, 3 mM NaCN	12.1
			7 mM NaOH	
			300-fold dilution of zinc cyanide bath, simulating rinsing water	
	V	Zn III	1 mM $ZnCl_2$, 2 mM NH_4Cl	5.7
			5 mM KCl	
			300-fold dilution of weakly acidic plating bath, simulating rinsing water	
	I		0.3-4.6 mM zinc waste	10- 12.5
Cd	V	Cd I	1 mM $CdCl_2$ reference solution	6.6
	V	Cd II	1 mM CdO, 10 mM NaCN	11.3
			220-fold dilution of cadmium cyanide bath, simulating rinsing water	
	V	Cd III	1 mM Cd (metal) , 10 mM NH_4NO_3	8.7
			130-fold dilution of cadmium removal bath	

4.3. Test procedures

4.3.1 Batch mode tests

In the batch procedure exchanger and test liquid were equilibrated in sealed vials and finally a solid phase was separated from the liquid phase by centrifuging, solution/ exchanger ratio varied in the range 100-300 ml/g . Equilibrating time varied in the range of 1-7 days. The metal concentration and pH was determined from the liquid. Metal concentrations were used to calculate the distribution coefficient or separation percentage.

4.3.2 Column mode tests

Column mode tests (I, II, V) were used to determine the practical cleaning performance of most promising exchangers evaluated in the batch tests. Column tests were carried out in mini columns (D = 4-7 mm) with simulated and actual waste solutions. Liquid was pumped through a packed bed at a rate of 2-34 bed volumes per hour, fractions of 5-20 bed volumes were collected and the metal concentration and pH were determined for each fraction. Fractions were collected until at least 50 percentage breakthrough was obtained.

From the breakthrough curve the cumulative decontamination factor (DF) was calculated as a function of eluted liquid volume, and 5% and 50% breakthough loading. Uptake at the 5% and 50% breakthrough levels are presumed to indicate the process and practical capacity respectively.

4.3.3 The Colmenu program

The Colmenu program was developed in this study for calculating column performance parameters from experimental data. In column tests with effective exchangers metal concentration in the eluate is so low that experimental data points are often quite scattered. The Colmenu program uses measured data points of the breakthrough curve for smoothing the curve and integrates the curve between given limits. The result can be printed in linear or in logarithmic form. Column performance parameters are given as cumulative DF values and breakthrough percentage values. Both values are calculated from the ratio of two areas A and B, between the integration limits. Cumulative DF values can also be plotted on a graph

(Figure 5), which helps in estimating optimal breakthrough capacity in a practical operation.
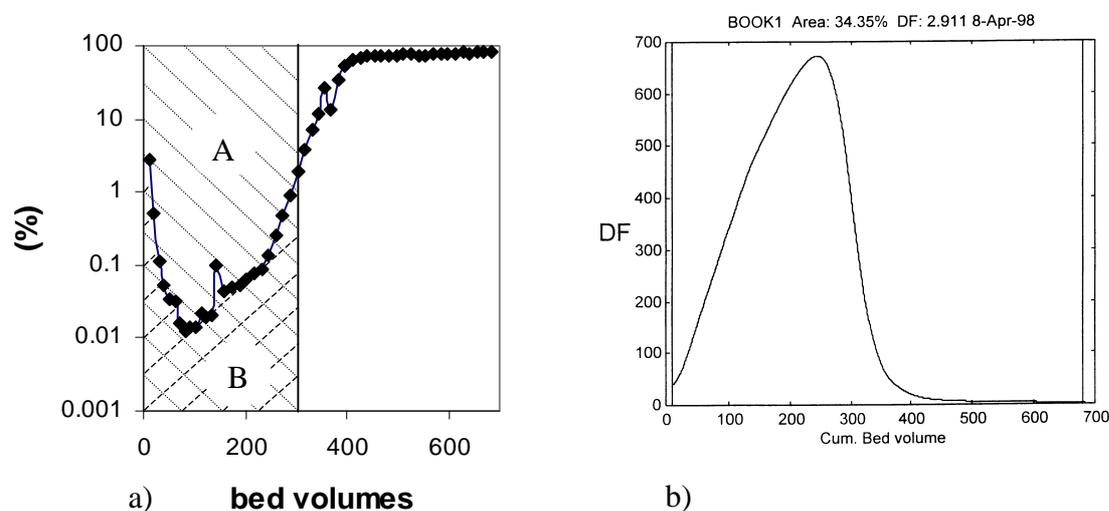
Figure 5. a) Calculation of cumulative DF value ($= {}^{A}/_{B}$) from the breakthrough curve   b) DF value as a function of the eluted solution volume

4.4. Tracer studies

Change in metal concentrations excluding Cu were determined with the radioactive tracer technique. All radioactive copper isotopes are too short lived for practical purposes and Cu concentrations were therefore determined with atomic absorption spectrophotometry (AAS).

