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Elimination of Health-Relevant Heavy Metals From Raw Waters of The Drinking Water Supply in the PR China by Means of Weakly Basic Anion Exchange Resins

Abstract

The selective elimination of traces of heavy metals from raw waters of the drinking water supply by means of commercially available weakly basic anion exchangers has been investigated. Target species were heavy metal cations (of Hg, Cd, Zn, Ni, Cu, Pb) and chromate (Cr(VI)) anions.

In the laboratory investigations, suitable anion exchangers were indentified. The phenol formaldehyde-based resin Duolite A7 revealed optimum properties for sorption of practically all heavy metal cations. Acrylic weakly basic exchangers provide optimum properties for chromate removal. Both kinds of exchangers also remove part of the natural organic matter. In parallel investigations in China Chinese anion exchangers were investigated. Further fundamental investigations comprised the sorption mechanism, the rate-controlling step and the conditions of optimum regeneration and rinsing. Furthermore, a mathematical approach for prediction of the filter breakthrough performance was tested.

In the pilot scale experiments were carried out at several sites in China to demonstrate the processes and to obtain economic data about the application. Experiments at Shenyang showed that chromate concentrations of about 100 µg/L Cr(VI) can be decreased below the standard of 50 µg/L for about 4000 bed volumes. Experiments at Haikou showed that mercury concentrations of about 2 µg/L can be diminished below 1 µg/L for more than 15000 m^3/m^3 of exchanger. The experiments at Huludao demonstrated that a simultaneous elimination of copper and mercury species, again at very large specific throughputs is achieved. In all cases only few m^3 of sulfuric acid, NaOH solution and rinsing water were required. Evaluation of the cost of chemicals and energy revealed that the specific operating cost of the selective elimination are in the range of € 0.02/m^3 to € 0.05/m^3

Elimination gesundheitsbedenklicher Schwermetalle aus Rohwässern der Trinkwasserversorgung in China mit Hilfe schwach basischer Ionenaustauscherharze

Zusammenfassung

In Grundlagenuntersuchungen und Vor-Ort-Feldversuchen im Pilotmaßstab wurde die selektive Elimination von Spuren von Schwermetallen aus Rohwässern der Trinkwasserversorgung in China mit Hilfe handelsüblicher schwach basischer Anionenaustauscher untersucht. Ziele waren die Elimination von Schwermetallkationen, insbesondere von Hg, Cd, Zn, Ni, Cu, Pb sowie von Chromat (Cr(VI)).

In Grundlagenversuchen im Laboratoriumsmaßstab wurden geeignete Anionenaustauscher identifiziert. Der auf der Basis von Phenol und Formaldehyd hergestellte Austauscher Duolite A7 weist optimale Eigenschaften für die Sorption praktisch sämtlicher Schwermetallkationen auf. Chromat kann am besten mit Austauschern auf Acrylamidbasis entfernt werden. Beide Arten von Austauschern entfernen gleichzeitig auch einen Teil der natürlichen organischen Wasserinhaltsstoffe. In parallelen Untersuchungen in China wurden Austauscher chinesischer Produktion getestet. Weitere Grundlagenversuche konzentrierten sich auf den Sorptionsmechanismus und die Bedingungen einer optimalen Regeneration und Spülung. Ferner wurde ein mathematischer Ansatz zur Simulation des Filterbetriebs getestet.

In Vor-Ort-Versuchen wurden die Prozesse im Pilotmaßstab an mehreren Standorten in China demonstriert. Die Versuche wiesen nach, daß eine selektive Verminderung des Cr(VI)-Gehalts von 100 µg/L unter den Grenzwert von 50 µg/L erreicht wird. Pro m³ Austauscher können dabei ca. 4000 m³ Wasser behandelt werden. Bei Quecksilber gelingt eine selektive Elimination von etwa 2 µg/L auf weniger als 1 µg/L für mehr als 15000 m³ Wasser pro m³ Austauscher. Regeneration und Spülung benötigen wenige m³ Schwefelsäure, Natronlauge und Spülwasser. Die spezifischen Betriebskosten liegen im Bereich von < € 0.05/m³

Contents

1. Introduction

1.1 Occurrence of heavy metals in raw water

1.1.1 Surface and ground waters

In the past 50 years the drinking water resources in China have been strongly contaminated because of the discharge of hazardous substances either as solid materials or as non-treated waste waters [1].

According to an estimation of the National Environmental Agency for the years 1990 - 1995 mercury is the main contaminant among heavy metals in rivers, lakes and barrier lakes used for drinking water supply [2]. In about 35% of the river sections in cities the concentration of total mercury is above 1 μg/l and, therefore, above the quality class 3. On 21 % of these river sections tha anuual average of mercury was above the river standard 3 [3]. In some regions the mercury content even amounted to more than 22 μg/L. The biggest river in China, the Yang-zi River, is the drinking water source for many cities. In 1999 its annual average mercury concentration was 2 μg/L and, therefore twice the standard for drinking water. For the Huang-Ho (Yellow River) the concentration of total mercury is above 1 μg/l for 90% of the lenght of the river. On 80% also the annual average concentration lies above this standard. Because of the concentrations and the toxicity mercury poses the most serious problem among the heavy metals [2].

Cadmium is a further element among the contaminations of drinking water. Studies have shown that on 18 % of river streches its concentration was above the river quality standard 3 of 10 μg/L. On 9.2 % the annual average value exceeded this value. In some cities, e.g. Qinhuangdao City, the concentration in surface waters even reached 40 μgL. In the Yang-zi River Cadmium is the contaminant with the fifth highest concentration. Cadmium contaminations are not limited to river waters. 68 % of the samples from barrier lakes like the Fenhe Reservoir were above the drinking water standard of 10 μg/L [2].

The situation in surface waters was also difficult with respect to other (heavy) metals like nickel, thallium, beryllium, chromium, copper and lead. In the Daliao River in North Eastern China the contents of lead was above μg/L for 80 % of the streches of the river. Table 1-1 shows the situation of some surface waters during the period before 1995.

Organic impurities like volatile phenol and petrolleum compounds are the main contaminants in all surface waters. In some river stretches phenol concentrations of up to 0.6 mg/L are encountered. In the Yellow-River basin which suplies four provines with drinking water the biological oxygen demand BOD exceed the standard on 78 % of the streches, the chemical oxygen demand (COD) even on 89 % [3, 4].

Drinking water quality is also endangered by the contamination of ground water bodies in cities [5]. Contamination by households and industry, irrigation of waste water and the geogenic situation are the main reasons. 11% of all cities have ground water resources of more than 200 km^2 in which the contaminant concentration exceeds the quality level 3. 11.5% of the cities cover areas between 100 and 200 km^2 and 48.2% of the cities between 20 and 100 km^2. The main contaminants are heavy metals, organic compounds, ammonia, nitrate, and further hazardous substances. E.g. in Xi'an the concentration of Chromium (VI) exceed the quality standard 3 (50 μg/L) on an area of 52.8 km^2. In the ground water of the sity of Guiyang in South West China 60 - 70 % of the water samples contain Lead in concentrations >50 μg/L and zinc > 1 mg/L. In Qiqihaer the concentration of phenol amounts to 0.01 mg/L, that of ammonia is around 80 mg/L and that of nitrate about 166 mg/L. It has been assumed that the ground water of cities like Beijing, Tianjin, and Tangshan contains at least 130 organic main contaminants. The main contaminants in 32 cities are listed in Table 1-2.

Table 1-1: Concentrations of contaminants in different Chinese surface waters.

Gewässer	**CSB (mg/L**	**BSB_5 (mg/L)**	**NH_3-N (mg/L**	**Phenol (mg/L)**	**Hg (µg/L)**	**Cr(VI) (µg/L)**	**Pb (µg/L)**	**Cd mg/L)**	**Petrol. (mg/L)**
Nanfenhe-Fluß (Hefei city)	50.1	26.12	0.46	0.11	1.820	< 50	< 50	10	17.44
Huanghe-Fluß (Wufosi)	24.15	6.48		0.007	0.300	60	190	10	
Fenhe-Fluß (Taiyuan city)	68.55	39.68	1.43	1.51	2.250	< 50	< 50	< 5	1.03
Jingpo-See	34.05	5.00		0.006	1.140	60	110	20	
Fenhe-Fluß (Linfen city)	301.5	25.60	0.21	< 0.005	0.19	< 50	110	20	10.31
Suzhou-Fluß (Shanghai city)	38.40	22.80	0.57	0.08	2.250	< 50	120	20	1.03
Songhuanjiang-Fluß (Honqing)	34.65	6.44	0.02	0.01	4.97	100	60	10	
Fenhe-Reservoir	22.20	7.00	0.04	0.007	0.120	100	110	6000	

Table 1-2: Percentage of cities where the contamination of the groundwater is above the quality standard 3 [5].

Parameter	**As**	**Hg**	**Cr**	**F**	**Fe**	**Mn**
% Cities	31.3	31.3	40.6	34.4	28.1	25.0

It has been estimated that the heavy metal dontaminations of the Chinese waters have considerable effects on the health of the publication. It may be assumed that a high percentage of certain kinds of cancer in the city Xingtai, close to Beijing, is due to elevated concentrations of nickel and cobalt in the drinking water.

1.1.2 Drinking water

In Northern China drinking water is generated by about 50 % from both ground and surface water whereas almost exclusively from surface water in Southerm China. To have enough drinking water more and more rersources with elevated concentrations of contaminants have to be used. In the absence of a suitable treatment, therefore, also drinking water contains contaminants at elevated concentrations. As an example, Table 3 shows the annual average concentrations in the drinking water of the city of Huainan / Anhui province in 1995 and 1996. The city has three water works with capacities of 70.000 m^3/d bzw. 2 x 100.000 m^3/d.

Table 1-3: Concentrations of contaminants in raw and drinking water of Huainan city , mg/L

Parameter	Raw water (1995)	Product water (1995)	Raw water (1996)	Product water (1996)
Fe	0.33 - 3.83	0.05 - 0.60	0.51 - 8.69	0.05 - 0.93
Mn	0.1 - 1.00	0.10 - 0.29	0.10 - 1.05	0.10 - 0.28
Cu	< 0.02	< 0.02	< 0.02	< 0.02
Zn	0.05 - 0.20	0.05 - 0.06	0.10 - 2.0	0.05 - 0.4
Se	0.005 - 0.02	0.005 -0.008	0.005 - 0.01	0.005 - 0.008
As	0.01 - 0.025	0.01 - 0.02	0.01 - 0.02	0.01 - 0.02
Hg	< 0.0008	< 0.0008	< 0.001	< 0.001
Cd	0.005 -0.01	0.005 -0.01	0.005 - 0.01	0.005 - 0.01
Cr(VI)	0.01 - 0.09	0.01 - 0.09	0.016 - 0.1	0.016 - 0.1
Pb	0.02 - 0.04	0.02 - 0.04	< 0.05	< 0.05

1.1.3 Drinking water quality standards in the PR China

Actual Chinese standards of contaminants in drinking water are summarized in the national act GB 5749-85 enthalten [6]. The respective maximum concentrations for heavy metals are summarized in Table 4.

Table 1-4: Standards in China, EU and WHO for heavy metals in drinking water, mg/L [6, 7].