The tracer technique is a sensitive and fast method to analyse a large number of specimens (Table 5). The test solutions were spiked with tracer and after isotopic equilibration their initial activity was 40 kBq / l . Inactive carrier in the trace solution brings only insignificant change in total metal concentration (less than 10^{-8} mol/l). A targeted total activity for the counting sample was set at the level where the activity determination could be done with one percent error.

Table 5.   Tracer nuclides for metal concentration determination

metal	tracer nuclide	radiation	determination method
Cadmium	Cd-109	γ	gamma counter
Cobalt	Co-57	γ	gamma counter
Chromium(III)	Cr-51	γ	gamma counter
Chromium (VI)	Cr-51	γ	gamma counter
Nickel	Ni-63	β	liquid scintillation counter
Zinc	Zn-65	γ	gamma counter

gamma counter   : Wallac/ Wizard or Ultrogamma

liquid scintillation counter   : Wallac/ Racbeta

After activity determination distribution coefficient was calculated as follows:

$$K_D = \left(\frac{A_0}{A_{eq}} - 1 \right) \frac{V}{m} \tag{13}$$

Where A_0 is metal concentration or tracer activity before ion exchange, A_{eq} is metal concentration or tracer activity at equilibrium. Instead of the activity the count rate could be used if the measuring conditions are comparable.

5. Results and discussion

5.1. Evaluation of exchangers and sorbents

5.1.1 Evaluation of exchangers and sorbents for Ni and Zn in actual waste solution

The first batch evaluation of organic and inorganic exchangers and sorbents gave very promising results for four chelating exchangers; which were Amberlite IRC 718, Duolite ES 467, Spheron Oxin, and oxine impregnated active carbon. Inorganic sodium titanate exchanger performed also well. Chelating exchangers have three different amines as functional groups (Figure 6).
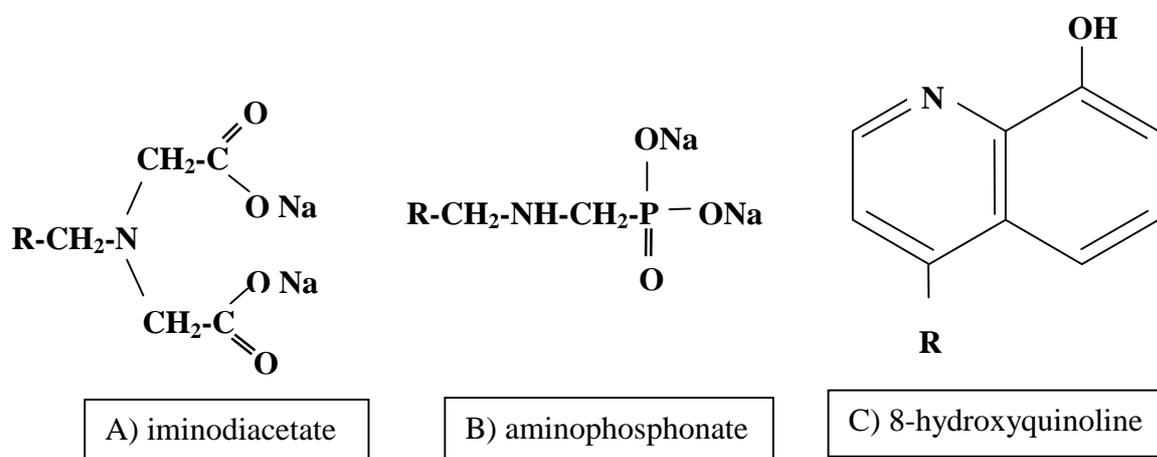
Figure 6 . Functional groups of Amberlite IRC 718 (A), Duolite ES 467 (B) and Spheron Oxin/oxine impregnated active carbon (C)

Sodium titanate is a totally inorganic compound prepared from an industrial intermediate product of a titanium dioxide process (Heinonen). It is probably a layered compound (Clearfield) with an ideal composition of $Na_4Ti_9O_{20} \bullet XH_2O$ in which the sodium ions are located between the titanium oxide layers.

These five exchangers removed more than 99% of Ni and Zn from solution, which corresponds to a K_D value higher than 10000 ml/g. The only exception was nickel sorption to Spheron oxin. The separation percentage was only 81% (K_D= 400 ml/g), this was because the practical nickel capacity of the exchanger in this waste liquid was

almost exceeded. In column experiments with this exchanger Ni capacity was found to be only 0.1 meq/g with 0.5 mM waste and in the batch experiment the Ni uptake was 0.08meq/g .

These five promising exchangers were tested (I) in mini columns, using typical Ni and Zn bearing waste solutions from plating plants. Sodium titanate was most efficient for the separation of nickel, and Duolite ES467 for the separation of zinc. The metal loadings of exchangers were 0.65 meq/g nickel for sodium titanate and 1.78 meq/g zinc for Duolite ES467, calculated at the 50% breakthrough point. The concentrations of nickel and zinc were respectively 0.1% and 0.5% of the initial metal concentration, prior to breakthrough. Amberlite IRC 718 was the second best exchanger for both Ni and Zn; metal loadings were 0.61 and 0.64 meq/g respectively (Tables 5 and 6 in (I)).

5.1.2 Evaluation of organic exchangers for Cr sorption

Fiban AK-22 showed undisputably the best separation performance for all Cr species. The exchanger could remove 97.6% of Cr^{3+} (K_D=4400ml/g) and 99.6% of $Cr_2O_7^{2-}$ (K_D= 27000ml/g) at pH 3.1 , and at pH 7.4 the removal of CrO_4^{2-} was 99.7% (K_D= 36000ml/g). Fiban AK-22 has been developed at the Institute of Physical Organic Chemistry in Minsk, Belorussia (Soldatov). This exchanger has two kinds of functional groups on polypropylene fibres (Figure 7).
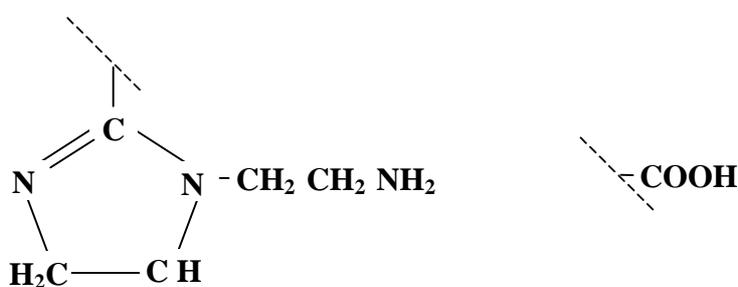
Figure 7. Functional groups of Fiban AK-22, imidatsoline and carboxylic acid

Since Fiban AK-22 has carboxylic groups, it works as a cation exchanger and due to the protonation of imidatzolene groups it can work as an anion exchanger as well. In addition, the nitrogen atoms in the imidatzoline group also form chelates with transition metal ions.

Column experiments were done with contaminated effluents from rinsing baths. Fiban AK-22 removed chromium rather efficiently from a 1 mM waste effluent (pH 6.1).

The level of Cr in the effluent prior to breakthrough was very low, only 0.01% and the chromium loading was 0.47 mmol/g, calculated from the 50% breakthrough value. The pH of effluent remained constant at pH 6.8-7, which indicates that the chromium in this solution was probably in the chromate form. The behaviour of acidic (pH=1.3 , [Cr]=28 mM) solution was rather complicated. Strong changes in effluent pH value points to a varying mixture of several forms of chromium in the effluent.

5.1.3. Evaluation of zeolites and activated carbons for Cr, Co, Ni, Cu, Zn, and Cd sorption

A third set of evaluations was done with zeolites and activated carbons in waste simulants. Zeolites A and X (Si/Al ratio 1-1.2) gave K_D values higher than 70 000 ml/g for both Ni and Zn in all the tested solutions. Zeolite L (Si/Al ratio 3.1) gave K_D values higher than 60 000 ml/g for Ni in all three nickel solutions and ferrierite (Si/Al ratio 6.1) gave K_D values higher than 10 000 ml/g for Zn in both tested solutions. These K_D values are one or two orders of magnitude higher than the values obtained with high-silica zeolite Y (Si/Al ratio 6.5-10), the K_D values were only in the range of 100 – 1000 ml/g (Table 4 in (V)).

Zeolites A and X showed good performance also for Cd, Cu and Co in all the tested solutions. The distribution coefficients for Cd were in the range 18 000 – 33 000 ml/g in a 1mM $CdCl_2$ solution. The separation performance was even better in solutions which contained 10 mM NH_4NO_3 as the complexing substance for Cd : the K_D values were in the range of 74 000-440 000 ml/g. The lowest K_D values, 230-460 ml/g, for Cd in both solutions were observed with zeolite ZSM5 (Table 5 in (V)). Zeolites having low Si/Al ratios showed good separation performances for all the metals of interest.

In the column tests four zeolites, A , X , L, and ferrierite were tested for Zn, Ni, Cd, and Cu, in five simulants and in the reference solutions (Table 8 in (V)). X zeolite showed best performance in nickel solutions, the uptake values in all three solution were in the range 2-2.4 meq/g at the 50% breakthrough point. A and L zeolites performed corresponding values around 0.6 meq/g . The efficiency in column operations are dependent on the ion exchange equilibrium and kinetic parameters. In this study column parameters, such as flow rate, were not optimized, but this should not have a significant effect on uptake at the 50% breakthrough point in present study.

Every exchanger was tested in the same manner, using the same grain size, flow rate and bed dimensions. Thus, the uptake and the cumulative DF value at the 5% breakthrough point can be compared within these experiments. Uptake at the 5% breakthrough point was selected to represent a processing capacity for typical column operations.