Parameter	Standard, CN	Standard EU	Standard WHO
Arsenic (As)	0.05	0.05	0.01
Chromium (Cr(VI)	0.05	0.05	0.05
Lead (Pb)	0.05	0.05	0.01
Nickel (Ni)	0.05	0.05	0.02
Mercury (Hg)	0.001	0.001	0.001
Cadmium (Cd)	0.01	0.005	0.003
Antimony (Sb)	0.01	0.01	0.05
Iron (Fe)	0.3	0.2	-
Manganese (Mn)	0.1	0.05	0.05

1.2 Relevance

Heavy metals are essential for life. However, above certain individual levels they are toxic and can lead to spontaneous or chronic diseases. The main threats to human beings in China are associated with cadmium, mercury, arsenic and lead in water supplies.

Cadmium accumulates in the kidneys and is involved in a range of kidney diseases. The principal health risks associated with mercury are to damage the nervous system. I children are exposed to mercury, the foetal and embryonic nervous systems will be damaged with subsequent learning difficulties, poor memory and shortened attention spans. High concentration of arsenic in drinking water will cause cardiovascular problems, skin cancer and other skin effects and kidney damage. Lead poisoning in children causes neurological damage leading to a reduction in intelligence, loss of short-term memory, learning disabilities and problem with coordination [8].

The importance of water to China is more obvious than ever before, growing populations, endangered ecosystems, developing economy, deteriorating geological conditions and acid rain lead to worsening the quality of drinking water supply sources and subsequently to a decrease of available fresh water resources. Therefore water demands have emerged for drinking water in China because of pollution, and water quality degradation in the main water supply sources which are formed by the seven biggest water systems including Yellow River, Yangzi River, Huaihe River, Songhuajiang River, Zhujiang River, Heilan River and Daliaohe River. These resources are mainly polluted by trace amounts of heavy metals and micro-organic substances. Among these pollutants mercury and cadmium are predominant because of their toxicity, among the organic pollutants the main compound is phenol [8, 9].

1.3 Conventional methods for removal of heavy metals

Heavy metals can be removed from water by means of different methods:

- Precipitation processes
- Membrane processes
- Sorption processes

1.3.1 Precipitation processes

With respect to the removal of heavy metals from industrial waste waters there is much experience for a large variety of cases. However, the elimination of heavy metals from drinking water is a new task for which only little knowledge is available.

Heavy metals can be eliminated by adding hydroxides ($Ca(OH)_2$, NaOH) or $NaCO_3$ and the subsequent increase of pH. The elimination rates achievable for different metals (aluminium, arsenic, lead, cadmium, chrom(III), cobalt, nickel, silver, zink) depend on the technical conditions and vary between 10% and 95 % [10]. A much better precipitation is possible if sulphides or organosulphides are applied. However, because of the toxicity of the additives these methods cannot be applied to drinking water [11, 12].Traces of heavy metals can also be eliminated during softening / dealkalization [13, 14]. This process has advantages if the water has increased alkalinity levels. At small alkalinity this approach is less useful.

A co-elimination of heavy metals also occurs during conventional removal of manganese and iron. Manganese dioxide has properties of a cation exchanger and, therefore, adsorbs heavy metal species like nickel. The phenomenon has been observed by different authors [15].

1.3.2 Membrane processes

Membrane processes, especially reverse osmosis and nanofiltration allow an elimination also of heavy metal species [10]. Unfortunately, these processes do not lead to a selective or exccusive elimination of heavy metals. Furthermore, a relatively large waste water stream is generated which has to be post-treated.

1.3.3 Sorption processes

Heavy metals can be eliminated by means of an ion exchange with suitable sorbents. In the treatment fo industrial waste waters especially chelating exchangers have been introduced. They show a strong preference of heavy metal cations over alkaline earth species. Resins with imino diacetic acid groups also allow n elimination fo nickel from drinking water. This has successfully been demonstrated in a German research project. The resins are applied in the calcium form. Therefore, any exchange of alkaline earth ions and, thus a strong change of the background composition of the water is avoided [16, 17]. Mercury can also be eliminated using selective resins. These resins, however, are not regenerated but put to landfill deposits.

Heavy metal cations an also be adsorbed by activated carbon or organic materials like peat. However, both their selectivities and sorption capacities are poor [18, 19].

Chromate anions can be eliminated by means of strongly or weakly basic anion exchangers through an exchange for chloride ions. The disadvantage lies in the fact that apart from the trace chromate species also sulfate anions are adsorbed. Therefore, the effective capacity is strongly reduced. Furthermore, regeneration is complicated [20, 21]. Chromate anions care also eliminated using weakly basic anion exchangers in the hydrochloric acid form [22]. The disadvantage of this approach lies in the fact that the exchangers also adsorb all sulfate from the water which, therefore, strongly reduces the effective capacity.

The chromate-bearing waste waters are treated with reducing agents like SO_2, sulfite or divalent iron to achieve a reduction to Cr^{3+} and a subsequent preciptation as hydroxide [10].

1.4 Methods selected for the research project

1.4.1 Elimination of heavy metal cations

The ability of selective exchange resins for selectively adsorbing transition metals is generally due to the presence of electron donor atoms (e.g. nitrogen or oxygen) in their functional groups. By this means these resins have Lewis base properties and can undergo coordination bonds with Lewis acids [23, 24].

Weakly basic exchangers possess nitrogen atoms in their amino groups. At pH values above 5, therefore, they can adsorb transition metal ions. If a weakly basic resin in its free base form is contacted with a heavy metal-bearing solution metal cations will be adsorbed. However, to maintain the condition of electroneutrality in the liquid and exchanger phases this uptake of metal cations has to be accompanied by a parallel adsorption of equivalent amounts of anions of strong acids, preferably of sulphate [25 - 27]. Using cadmium and sulphate as an example, the service cycle can be written as:

$$\overline{R-NH_2} + Cd^{2+} + SO_4^{2-} \Leftrightarrow \overline{R-NH_2\left(Cd^{2+}, SO_4^{2-}\right)} \qquad (1)$$

The elimination of heavy metal salts other than $CdSO_4$ develops in a similar way. Unlike heavy or transition metals alkaline earth ions have extremely poor Lewis acid properties. As a consequence their adsorption is practically excluded. This means that weakly basic resins exhibit an extremely selective adsorption of heavy metal salts.

Protons are strongly preferred over heavy metal species by the nitrogen atoms of the functional groups. With decreasing pH, therefore, the uptake of acids increases and the metal salts are removed. Consequently, desorption of heavy metals can be achieved by treatment with a sufficiently strong acid.

$$\overline{R-NH_2\left(Cd^{2+},SO_4^{2-}\right)}+H_2SO_4 \quad \Leftrightarrow \quad \overline{R-NH_3^+HSO_4^-}+CdSO_4 \tag{2}$$

The uptake of sulphuric acid develops as a reaction-coupled exchange process for which only slightly more than the stoichiometric amount of acid is needed. Because of the strong preference of the acid the exchanger cannot be reused in this form but has to be reconverted to the free base form in a second step of the entire regeneration. For this neutralisation sodium hydroxide can be applied:

$$\overline{R-NH_3^+HSO_4^-}+2\,NaOH \quad \Leftrightarrow \quad \overline{R-NH_2}+Na_2SO_4+2H_2O \tag{3}$$

Again, a reaction-coupled exchange process develops which needs only small excess amount of NaOH over the stoichiometric quantity.

There should be a wide variety of suitable weakly basic anion exchangers which are capable to adsorb heavy metal salts. It can be estimated that the competitive sorption of strong acids is suppressed with very weakly basic resins. However, the properties of the individual functional groups might be more important.

1.4.2 Elimination of chromium(VI)

In natural water and at neutral pH chromium usually occurs as CrO_4^{2-} and $HCrO_4^-$. Chromate species cannot be eliminated in a similar selective way as described above. However, it is well known that chromate anions are preferred over the usual anions of natural waters by all types of anion exchangers. As a consequence, a preferred elimination should be possible by means of weakly basic exchangers which are sufficiently protonated in neutral solutions. This property is found with acrylic weakly basic resins which, therefore, should be the appropriate exchangers [34]. Assuming $HCrO_4^-$ species the elimination by means of the resin in the free base form can be written as:

$$\overline{R\text{–}NH_2\cdot H_2O}+HCrO_4^- \quad \Leftrightarrow \quad \overline{R\text{–}NH_3^+HCrO_4^-}+OH^- \tag{4}$$

The elimination should work despite of the much higher concentrations of chloride and especially sulfate in normal raw waters because chromate speces are preferred over both competitors. Using anion exchangers with a relatively high degree of protonation some exchange of sulfate and chloride for hydroxyl ions can be expected. Consequently, the above-mentioned elimination of chromate leads to a slight temporary increase of the effluent pH. This increase can, however, be suppressed by pre-neutralising the exchanger with a NaCl solution. This does not affect the uptake of chromate species. The exchange of chromate species in trace concentrations for OH- has no measurable influence on the pH value.

For regeneration the exchanger has to be converted to the free base form by means of caustic or lime.

$$\overline{R\text{–}NH_3^+HCrO_4^-}+NaOH \quad \Leftrightarrow \quad \overline{R\text{–}NH_2\cdot H_2O}+Na^+ +HCrO_4^- \tag{5}$$

Due to the strong preference of hydroxyl ions at high pH values regenerations needs only slightly more NaOH than the stoichiomeric amount.

1.5 Scientific and technical objectives of the projects

Especially in Northern China surface waters which serve as sources of drinking water are contaminated with organic compounds and with the heavy metalss mercury, cadmium, chromium arsenic, lead and zinc. Groundwaters contaminations mainly consist of lead, zinc, arsenic and chromium (VI). Because of the increasing demand of qualitatively good drinking water and the contamination of some of the possible sources an increasing water shortage is results. The general objective of the project was, therefore, to develop methods and processes for the selective removal of trace contaminations from drinking water resources.

The developments were based on earlier research work about the adsorption of heavy metal salts by weakly basic anion exchangers. This elimination had been demonstrated for the removal of nickel from tap water. Furthermore, results from the selective removal of chromate species were available.

The scientific investigations of this project were subdivided into different categories:

- In fundamental investigations in the laboratory scale sorption equilibria and kinetics were to be studied to derive parameters for the description and for application in mathematical simulations of the eadsorption.
- A broad series of filter experiments was to demonstrate the dynamic performance of this kind of elimination.
- Based on scientific approaches a method for the prediction fo the filter performance of technical filters was to be developed.

As a result of the scientific part suitable ion exchange resins and operating conditions for optimum application should be identified. This first part was the contents of the tasks of the Institute of Technical Chemistry of Forschungszentrum Karlsruhe and opf the Institute of Nuclear Energy Technology of Tsinghua University, Beijing.

Based on the results of the laboratory scale experiments the elimination fo trace heavy metals was to be demonstrated in the pilot scale during a demonstration campaign in China. Design and construction of this pilot plant was to be made by VA TECH WABAG Company. The plant was to be operated at three cities in China with metal contaminations in the raw water. The results should show the economics of the process and should allow the design of a full-scale installation.