5.1.4 Selecting the most promising exchangers

Evaluation showed that sodium titanate, zeolites A and X, aminophosphonic resin (Duolite ES 467), iminodiacetate resin (Amberlite IRC 718), and the combined imidatzolene – carboxylic exchanger (Fiban AK-22) may have potential for new applications in waste treatment. In bench-scale column tests at Finnair's plating shop sodium titanate (SrTreat) had the best separation performance for Ni but its regeneration properties were not as good as those for iminodiacetate and aminophosphonate resins (VI). For practical applications exchangers must be commonly available and their price compared to the effort involved must be reasonable. All the named exchangers are available commercially and most of them are commonly in use. Another criteria used in the selection is the cost of the cleaning operation, which can be derived from the capacity of exchanger compared to price of exchanger and the operating costs of the ion exchange plant. The facilities and labour used for granular or bead form exchangers are basically the same. The price of the organic resins, including materials from practical grade strong cation exchanger to chelating cation exchanger, is in the range 2-20€/kg and price of the synthetic zeolites and highly selective inorganic exchangers is in range 20-200€/kg. Although inorganic exchangers have a higher capacity, the advantageous price and regeneration properties and chemical stability of chelating organic resins make chelating exchangers preferable for waste treatment.

5.2 Ion exchange equilibria of transition metals on chelating resins and zeolites

As stated before, in waste solutions there are several species and phenomena which interact in ion exchange, such as hydrolysis of the ion exchanger, dissolved atmospheric carbon dioxide, competing cations and process chemicals. Usually, these interactions have a negative effect on the performance of an ion exchanger but

sometimes certain complexing agents or an excess of co-ion make the conditions more favourable for metal sorption.

5.2.1. The effects of pH value and competing complexation

It was found that the chelating ion exchangers studied, iminodiacetate and aminophosphonate resins and amphoteric fibrous exchanger, have a maximum K_D value in a certain pH range. Iminodiacetate resin with zinc and nickel, and aminophosphonate resin with zinc had a maximum distribution coefficient in the 5-6 pH range (I, III ,IV) . The amphoteric Fiban AK-22 exchanger has a maximum distribution for chromium in the 3-4 pH range(II).
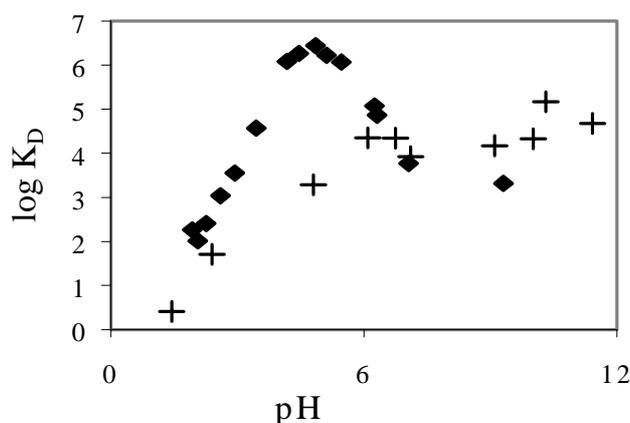
Figure 8   Distribution coefficient (K_D) of Ni on (♦) iminodiacetate exchanger Chelex 100 and on (+) sodium titanate as a function of pH , initial nickel concentrations 0.01 mM and 0.34 mM
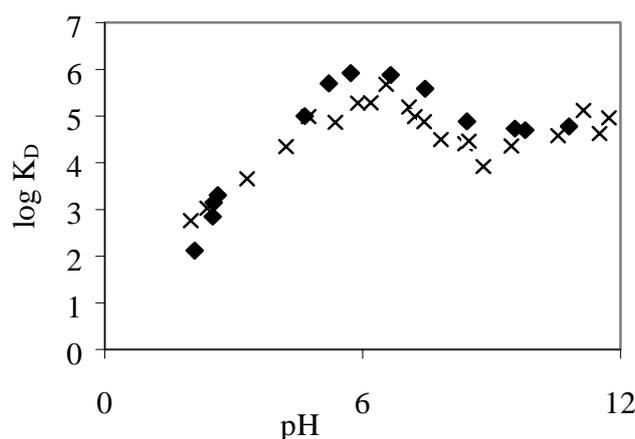
Figure 9   Distribution coefficient (K_D) of Zn on amiphosphonate exchanger as a function of pH, from (♦) 0.31 mM $ZnSO_4$ solution and from (✕) 1 M NaCl solution which contains 6×10^{-7} M Zn tracer