2. Materials and methods

2.1 Ion exchangers

Experiments for heavy metals removal from natural water were carried using commercially available weakly basic anion exchangers manufactures by Western and Chinese companies. The resins and their basic properties are summarized in Table 2-1.

Table 2-1: Data of resins applied

Resin	Matrix	Functional groups	Particle size, (mm)	Moisture content (%)	Anion exchange capacity (eq/L)	Density (dry) (g/L)
Amberlite IRA 67	Acrylic-DVB	Tertiary amine	0.36-0.76	56-62	1.6	690-720
Amberlite IRA 93						
Amberlite IRA 96						
Duolite A 7	Phenol / formaldehyde	Secondary amine	0.3-1.2	53-60	2.0	555-620
Purolite A 830	Styrene / divinylbenzene	Primary and secondary amine	0.3-1.2	47-53	2.75	690-725
Purolite A 832	Styrene / divinylbenze	Primary and secondary amine	0.3-1.2	45-55		690-720
Purolite A 845	Acrylic-DVB	Tertiary amine		52-60	1.6	690-720
Fuji PEI-CS-07	Chitosan	Promary, secondary, tertiary amine	0.3 - 0.8	52-60	No data	No data
701	Epoxy	Primary and secondary amine	0.3-2.0	60-70	No data	650-900
705	Acrylic-DVB	Tertiary amine	0.3-1.25	42-52	No data	700-800
703	Acrylic-DVB	Tertiary amine	0.3-1.25	52-62	No data	650-750
709	Styrene	Tertiary amine	0.3-1.25	47-57	No data	650-750
700	Styrene	Primary amine		55-60	No data	
708	Styrene	Tertiary amine		45-55	No data	630-730
D301	Styrene	Tertiary and quarternary amine	0.36-1.25	50-60	No data	650-720
D314	Acrylic-DVB	Tertiary amine	0.35-1.25	60-65	No data	650-750
SM1	Acrylic-DVB	Secondary (45%) and quarternary (55%) amine	0.60-1.25	59.3	No data	700
SM2	Acrylic-DVB		0.32-0.60	58.9	No data	710
WC1	Styrene	Tertiary (85%) and quarternary (15%) amine	0.6-1.3	57.6	No data	680
WC2	Styrene		0.3-0.6	53.4	No data	700
WM1	Acrylic-DVB	Secondary amine	0.6-1.3	59.4	No data	700
WM2	Acrylic-DVB	Secondary amine	0.3-1.2	59.4	No data	710

For the experiments the resins were first pretreated with hydrochloric acid and sodium hydroxide to remove impurities from their synthesis. After extensive rinsing with distilled water the exchangers were applied for the experiments. Narrow particle size fractions have not been sieved out.

2.2 Raw waters

Table 2-2: Main components of the tap water of the Karlsruhe Research Centre

Parameter	Value	
	Karlsruhe	INET
Calcium, mg/L	98,1	92.8
Magnesium, mg/L	12,6	35.4
Natrium, mg/L	18,9	17.7
Chloride, mg/L	35,6	55
Nitrate, mg/L	4,5	22.1
Sulphate, mg/L	76,1	68.5
m-Alkalinity, mmol/L	4.33	4.23
p-Alkalinity, mmol/L	0.43	n.d.
DOC, mg/L	0.75	n.d

2.3 Analytical methods

Heavy metals concentrations were determined by means of flame atomic absorptions spectroscopy using a Varian SpectrAA-300 device (Forschungszentrum Karlsruhe) or an Analytik Jena AAS-6 Vario analyzer (at INET). The concentration of organic matter (DOC) was measured by means of a Shimadzu TOC 5000 analyzer (Forschungszentrum Karlsruhe) and a High TOC 5000 Instrument (INET). pH values were determined by means of standard Schott electrodes and Knick digital pH meters 646. Anion concentrations were measured by means of a Dionex ion chromatograph 2000i.

3. Sorption equilibria

3.1 Experimental methods

For determination of the sorption equilibrium samples of centrifuged resin material (0.5 - 10 g) were equilibrated with 200 ml heavy metal salts bearing demineralized water having a fixed initial concentration. For investigation of the influence of background composition on the uptake of heavy metals different amounts of NaCl, $NaNO_3$ or humic acid were added. Resin loadings were determined from the difference between initial and equilibrium concentrations of solutions.

The second method to achieve adsorption isotherms of heavy metals at trace concentration level was to use shallow bed column, in which the resin material was packed and heavy metal-bearing solution passed through the resin materials continuously. Equilibrium was regarded to be reached when the feed and effluent heavy metal concentrations were equal approximately. Resin loading of heavy metals was driven by regenerating resin material and monitoring heavy metals in the spent regenerant. Adsorption isotherms could be achieved by plotting the relationship curves between the different Cr concentration in the feed water of shallow bed and corresponding resin loading.

3.2 Exchange capacity

For measurement of the exchange capacity two samples of about 1 g (centrifuged) were contacted for one day with 0.2 L of hydrochloric acid (0.01 mol/L). Capacity was calculated from the decrease of chloride concentration.

Capacities for the uptake of heavy metal salts have not been determined because the maximum loading occurs only at rather high metal concentrations which were outside of the range to be considered in this research project.

3.3 Results

3.3.1 Sorption of heavy metal cations

Isotherms of the adsorption of cadmium and nitrate from demineralized water onto Purolite A 830 and A 832 are plotted in Fig 3-1. For both exchanges studied there is a linear dependency of Cadmium loading at trace concentration level.

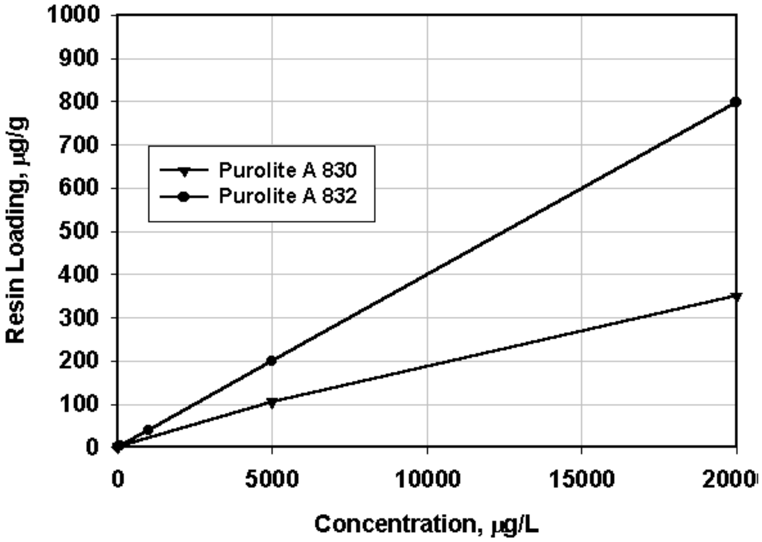

Figure 3-1: Isotherms of the sorption of Cadmium for Purolite A 830 and A 832 [28]

The results demonstrate that linear equilibrium relationships are encountered in the trace concentration region.

In addition the adsorption capacity for cadmium was also studied at increased chloride concentration, increased ionic strength μ (addition of nitrate salts), and increased content of dissolved organic matter. The resulting data are summarized in Table 3-1. The influence of the chloride concentration on the amount of cadmium adsorbed reveals that the chloride concentration has only a minor influence on the amount of cadmium adsorbed. Similar results have been obtained at increased nitrate and DOC concentrations.

Table 3-1: Sorption of Cadmium from different solutions by Duolite A7. Initial Cadmium concentration: 1 mg/L

No.	Additional composition of initial solution	Cadmium adsorbed, µg/g
1	Demineralized water	77,29
2	Demineralized water, $c(Cl^-)$ = 5 µmol/L	77,23
3	Demineralized water, $c(Cl^-)$ = 50 µmol/L	77,19
4	Demineralized water, $c(Cl^-)$ = 200µmol/L	77,23
5	Demineralized water, $c(Cl^-)$ = 500 µmol/L	77,19
6	Demineralized water, $c(Cl^-)$ = 2000µmol/L	77,15
7	Demineralized water, $\mu=2,5\times10^{-6}$ mol/L	77,21
8	Demineralized water, $\mu=50\times10^{-6}$ mol/L	77,02
9	Demineralized water, $\mu=1000\times10^{-6}$ mol/L	77,02
10	Demineralized water, $\mu=2000\times10^{-6}$ mol/L	77,02
11	Demineralized water, DOC = 0,1mg/L	77,02
12	Demineralized water, DOC = 1mg/L	76,77
13	Demineralized water, DOC = 10 mg/L	76,67
14	Demineralized water, DOC = 40 mg/L	76,05

At low pH value numerous amino groups of weakly base anion resins are protonated and therefore cannot provide free electron pairs as LEWIS base for heavy metals. In addition, the resin in protonated form has a greater Donnan potential by which cations are repelled from the resin phase. As shown in Table 3-2, the uptake of heavy metals into the resin phase can be promoted by increasing the pH value. For weakly or strongly alkaline solutions, a very favorable distribution of heavy metals between resin and solution phase can be observed. Consequently, a significant increase of acidity of the solution promotes the destruction of the complex between resin and heavy metal in view of the stronger stability of N-H bond. Regeneration of the resin can be therefore achieved by applying a strong acid.

Table 3-2: Sorption of cadmium at different pH values. Resin: Duolite A7.

pH value	Equivalent fraction in resin phase at equilibrium, %
2.0	4
4.0	5
5.8	62
8.0	98
11.0	97

3.3.2 Sorption of chromate anions

As shown in Fig 3-2, adsorption isotherms of Cr were obtained by means of the method of shallow bed column.

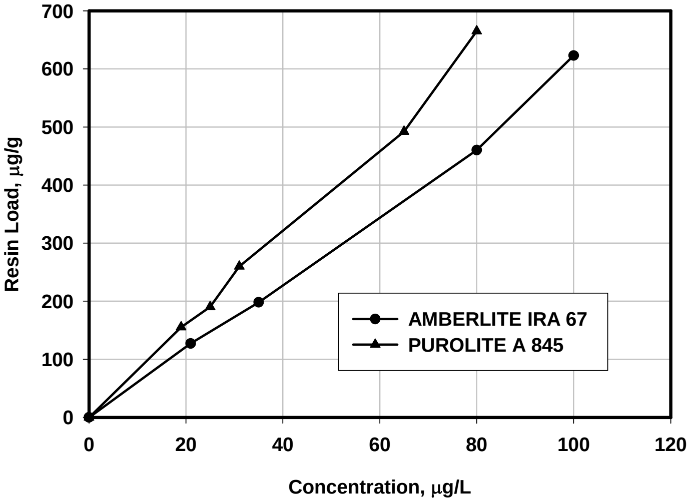

Figure 3-2: Chromate isotherms for Purolite A 845 and IRA 67.

Again the equilibrium relationship in the trace concentration region develops as a linear isotherm.

Chromate uptake is influenced by the competitive sorption of other anions, especially of sulfate. The adverse effect of inscreasing sulfate concentrations is demonstrated by the data of Table 3-3. The data show that with increasing concentration of SO_4^{2-} in the original solution there is a corrresponding decrease of the equivalent fraction of Chromate inthe exchanger phase.

Table 3-3: Equivalent fraction of Cr in exchanger phase with the increase of SO_4^{2-} in the original solution. Initial Cr concentration: 1 mg/L

Concentration of SO_4^{2-} (mol/L)	**Equivalent fraction of Cr in exchanger phase at equilibrium, (%)**	
	IRA-67	**Purolite A845**
0.001	95	95
0.01	46.5	90
0.1	10	27.7
0.5	7	6.3

3.4 Evaluation of equilibria

3.4.1 Surface complexation theory

In the surface complexation theory it is assumed that the ion exchanger can be considered as a plane surface across which the functional groups are uniformly distributed. Surface charges are generated by the dissociation or protonation of surface groups. As a consequence, it can be assumed that protons are adsorbed directly on the surface. The majority of the other ions are located in individual STERN layers parallel to the surface: Heavy metal cations in different layers further away and of different distance from the surface, and monovalent and divalent anions which neutralise the surface in one further common layer. The latter assumption is due to the results of earlier investigations. The remaining part of counterions and coions is distributed across the diffuse layer which normally can be neglected as shown in previous publications. Due to the electrical charges of each layer the entire sequence can be considered as an electric capacitor. It is furthermore assumed that electrostatic interactions as well as swelling phenomena can be neglected. Activity coefficients in the resin phase are assumed to be 1. Figure 3-3 shows a schematic diagram of the layers of a system with protons, two kinds of divalent metal cations, and monovalent and divalent anions. The corresponding development of electric potentials is shown in figure 3-4 [27, 29].

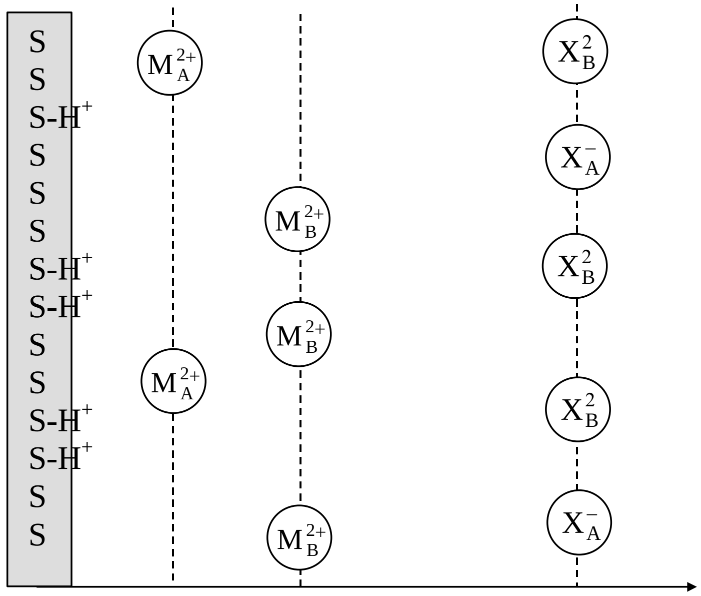

Figure 3-3: Scheme of the arrangement of layers at the surface

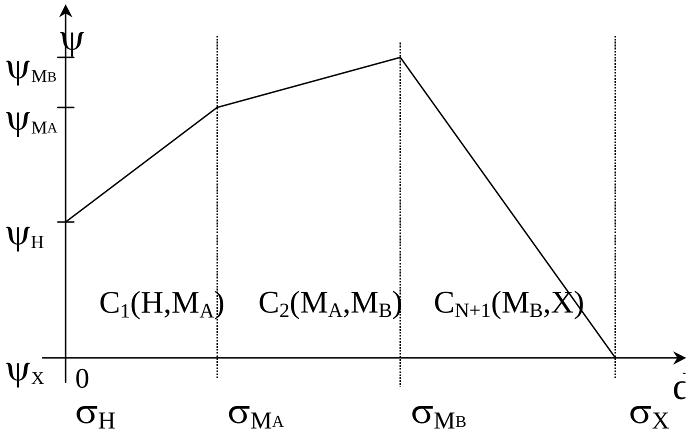

Figure 3-4: Simplified development of electric potential close to the surface

Heavy metals in the liquid phase are assumed to exist exclusively as divalent cations. For derivation of equilibrium relationships a system is considered which contains protons (H^+), one kind of heavy metals cations (M^{2+}), and one kind of anion species ($X^{z(X)}$). The surface valency corresponds to the smallest common multiple of the ions sorbed. In the case of divalent metal ions the valency is 2 [27].

The formation of surface complexes can be written as follows:

Sorption of strong acid H_2X_n:

$$S + 2H^+ \Leftrightarrow SH_2^{2+} \tag{3.1}$$

$$SH_2^{2+} + n\,X^{z(X)} \Leftrightarrow SH_2X_n \tag{3.2}$$

$$S + 2H^{+} + n\,X^{z(X)} \quad \Leftrightarrow \quad SH_2X_n \tag{3.3}$$

<u>Sorption of heavy metal salt:</u>

$$S + M^{2+} \quad \Leftrightarrow \quad SM^{2+} \tag{3.4}$$

$$SM^{2+} + \quad n\,X^{z(X)} \quad \Leftrightarrow \quad SMX_n \tag{3.5}$$

$$S + M^{2+} + n\,X^{z(X)} \quad \Leftrightarrow \quad SMX_n \tag{3.6}$$

The concentrations of surface complexes SH_2X_n and SMX_n correspond to the loadings q(i) of the resin phase with acid and metal salt, if expressed in meq/g.

Applying the mass action law to equations (3.3) and (3.6) and by means of the dimensionless resin loading $y(i) = q(i)/q_{max}$ the formation constants of the two kinds of surface complexes can be derived (For simplicity y(H), y(M) and y(S) are used for the loading with acid and metal salt, respectively and for the relative amount of non-charged functional groups):

$$K_{H_2X_n} \quad = \quad \frac{y(H)}{y(S)\cdot c_{ST}(M^{2+})\cdot c_{ST}(X^{x(X)})^n} \tag{3.7}$$

$$K_{MX_n} \quad = \quad \frac{y(M)}{y(S)\cdot c_{ST}(M^{2+})\cdot c_{ST}(X^{z(X)})^n} \tag{3.8}$$

These equilibrium constants contain all possible interaction phenomena between surface and acid or salt. In eqns. (3.7) and (3,8) c_{ST} designates the concentrations in the respective STERN layers which can be related to the concentrations in the free solution by means of the POISSON-BOLTZMANN relationship as a function of the electric potential Ψ_r:

$$c_r(i) \quad = \quad c_L(i)\cdot \exp\left\{-\frac{z(i)\cdot F}{R\cdot T}\Psi_r\right\} \tag{3.9}$$

the following two relationships can be derived:

$$\log\frac{y(H)}{y(S)\cdot c_L^2(H^+)\cdot c_L^n(X^{z(X)})} \quad = \quad \log K_{H_2X_n} - \frac{2F}{\ln 10\cdot R\cdot T}\cdot\left(\Psi_H - \Psi_X\right) \tag{3.10}$$

$$\log\frac{y(M)}{y(S)\cdot c_L(M^{2+})\cdot c_L(X^{z(X)})^n} \quad = \quad \log K_{H_2X_n} - \frac{2F}{\ln 10\cdot R\cdot T}\cdot\left(\Psi_M - \Psi_X\right) \tag{3.11}$$

In both equations the left hand sides contain exclusively quantities which can be determined from experimental data. Both quotients are designated as *generalized separation factors* [30].

For elimination of the unknown electrical potentials pairs of always two STERN layers are considered as electric capacitor. As has been demonstrated before the consideration of potentials, surface charge densities, and electric capacities of these capacitors two relationships are eventually obtained which give the logarithm of the generalized separation factors as a function of the resin loading with acid and metal salt, respectively [27]:

$$\log Q_{MX_n} \quad = \quad \log K_{MX_n} - \frac{2\cdot F^2\cdot q_{max}}{\ln 10\cdot R\cdot T\cdot A_0\cdot C_2}\cdot y(X) \tag{3.12}$$

$$\log Q_{H_2X_n} \quad = \quad \log K_{H_2X_n} - \frac{2\cdot F^2\cdot q_{max}}{\ln 10\cdot R\cdot T\cdot A_0\cdot C_1}\cdot y(H) - \frac{2\cdot F^2\cdot q_{max}}{\ln 10\cdot R\cdot T\cdot A_0\cdot C_2}\cdot y(X) \tag{3.13}$$

In a simplified way both equations can be written as:

$$\log Q_{MX_n} = \log K_{MX_n} + m_2 \cdot y(X) \tag{3.14}$$

$$\log Q_{H_2X_n} = \log K_{H_2X_n} + m_1 \cdot y(H) + m_2 \cdot y(X) \tag{3.15}$$

with the abbreviations

$$m_1 = -\frac{B}{C_1(H,M)} \tag{3.16a}$$

$$m_2 = -\frac{B}{C_2(H,M)} \tag{3.16b}$$

$$B = \frac{2 \cdot F^2 \cdot q_{max}}{\ln 10 \cdot R \cdot T \cdot A_0 \cdot} \tag{3.16c}$$

For description of the equilibrium, therefore, four constants are needed: m_1, and m_2 and the ratios of formation constants K_{MX_n} and $K_{H_2X_n}$ These quantities can be evaluated from experimental data. Their determination is as follows: In a first step the quantity $\log Q_{MX_n}$ has to be plotted vs. the dimensionless loading with anions y(X). Linear regression yields the parameter $\log K_{MX_n}$ as the intersection with the vertical axis and m_1 as the slope of the regression line. By means of this value of m_2 the quantity $\log Q_{MX_n}$ – m_2 y(X) has now to be plotted vs y(H). Linear regression again leads to the parameters $K_{H_2X_n}$ and m_1.

The description of systems with two or more heavy metal salts is straightforward [27, 29].

Diagrams for evaluation of the binary model parameters are plotted in Figures 5 and 6 for chloride and sulfate-bearing systems and the resin Purolite A109.

The plots for deducing the equilibrium parameters for the metal sorption (upper diagrams) demonstrate the linear relationships rather well. Contrary to that evaluation of the parameters for the adsorption of the acids are less reliable, mainly for systems with chloride and the resin Purolite A 109. The reasons for this phenomenon are the use of the pH values in the liquid phase for determination of the loading with acid and also the fact that deviations and uncertainties from the determination of the first set of parameters are introduced into the evaluation of the second set. A further reason is probably due to the simplicity of the model assumption: It is assumed that the resin matrix occupies two coordination sites of the metal cation. However, this is only an average value. It is possible that the metal cations are either linked to one to four nitrogen atom which cannot be taken into account. The number of coordination sites occupied depends on the concentration and kind of the heavy metal, the flexibility of the matrix and the kind of functional group. It is rather likely that there is no uniform state of bonding. Table 2 summarises the equilibrium parameters deduced in these investigations.