29
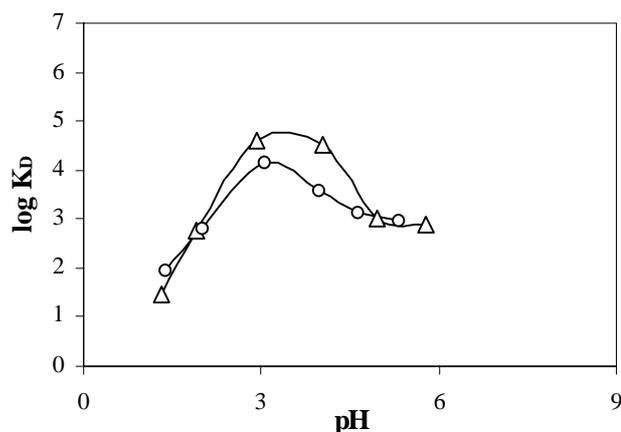
Figure 10   Distribution coefficient of Cr from citrate buffer on polyampholyte exchanger Fiban AK22; ($\triangle$) Cr^{3+} and (o) $Cr_2O_7^{2-}$, initial chromium concentration 10^{-4} mol/l.

Sodium titanate did not have a similar maximum in the K_D values, but all exchangers have the same trends in K_D's in the acidic region.

The chelating resins and inorganic exchangers, which were studied, are weakly acidic in nature and thus very selective for the hydronium ion. In the alkali metal form these exchangers react alkalically in water, the pH value rises when the counter ion exchanges with H^+ from water. The equilibrium pH value has a very strong effect on the distribution of metals. Metal sorption starts when the pH rises to the range where most acidic ion exchange sites start to exchange hydronium ion for metal and the capacity reaches the maximum value in the pH range where all the ion exchange sites take part in the reaction and the functional group is able to form chelate rings with the metal cations. In Figures 8-10 before the maximum there are linear ranges with upward trends because the degree of dissociation increases and H^+ concentration in solution decreases (Equation (14)). The same kind of dissociation phenomenon occurs with sodium titanate but with no chelate formation.

$$\begin{array}{ccc} CH_2\text{-}COOH & CH_2\text{-}COO^- & CH_2\text{-}COO \\ \backslash & \backslash & \backslash \quad / \\ R\text{-}CH_2\text{-}N \quad + Ni^{2+} \rightleftharpoons & R\text{-}CH_2\text{-}N \quad + Ni^{2+} + H^+ \rightleftharpoons & R\text{-}CH_2\text{-}N \longrightarrow Ni + 2H^+ \\ / & / & / \\ CH_2\text{-}COOH & CH_2\text{-}COOH & CH_2\text{-}COO \end{array} \qquad (14)$$
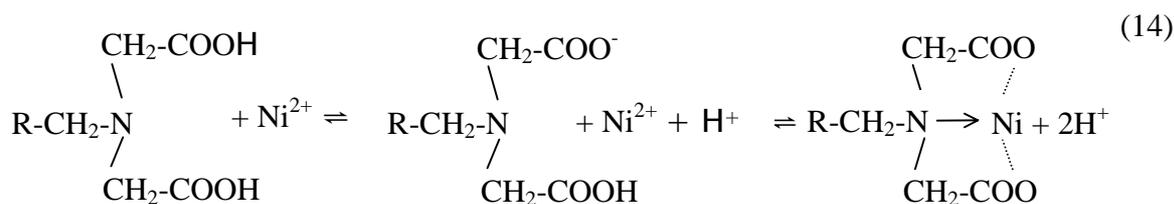
The decrease in K_D-values after the maximum in the neutral and alkaline region can be explained by the complex formation with different ligands. The pH has a strong effect on the competing complexation. In waste solutions there are complex forming agents which dissociate and become reactive as hydronium ion concentration decreases. In the neutral region the autoprotolysis of water produces hydroxide ions, and in the alkaline pH range hydrolysis of cations and complexation with dissolved atmospheric carbonate takes place, which interferes with metal sorption at trace concentrations (Equation (15)). The decrease of K_D of Zn and Cr in Figures 9 and 10 can be explained rather well by hydrolysis of cations, driven by pH change. In Figure 8 competing complexation with carbonate and hydroxide could not entirely explain the decrease of K_D values. It was concluded that very small resin fragments or other colloidal nickel bearing particles released by the exchanger were responsible for this anomaly.

$$
\begin{array}{l}
\quad\quad\quad \text{O} \cdots \text{Zn}^{2+} \\
\quad\quad\quad |\quad\ \vdots \\
\text{R-CH}_2\text{-NH-CH}_2\text{-P} \!\!-\!\! \text{O}\ \ + \text{Na}^+ + \text{OH}^- + \text{HCO}_3^- + \text{CO}_3^{2-} \rightleftharpoons \\
\quad\quad\quad\quad\quad \| \\
\quad\quad\quad\quad\quad \text{O}
\end{array}
\tag{15}
$$

$$
\begin{array}{l}
\quad\quad\quad\quad\quad\quad \text{ONa} \\
\quad\quad\quad\quad\quad\quad | \\
\quad\quad \text{R-CH}_2\text{-NH-CH}_2\text{-P} \!\!-\!\! \text{ONa}\ \ + \text{ZnOH}^+ + \text{Zn(OH)}_2 + 2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2 \\
\quad\quad\quad\quad\quad\quad \| \\
\quad\quad\quad\quad\quad\quad \text{O}
\end{array}
$$
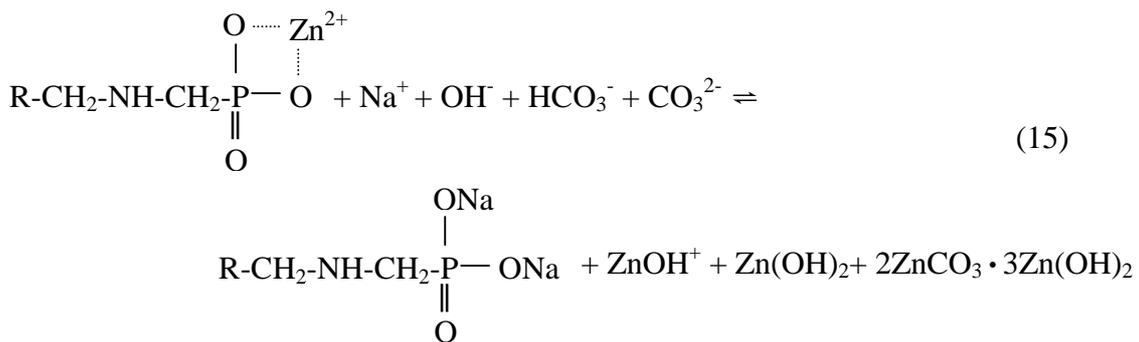
In the batch tests it was observed that aminophosphonate resin may break the zinc cyanide complexes. This has been studied by determining K_D values of zinc as a function of cyanide concentration. Experiments were done at two zinc concentrations, 1 mM and 6×10^{-7} M, the cyanide concentration was in the range $10^{-5} - 0.1$ M. In these chemical conditions Zn forms several complexes. with cyanide and hydroxyl and experiments showed that aminophosphonate-resin can strip zinc from other cyanide and hydroxide complexes but not from Zn(CN)_4^{2-}. Etylenediaminetetra-acetic acid (EDTA) dramatically suppresses metal sorption compared to the effects of citrate or gluconate. The inhibiting effect of EDTA on Zn sorption starts at a concentration of 1μM of the ligand, and a 2 mM solution practically prevents all metal sorption , Figure 6 in (III). Citrate has a much weaker

effect, the ligand starts to interfere with Zn sorption only at concentrations higher than 10 mM and gluconate causes no interference at all.

5.2.2.The effect of counter ion concentration

The effect of counter ion concentration was studied in trace nickel and zinc sorption to iminodiacetate and aminophosphonate resins respectively and to Cr sorption to Fiban AK22. Na is a common counter-ion in weakly acidic chelating exchangers and in hydrometallurgical processes additives are often used as sodium salts, therefore in systems with waste effluents it is possible that Na concentrations are several orders of magnitude higher than those of transition metal concentrations. Even the hydrolysis of the sodium form exchanger can produce 10^{-4} M (Lehto 1994) sodium concentrations in dilute solutions.

The initial nickel concentration was 10^{-3} M and the initial Zn concentration was $6x$ 10^{-7} M . Metal concentrations were so low that the exchangers were not essentially converted to the transition metal form. The increasing sodium ion concentration in the solution drives the reaction (5) to the left-hand side and thus the increase in sodium concentration brings the pH down and only slightly increases the sodium uptake. In both cases, (Figures 3 in (III) and (IV)) an increase in sodium concentration decreases pH almost linearly and the K_D increases until the sodium reaches a concentration of 0.7 M. At higher sodium concentrations pH still decreases but in the Ni/ iminodiacetate system the distribution coefficient of the metal increases, and in the Zn/ aminophosphonate system the distribution coefficient of metal decreases. This kind of ternary ion exchange equilibrium is quite a complex system. Even though the transition metals and hydronium dominate the equilibrium (IV) it is impossible to make straightforward conclusions from the H/Na/metal equilibrium, because total electrolyte concentration in solution phase varies in a wide scale. However, the equilibrium can be described by plotting binary selectivity coefficients ($K_{Ni/H}$, $K_{Na/H}$, $K_{Ni/Na}$) vs. Ni loading in exchanger (Figure 11). It can be seen that in case of iminodiacetic exchanger, $K_{Ni/H}$ has two ranges corresponding to 0.00001-0.001 mmol/g and 1-1.7 mmol/g Ni loadings in which it is practically constant as a function of Ni loading. In the range of 0.00001-0.001 mmol/g Ni-loading only trace nickel exchange takes place and in the range of 1-1.7 mmol/g Ni-loading, equilibrium is practically controlled by binary Ni/H exchange.
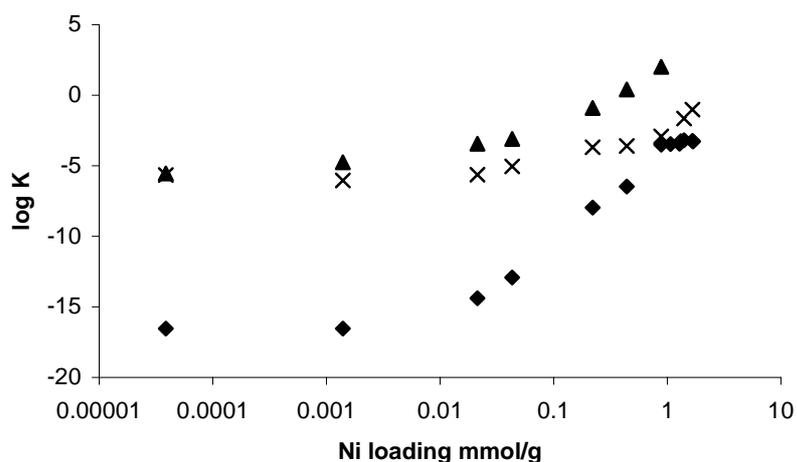
Figure 11   Binary selectivity coefficients of $H^+/Na^+/Ni^{++}$-equilibrium vs.
hydronium loading of Chelex 100 exchanger, ▲ $logK_{Ni/Na}$,◆ $logK_{Ni/H}$ and ✕
$logK_{Na/H}$.