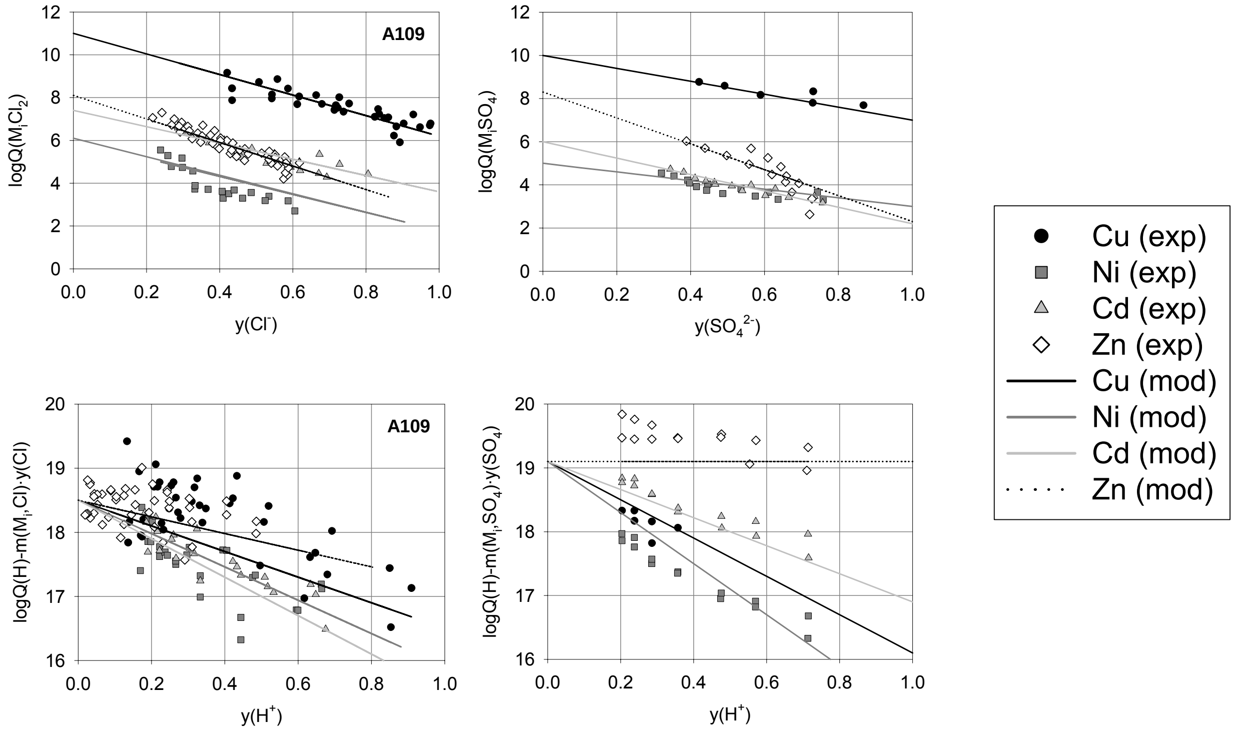

Figure 3-5: Evaluation of equilibrium parameters for the uptake of heavy metal salts by weakly basic anion exchangers [29].

Table 3-4: Equilibrium parameters for the uptake of acid and heavy metal salt, derived from binary data

	Purolite A 109		Fuji PEI-CS-07	
	chloride	sulphate	chloride	sulphate
log K(acid)	18.5	19.1	22.0	20.5
log K(Cu salt)	11.0	10.0	15.0	11.2
log K(Ni salt)	6.1	5.0	14.0	10.5
log K(Cd salt)	7.4	6.0	13.7	10.3
log K(Zn salt)	8.1	8.3	13.5	10.0
m (Cu salt)	- 2.0	- 3.0	- 8.5	- 10.5
m (Ni salt)	- 2.6	- 4.0	- 5.0	- 8.0
m (Cd salt)	- 3.0	- 2.2	- 4.5	- 4.
m (Zn salt)	- 1.3	0	- 4.0	0
m (Cu/anion)	- 4.8	- 3.0	- 15.2	-7.5
m (Ni/anion)	- 4.2	- 2.0	- 18.7	- 10.0
m (Cd/anion)	- 3.8	- 3.8	- 19.2	- 11.0
m (Zn/anion)	- 5.5	- 6.0	- 19.7	- 10.5

Experimental results and calculated isotherms for the uptake of heavy metal chlorides and sulphates in binary systems (metal salt and respective acid) are plotted in figures 9 and 10 for Purolite A 109 and Fuji PEI-CS-07.

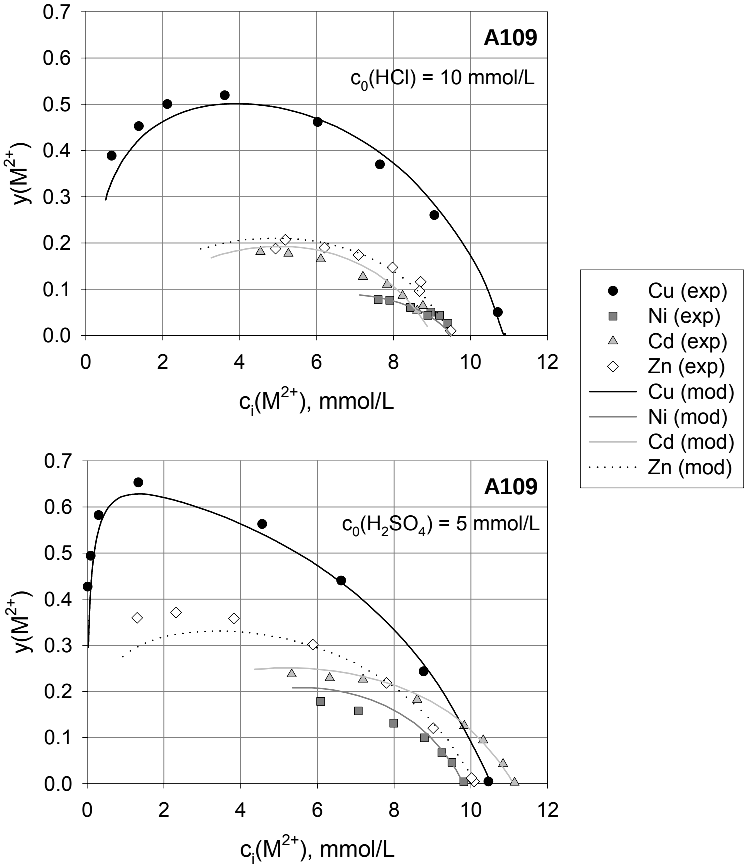

Figure 3-6: Isotherms of the uptake of metal chlorides (top) and metal sulfates (bottom) by the weakly basicc anion exchanger Purolite A 109 [29].

The development of metal loadings vs. metal concentrations depends on the experimental method with decreasing amounts of sorbent and constant volume of the liquid phase. The shape of the isotherms is typical for the less preferred component (metal salt) in a two-component system (metal salt + acid). The smaller the quantity of resin material in a sample the more the uptake of the preferred component will dominate. The result corresponds well with similar experimental data from the adsorption of two organic compounds onto activated carbon [31].

3.4.2 ADSA modeling adsorption of equilibria

The principle of the adsorption analysis (ADSA) consists of subdividing the unknown sorptives into a small number of components with pre-set adsorption properties. This principle has successfully been applied to adsorption of unknown organic compounds onto activated carbon. Usually the system is simplified in a way that four to six components are assumed. The adsorption equilibrium of these componds is desctibed by Freundlich isotherms with a constant exponent. The components vary in their Freundlich constants. The competition is expressed by means of the Ideal Adsorption Theory (IAS theory). The iteration then leads to initial shares of concentrations of each virtual component. The composition of the feed with these components in the calculated initial concentrations leads to an optimum description of the adsorption of the unknown mixture [32 - 34].

At INET an ADSA program for simulating adsorption of unknown organic mixtures by activated carbon has been used in this study to simplify the resin screening process.

The concentration of counterions at the equilibrium can be expressed by:

$$C_i = \frac{q_i}{\sum_{j=1}^{N} q_j}\left[\frac{\sum_{j=1}^{N}\frac{q_j}{n_j}}{\frac{k_i}{n_i}}\right]^{\frac{1}{n_i}} \qquad i=1,2\cdots N \qquad (3.17)$$

K_i, n_i are Freundlich coefficients of counterion of i. q_i is the concentration of species i in the resin phase. The pre-selected Freundlich constants and their meaning are summarised in Table 3-5.

Table 3-5: Relationship between K_i and adsorption ability of heavy metals

	Not adsorbable	**Poor**	**Normal**	**Good**	**Very good**
K_i	0	0~5	5~20	20~50	>50
n_i	<2		≥2		

Results from the adsorption of Hg^{2+} and Cd^{2+} on the resins of 703, 700 and SM_2 are summarized in table 3-6.

Table 3-6: Static experimental results on removing Hg^{2+} and Cd^{2+} by resins

Hg^{2+}						**Cd^{2+}**					
703		**700**		**SM_2**		**703**		**700**		**SM_2**	
K_i	**C_0(%)**	**K_i**	**C_0(%)**	**K_i**	**C_0(%)**	**K_i**	**C_0(%)**	**K_i**	**C_0(%)**	**K_i**	**C_0(%)**
0	0	0	5	0	2.4	0	0	0	0	0	20
5	20	10	1	3	0	5	10	20	10	3	76
10	20	15	1	5	97.6	25	60	30	10	5	1
25	40	20	1	10	0	30	10	50	40	8	1
50	10	25	91	15	0	50	10	75	20	10	1
100	10	40	1	20	0	90	10	90	20	15	1
n=2.75		n=3.00		n=2.75		n=2.50		n=2.00		n=1.00	
Error 1.65%		Error 1.65%		Error 1.65%		Error 1.65%		Error 1.40%		Error 1.26%	

For three resins and mercury and cadmium a heavy metals, the apparent distribution of shares of different adsorbability as deduced from investigation of the adsorption equilibrium are listed in table 3-7.

Despite of the difficulties of this kind of equilibrium description the shares of ions of different adsorbability reflect the fact that the affinity decreases with increasing metal load, that e.g. mercury salts generate a variety of species with different affinity toward the resin and that cadmium forms chloride complexes which are not adsorbable.

Table 3-7: Comparison of adsorption capability of Hg^{2+} and Cd^{2+}

Resin /Heavy metal	**Percentage of Hg^{2+} and Cd^{2+} in different categories of adsorbability**				
	Very good	**Good**	**Normal**	**Poor**	**Not adsorbable**
703/Hg^{2+}	20	40	20	20	-
700/Hg^{2+}	-	93	2	-	5
SM2/Hg^{2+}	-	-	97.6	-	-
703/Cd^{2+}	20	70	10	-	-
700/Cd^{2+}	80	20	-	-	-
SM2/Cd^{2+}	-	-	4	76	20

3.5 Conclusions

The equilibrium experiments have demonstrated the following:

- At concentrations in the mmol/L level the equilibrium can well be correlated by means of the surface complexation theory. Evaluation of the adsorption of one metal salt leads to two sets of equilibrium parameters which remain constant in mixtures. Thus, a fairly good prediction of the sorption of mistures becomes possible.
- At trace concentrations, the equilibrium can well be described by means of linera relationships as usual in chromatography. Such relationships hold for the uptake of both heavy metal salts and chromate species.
- The Adsorption Analysis allows a judgement of the adsorbability of meal salts for comparison of different kinds of ion exchangers.

4. Sorption kinetics

4.1 Experimental methods

4.1.1 Studies at elevated metal concentrations

At elevated metal salt concentrations the development of loading of single particles was followed by means of direct observation of loading profiles inside the exchanger phase. For investigation about 5 g of exchanger material in the free base form was filled into a glass column (diameter 12 mm) and contacted with a metal-bearing solutions in upstream direction at a flow rate of 12 L/ in a fluidized bed. In pre-set time intervals small amounts resin material were taken from the column and dried for 24 hours. The beands were then immersed into transparent polystyrene and cut, approximately in the equatorial plane. The cross-sectional area was then studied either by normal microscopy or by means of REM-EDX. In other cases the cross-sectional area was treated with an organic reagent which gave a colour with the metal adsorbed in the resin. Figure 4-1 shows an example from a partly copper-loaded resin particle from microscopy and from EDX measurements [35, 36].

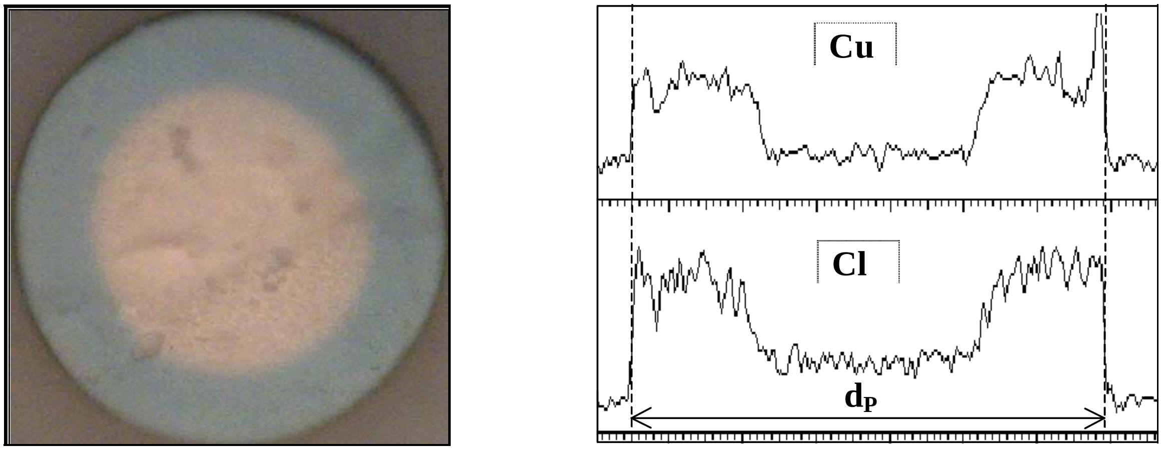

Figure 4-1: Loading profile resin A365, c($CuCl_2$)=5mmol/L, d_P=700 µm, t=10 min, light microscope (left). EDX profiles of cooper and chloride (right).

Figure 4-2: Loading profile resin A365, c($NiCl_2$)=5mmol/L, d_P=580 µm, t=30 min, light microscope

The optical observation revealed the progress of the copper loading with a sharp moving boundary. The EDX measurements demonstrated that there is a complete coincidence between the profiles of copper and of chloride species.

Unlike the uptake of copper the sorption of nickel does not develop with a similar sharp moving boundary. Figure 4-2 shows sthe profile during the sorption of nickel chloride. In this case the surface had been treated with dimethyldioxym to obtain a coloured nickel complex.

Measurements of the diameter of the moving boundary were also used for quantitative analyses of the rate-controlling step (see section 4.2).

4.1.2 Studies at trace metal concentrations

At trace concentrations the shallow-bed method was applied. Fig 4-2 shows the experimental apparatus of shallow bed. The inner diameter of the column is 2 cm. Resin material of two or three particle layers is placed between the layers of glass beads. The height of glass beads bed of each part was about 2 cm. In the experiments the resin material was contacted with Hg (II)-bearing solution. The development of sorption was followed by means of samples taken from the effluent of the column.

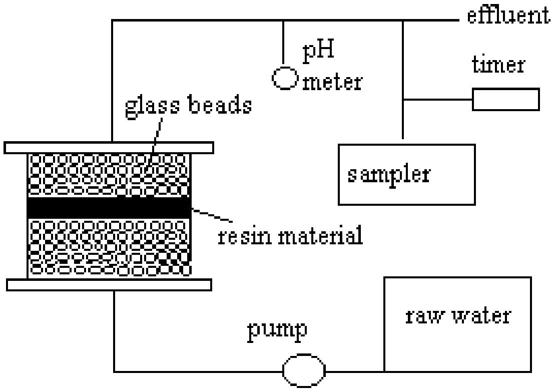

Figure. 4-3: Installations for shallow bed experiments

4.2 Evaluation of kinetic data

The qualitative investigations by means of microscopic methods have demonstrated that the sorption may develop with a sharp moving loading boundary inside the particles. The migration of these fronts can be controlled either by film diffusion across the liquid film surrounding the particle or by particle diffusion inside the beads. The case of chemical reaction control due to a slow adsorption reaction at the functional sites has bee claimed to be rate-controlling. However, despite of many attempts this hypothesis could never be proved. The respective concentration and loading profiles inside a single resin sphere are schematically shown on Figure 4-5.

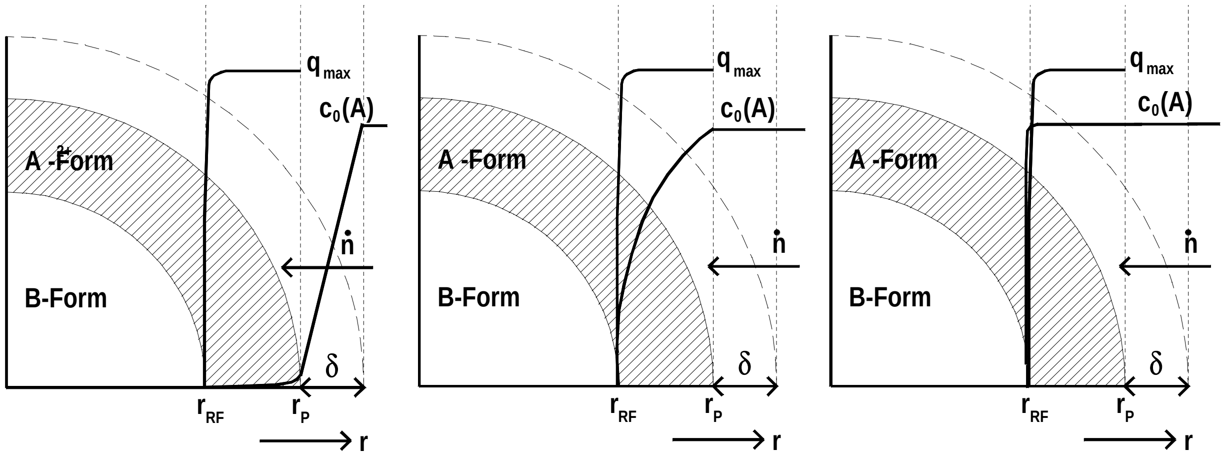

Figure 4-4: Concentration and loading profiles in the case of shrinking-core processes. Rate control by film diffusion (left), particle diffusion (center) and chemical reaction (right) [35].

Assuming spherical particles, constant liquid-phase concentration and with the simplified assumption of a pseudo-stationary transport the flux for species a penetrating into the resin phase is

$$\dot{N}_A = -\frac{dQ_A}{dt} \tag{4.1}$$

The number of sorption sites depends on the radius of the moving front and can be given by

$$Q_A(r_{RF}) = \frac{4}{3}\pi\, r_{RF}{}^3 q_{A,max}\rho_P \tag{4.2}$$

Initial condition is that the front radius is equal to the particle radius at time t = 0:

$$r_{RF}(t=0) = r_P \tag{4.3}$$

In the case of film diffusion the following boundary condition holds:

$$c_A(r_P + \delta) = c_{A,0} \tag{4.4}$$

Transport of ions across the liquid film results from

$$\dot{N}_A = 4\pi r_{RF}^2 \frac{D_{eff}}{\delta}(c_{A,0} - c_A^*) \tag{4.5}$$

with c_A^* being the surface concentration which initially is equal to zero.

$$\dot{N}_A = \frac{4\pi \overline{D}_{eff}}{\left(\frac{1}{r_{RF}} - \frac{1}{r_P}\right)} c_{A,0} \tag{4.6}$$

In the case of the chemical reaction controlling the sirption the concentration in the liquid film and in the shell are constant. Therefore, the condition at the moving boundary is:

$$c_A(r_{RF}) = c_{A,0} \tag{4.7}$$

Der reaction at the moving boundary can be described by a first-order approach:

$$\dot{N}_A = 4\pi r_{RF}^2 \, k \, c_{A,0} \tag{4.8}$$

Combination of the kinetic expressions, und with a mass balance at the moving boundary leads to three relationships for the development of the three different cases:

- Filmdiffusion:

$$F(y_A)_F = \frac{3D_{eff}}{q_{A,max}\,\rho_P\, r_P\, \delta}\, c_{A,0}\; t \tag{4.9}$$

- Particle diffusion:

$$F(y_A)_P = \left[1 - 3(1-y_A)^{2/3} + 2(1-y_A)\right] = \frac{6\overline{D}_{eff}}{q_{A,max}\,\rho_P\, r_P^2}\, c_{A,0}\; t \tag{4.10}$$

- Control by chemical reaction:

$$F(y_A)_C = \left[1 - (1-y_A)^{1/3}\right] = \frac{k}{q_{A,max}\,\rho_P\, r_P}\, c_{A,0}\; t \tag{4.11}$$

With F as the fractional attainment of equilibrium given by the relationship

$$F(y_A) = \left[1 - \left(\frac{r_{RF}}{r_P}\right)^3\right] \tag{4.12}$$

For identification of the rate-contolling step the function $F(y_A)$ from eqns and is plotted vs. time. For the rate-controlling mechanism a linear relationship should be found. From the respective slope the effective diffusion coefficients or kinetic reaction parameter can be deduced.

Figure 4-6 shows two examples of this kind of evaluation of experiments at relatively high metal salt concentrations.

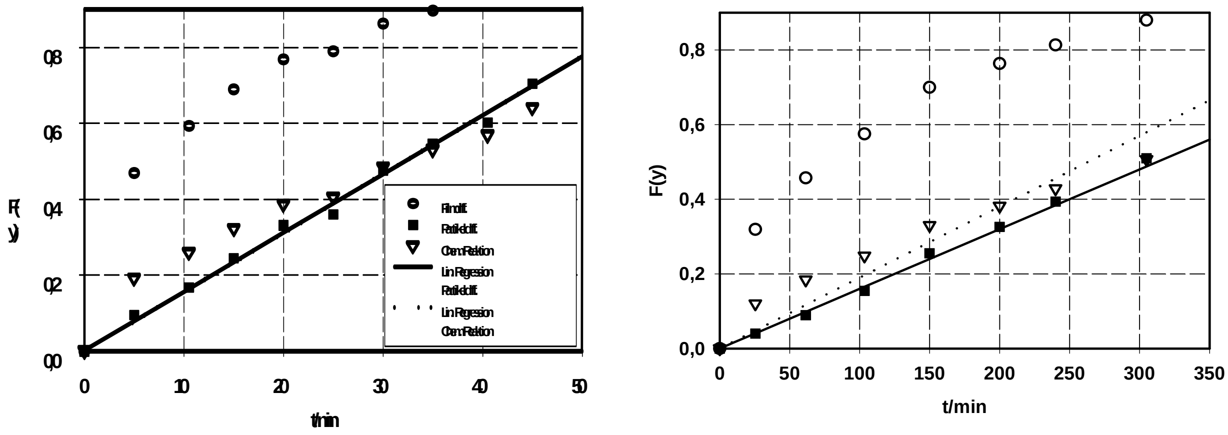

Figure 4-6: Fractional approach to equilibrium for the uptake of $CuCl_2$ by the resin A 365 at 5 mmol/L (left) and 2.5 mmol/L liquid phase concentrations [39].