Fiban AK22 was used to study the effect of K, Mg, Ca and Fe cations. Alkaline and
alkaline earth cations have no effect on the uptake of chromium(III) by Fiban at
concentrations below 0.1 M. However, the transition metal, iron, starts to interfere
with chromium sorption already at concentrations above 0.001 M, this is as expected
since as a transition metal, iron competes with chromium for complex formation with
the exchanger. The trivalent ion Fe^{3+} has a stronger interfering effect than Fe^{2+} (Figure
2 in (II)).

In the column tests there were signs of a positive effect of the strong electrolyte
background for the sorption of Cd on A type zeolite. Metal sorption from solutions
containing a large excess of NH_4NO_3 was considerably higher than metal sorption
from pure $CdCl_2$ (1 mM) solutions (Table 8 in (V)). One should assume that
competition between Cd^{++} and NH_4^+ suppresses the sorption of metal compared to
sorption from pure metal chloride solutions, which was not the case. To explain this
anomaly there are two alternatives either NH_4^+/NO_3^- ions or a relatively strong
electrolyte background (10 mM) have positive effects on the sorption of Cd. In the
NH_4^+ solution, the exchanger converts to some degree from H^+/Na^+-form to NH_4^+-
form , which may be more selective towards Cd. Cl^- forms stronger complexes with
Cd^{++} than NO_3^-, so chloride should prevent Cd sorption by the exchanger more

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strongly than nitrate and thus lower Cd uptake was obtained in $CdCl_2$ solution. Concerning the electrolyte background, it promotes the sorption of co-ion which enables complex formation between ammonia and Cd in the NH_4^+-form exchanger.

5.2.3. Effect of zeolite structure and composition

The pore structure of A type zeolite is a three-dimensional 8-member ring with a pore diameter of 4.1Å. The X type (faujasite) pore structure is a three-dimensional 12-member ring with a pore diameter of 7.4Å. Both exchangers, however, have silicon to aluminium ratios which are very similar, Si/Al =1 for zeolite A and Si/Al = 1.23 for zeolite X. Ni, Co, Zn, Cu, and Cd cations have a hydrated diameter in the range of 5.5 – 6.1 Å (Marcus) and thus they must be stripped at least partly from their hydration shells during sorption to the A type, but all hydrated cations should be able to enter the pores of the X type zeolite. The distribution coefficients of all five metals do not show a significant difference between A and X zeolites (Table 6 in (V)). Thus, we can conclude that the pore structure compared to the stability of hydration shell is not a critical factor in determining the selectivities in these cases.

If the distribution coefficient values of metals are compared with the values of the molar Gibbs energies of hydration of ions, it can be seen that the more negative their free energy of hydration, the higher are the K_D values of the metals (Table 6/V). Thus, we can conclude that in these cases the hydration of cations has a significant effect on selectivities. Because the high charge density in the A and X zeolite can strip water molecules from the shell and then the difference in hydration energies contributes to the overall energy change.

Among the tested zeolite materials there were five zeolites which have identical faujasite framework structures with pore diameters of 7.4 Å but their Si/Al ratio varied between 1.23-10. These exchangers were chosen to study the effect of Si/Al ratios on the ion exchange selectivities. As can be seen from Tables 4 and 5 in (V) the selectivities for these divalent metals increased with the aluminium content of the zeolite. The only exceptions to this rule were Zn and Cd in the reference solutions where Y type zeolites with Si/Al ratios of 4.5 to 6 had a higher selectivity than Y types with Si/Al ratios of 2.7 to 3.3 . Otherwise, sorption from the simulants had the same trends as sorption from the reference solutions (Figure 2-4 in (V)).