Evaluation obviously shows that particle diffusion controls the sorption at these liquid phase concentrations whereas film diffusion control can be ruled out by any means. Discrimination between particle and chemical reaction control is more difficult.

Kinetic studies at trace concentration levels were carried out using the shallow be methods as mentioned above. At trace conentration levels microphotographs are no longer possible C_s: concentration of heavy metal in film boundary to solid phase; C_l: concentration of heavy metal in film boundary to solution phase; D: diffusion coefficient; δ: the thickness of film. By mass balance, equation (2-4-2) can be driven:

$$-\frac{dq_A}{dt} = F\overset{\bullet}{N}_A \tag{4.13}$$

with

$$q=4\pi r^3 q_{A,max}/3,\ F=4\pi r^2, \tag{4.14}$$

$$-\frac{dC_s}{dt} = \frac{3}{r}\overset{\bullet}{N}_A \tag{4.15}$$

Assuming film diffusion as the rate-controlling step in the trace concentration level the fractional approach to equilibrium results from:

$$F(t) = \frac{q}{q_{eq}} = 1 - \exp(-\frac{3DtC_0}{r\delta}) \tag{4.16}$$

q: resin loading with heavy metal

q_{eq}: equilibrium resin loading.

Mathematical transformation leads to:

$$-\ln(1-F(t)) = \frac{3DC_0}{r\delta}t = kC_0 t \tag{4.17}$$

with the mass transfer coefficient

$$k = \frac{3D}{r\delta} \tag{4.18}$$

Plotting –ln(1-F(t)) as a function of time t should lead to linear relationships from which the mass transfer parameter k can be deduced [37].

Shallow bed experiments were carried out for sorption of $HgCl_2$ from spiked tap water. Feed concentration amounted to 0.03 mg/L. the linear velocity of feed water passing the shallow bed was 20 m/h. Results of experiments with two different resins are plotted in figures 4-7 and 4-8.

For both resins evaluation of data shows a more or less linear development which indicates that at the conditions given film diffusion might be the rate-controlling step. The larger slope of the straight line for Purolite A 832 should be due to the different particle size distribution with a greater share of smaller particles.

Figure 4-8 shows the effects of linear velocity of the feed water passing the shallow bed. Linear relationships are found for 11m/h, 19m/h, and 30 m/h.

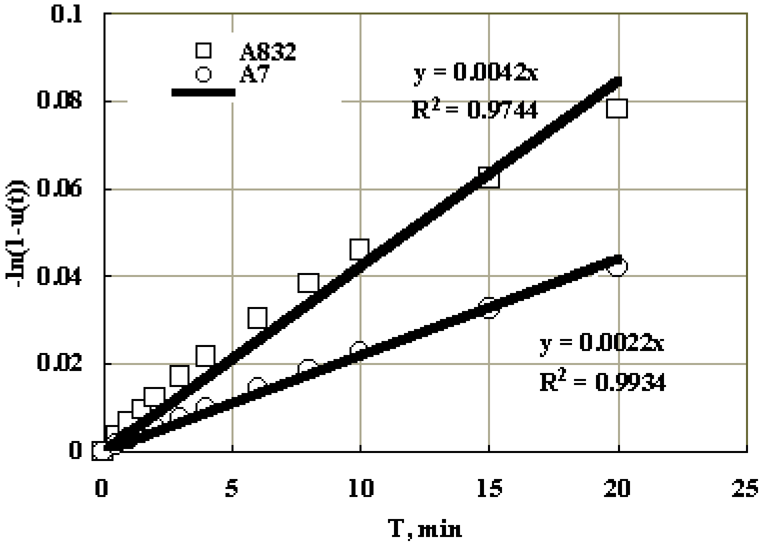

Figure 4-7: Evaluation of kinetic data for the resins Duolite A 7 and Purolite A 832.

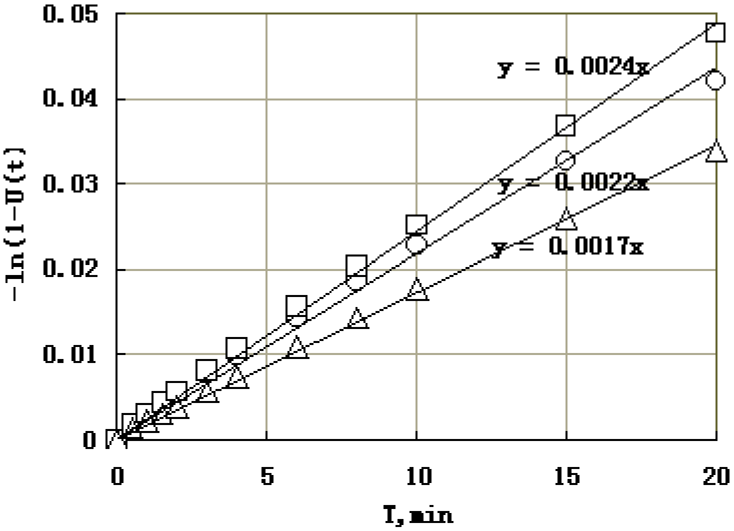

Figure 4-8: Effects of linear velocity on the diffusion

4.3 Effect of chloride ions and humic substance on sorption kinetics

Since heavy metals can be adsorbed by weakly basic anion exchange resin in terms of the formation of coordination compounds, the competitive uptake of ligands in waters (Cl^-, humic substance, etc.) may have an adverse affect on the sorption of metal species. Therefore, the influence of the concentrations of Cl^- and humic substance were studied as examples of inorganic and organic ligands. Furthermore, the effect of pH was investigated.

Experiments were carried by shallow bed experiments with tap water spiked with Cl^- and humic substance as feed water respectively. The corresponding transfer coefficient of diffusion was deduced in the same way as described above. For Duolite A 7 the results are shown in figure 4-9. It seems that the presence of Cl^- has little influence on the sorption kinetics in view of the neglectable variation of transfer coefficient k. The presence of humic substances, however, exhibits a considerable negative influence on the uptake of heavy metals. As shown in figure 4.10, the transfer parameter decreases with increasing content of humic substance in water. Similar results were obtained for Purolite A 832.

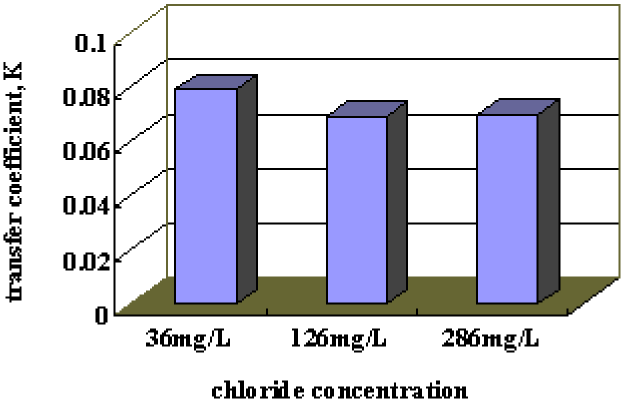

Figure 4.9: Effects of Cl$^-$ on the diffusion of trace heavy metals

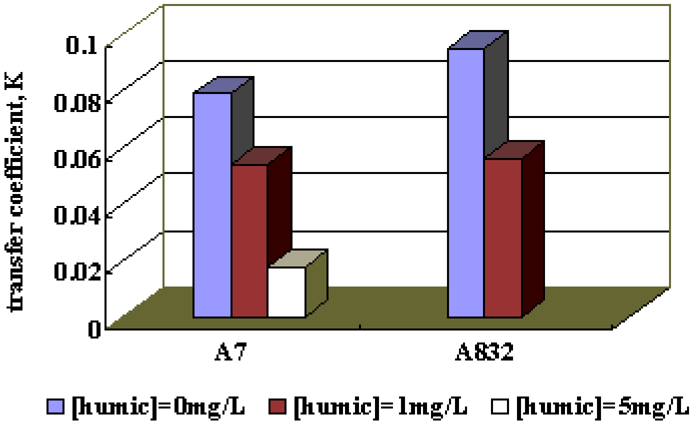

Figure 4-10: Effects of humic substance on the diffusion of trace heavy metals

For examination of the uptake of heavy metals at different pH values centrifuged resin material (2.0 – 5.0 g) were contacted with 200 mL heavy metal-bearing original solution in stirred Erlenmeyer flasks at constant temperature. Different initial pH values were adjusted by adding acid or caustic solution into the original solution. Liquid-phase samples were taken at preset time intervals of 1min, 10 min, 20min, 48hours. As shown in figure 4-11, the sorption rate of heavy metals increases with increasing pH. However, even at favourable pH values the time required for maximum uptake amounts to at least 20 minutes.

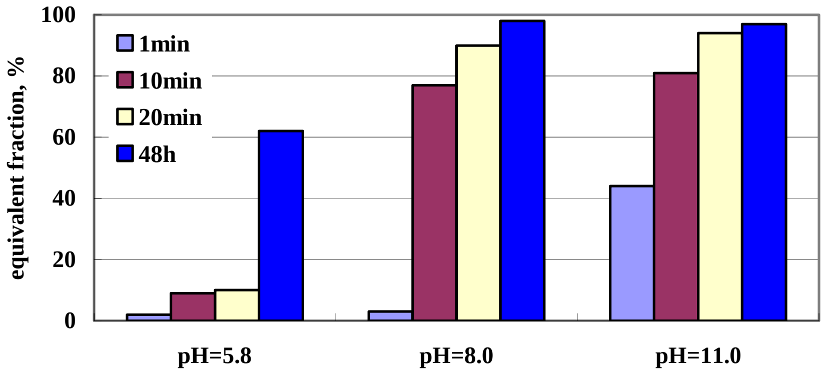

Figure 4-11: Effects of pH on the uptake of heavy metals,

4.4 Conclusions

Investigation of the kinetics of adsorption of heavy metal salts onto weakly basic anion exchangers has reveald the following facts:

- At higher heavy metal concentrations the sorption is controlled by the intraparticle diffusion of heavy metal salts. Diffusion across the liquid film can be ruled out by any means.
- At small concentrations film diffusion seems to be the limiting nmechanism. An increasing linear velocity of of the feed water in short fixed bed filters could accelerate the rate of sorption.
- The presence of inorganic ligands such as Cl^- ions has a negligible influence on the rate of uptake of heavy metals. However, the presence of humic substances may decrease the rate.