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6. Summary and conclusions

Selective ion exchange seems to be an almost ideal method of waste water treatment in certain applications such as purification rinse waters in metal plating plants. There are a wide variety of different applications and possible ion exchange materials but finding the most efficient choice of exchangers is laborious because there is no basic data for modelling multi-component systems or the available data bases are incomplete. Moreover, the multi-component models are quite complicated and laborious to use with real waste solutions.

The evaluation of exchangers produced equilibrium data that was used for successful selection of potential materials for further studies. Using the fast and simple batch method with the rapid tracer technique enabled us to evaluate a large group of ion exchangers and sorbents. In addition, the fast method also enabled us to use a wide variety of test solutions which contained the waste effluents that the plating industry commonly produces. The resulting K_D values were used as comparative measure of the efficiencies of exchangers. The use of K_D values is valid for this purpose if experimental conditions are more or less identical because K_D is strongly dependent on the experimental conditions. This kind of wide and fast evaluation is a useful method when there are a limited number of target applications and applications have relatively complicated chemistries.

The basic aim of the evaluation was to find a group of promising candidate exchangers for special applications and this target was achieved. Evaluation produced a heterogeneous group of exchangers, which were further tested in column experiments. The five selected organic ion exchangers were: aminophosphonate, iminodiacetate, and oxine resins, oxine impregnated carbon, and fibrous exchanger having imidatsoline and carboxylic groups. The five selected inorganic exchangers were: four zeolites A, X, L, and ferrierite, and sodium titanate. The two activated carbons selected were Hydrodarco 3000 and Norit Row Supra. The evaluation eliminated 37 of the group of 49 possible sorbents so that 12 promising candidates were left. The character common to all the selected sorbents was their selectivity towards one or more of the transition metals studied.

Column mode experiments were used for further testing of exchangers. Organic chelating exchangers gave the best performance in most cases, only sodium titanate and zeolites with high aluminium content showed performances comparable with resins. These exchangers showed high selectivities and process capacities. The use of mini columns and relatively high elution speed favours exchangers with fast kinetics and this experimental arrangement together with various economical factors were used as extra criteria for selection. The most promising exchangers were found to be chelating iminodiacetate, aminophosphonate and polyfunctional imidatsoline/carboxyl exchangers.

In evaluation and testing, the metals of interest were chromium, cobalt , nickel , copper , zinc, and cadmium. Chromium, nickel and zinc were used in equilibrium studies with the fibrous polyampholite exchanger, Fiban AK22; iminodiacetate exchanger, Chelex 100; and aminophosphonate exchanger, Duolite C467 respectively. In addition, the effect of pH on the performance of the sodium titanate and oxine resin Spheron Oxin was studied, and the selection of experimental conditions in batch tests produced data for the effect of zeolite structure and composition.

The aim of equilibrium studies was to find and study those parameters that control the ion exchange equilibrium in waste solutions. From a practical point of view, there are limited possibilities to adjust the chemical properties of waste effluents before ion exchange. The results shows that pH value is very significant for the performance of exchangers, thus pH adjustment may be a feasible alternative to preparing effluent for ion exchange. The pH adjustment is possible with cheap reagents or by mixing suitable waste effluents. There are two parallel ways by which the pH value can affect the ion exchange equilibrium. Firstly, by affecting the solution speciation, for instance hydroxyl complexation or dissociation/association of complexing ligands (e.g. EDTA) and secondly by competition between H^+ and transition metal. Chelating cation exchangers are particularly selective towards hydronium so that ion exchange with sodium form exchanger is at least a three-component system.

Moreover interfering counter ions and impurities e.g. carbonates or resin fragments originating from reagents and ion exchangers may interfere with the ion exchange

reaction at trace metal concentrations ($< 10^{-6}$mol/l). These phenomena increase breakthrough levels in column operation and may cause severe problems to the performance of the ion exchanger. Selecting an ion exchanger with an appropriate acidity, can solve the problem of right pH value in some cases, for instance oxine resins could be utilised in more acidic environments than iminodiacetate or aminophosphonate exchangers. In special conditions electrolyte background (excess of NH_4NO_3) may have a positive effect on the process capacity of exchanger but this study cannot explain this phenomenon.

In summary, several commercially available exchangers were identified for use in the purification of metal plating wastes, especially in applications where metal concentrations are low e.g. rinse waters or end of pipe polishing. With ion exchange technology it is possible to reach the most strict limits for the emissions and ion exchangers can be utilised as supporting systems for conventional purification technology. On the basis of this study, chelating ion exchangers have been applied to certain applications at Finnair's plating shop with promising results. The collected equilibrium data is not complete and cannot be applied to modelling of ion exchange equilibria but it is useful for the selection of materials used for waste management in the plating industry.

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