5. Column elimination experiments

5.1 Experimental methods

The column experiments in the laboratory scale were carried out in test installations whose schematic is shown on figure 1. The filter column for the laboratory scale experiments had an inner diameter of 1.2, 2 or 3 cm and the bed height amounted to 5-30 cm. Raw water from a reservoir was first pumped to an intermediate vessel from which it was conducted across the filter in upstream direction. pH was measured and recorded and samples were taken from the effluent. Throughput was adjusted to 5-20 bed volumes per hour.

The installations used at ITC-WGT and INET were basically identical.

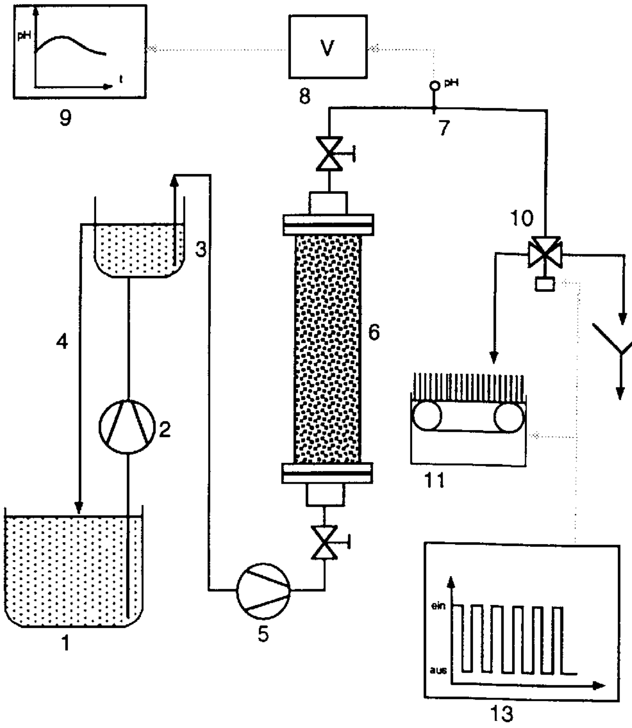

Figure 5-1: Schematic of test installation [38]. 1 = Raw water, 2 = pump, 3 = intermediate vessel, 4 = back flow, 5 = pump, 6 = resin filter, 7 = pH electrode, 8 = pH meter, 9 = recorder, 10 = three-way valve,11 = sampler, 12 = effluent, 13 = switch

The development of breakthrough was measured by means of samples taken by an automatic sampler. Furthermore, the effluent pH was measured and recorded. Throughput of raw water was varied between 5 and 40 bed volumes per hour (BV/h). Throughput during regeneration was usually 2 – 2.5 BV/h.

Raw water usually consisted of normal tap water which was spiked with heavy metal salts to achie the desired raw water concentrations.

5.2 Elimination of cadmium

5.2.1 Preliminary experiments

Preliminary eperiments have been carried out to find out the suitable flow rate and contact time to obtain a satisfactory elimination. Results of experiments with Duolite A7 at flow rates of 20 and 40 BV/h (corresponding to 3 and 1.5 min empty bed contact time, EBCT) are plotted in figure 5.2.

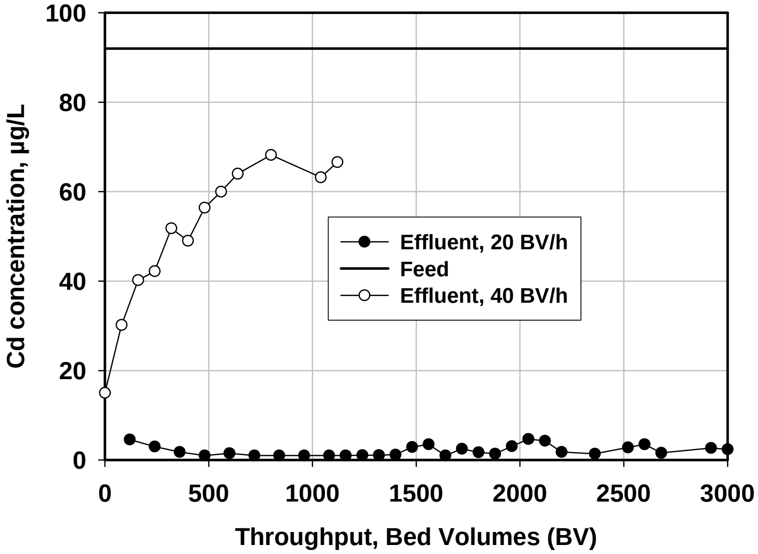

Figure 5-2: Cadmium breakthrough curves at throughputs of 20 and 40 BV/h.

The results indicate that the contact time should not be below 3 min. Therefore, 20 BV/h were selected for all following experiments.

Cadmium is forming chloro complexes which are anionic and, therefore, cannot be adsorbed at approximately neutral pH values [39 - 41]. The influence of the background chloride concentration has been investigated in tests with pure $Cd(NO_3)_2$ as feed water to which different amounts of NaCl had been added. The results are plotted in figure 5-3.

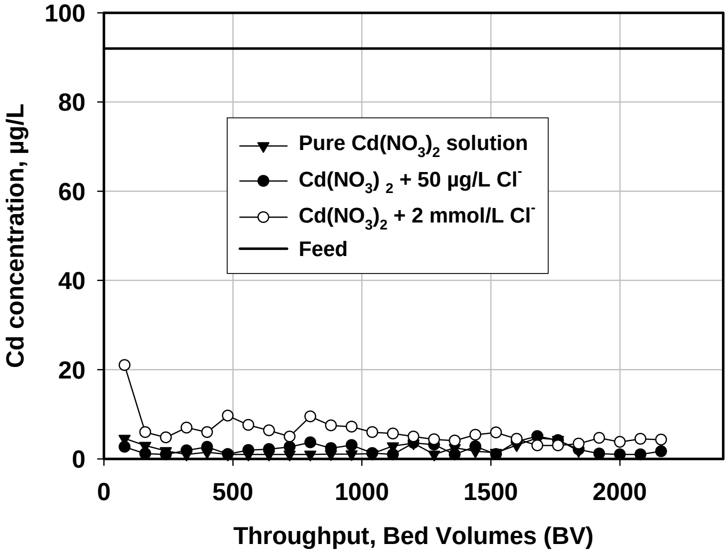

Figure 5-3: Elimination of cadmium from a pure solution and from NaCl-spiked pure solutions. Exchanger: Duolite A7. Throughput: 20 BV/h.

The experiments demonstrated that the uptake of cadmium is more or less slightly affected by the presence of chloride ions. Fortunately, this influence is of minor importance in natural waters. The difference becomes obvious from a comparison of the initial breakthrough curves with destilled and natural water of the same cadmium concentration. As can be seen from the results plotted in figure 5-4 the effluent concentrations for the natural water are smaller and more stable. This is a consequence of the buffer properties.

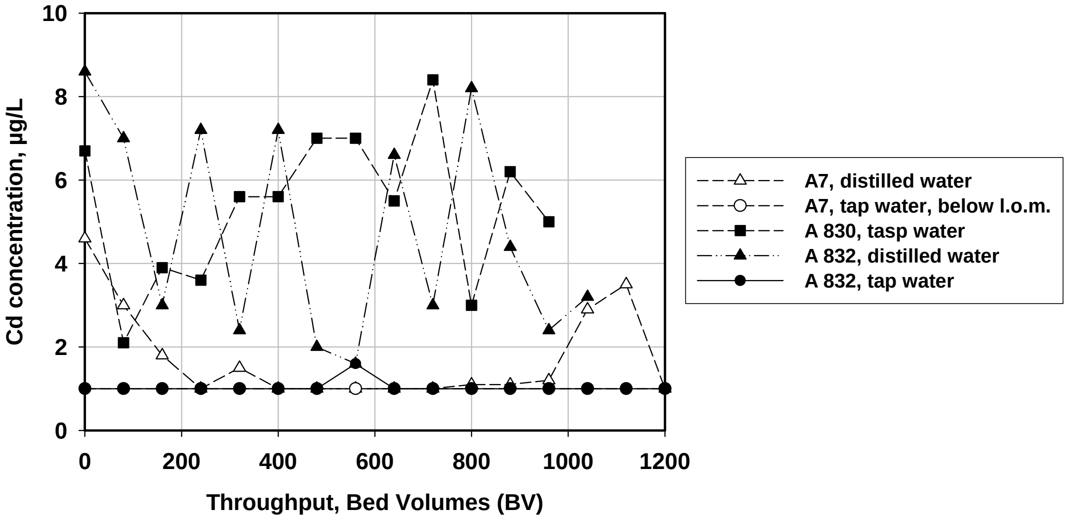

Figure 5-4: Comparison of cadmium elimination from distilled and tap water. Throughput: 20 BV/h (l.o.m. = limit of measurement).

Weakly basic anion exchangers have the ability to adsorb dissolved organic compounds (DOC). To judge the respective elimination some experiments have been carried out with distilled water and commercially available humic acid. The respective results are presented in figure 5-5. They reveal, that the elimination of heavy metals will always be combined with a substantial decrease of the content of dissolved organic matter.

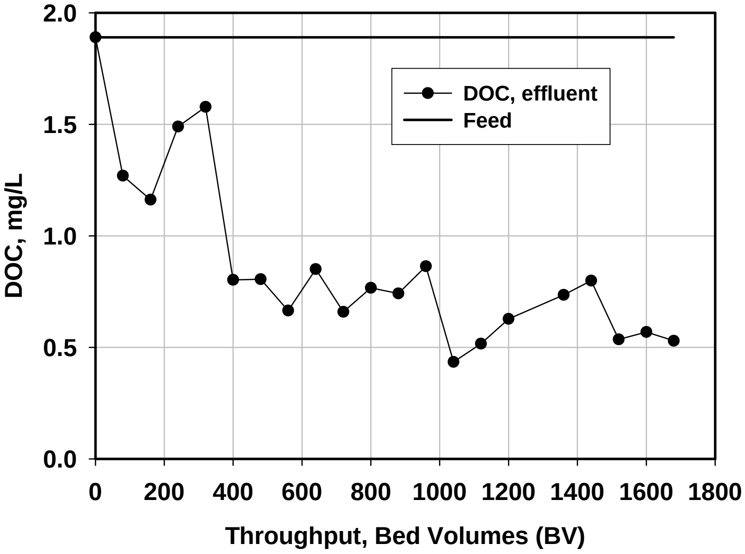

Figure 5-5: Development of DOC elimination. Exchanger: Duolite A7, throughput: 20 BV/h.

5.2.2 Elimination from spiked tap water

Figure 5-6 shows the breakthrough curve of an for cadmium removal experiment with the exchanger Duolite A7. Feed concentration amounted to about 92 µg/L. The development of the breakthrough curve shows that for about 7000 bed volumes the effluent concentration is below the limit of measurement for flame AAS (1 µg/L) and, therefore, also below the desired maximum concentration of 5 µg/L. Due to the non-suppressed exchange of sulphate for hydroxyl ions the effluent pH is initially greater than 8. However, it drops rather quickly and corresponds with the feed pH after 2000 BV. For the given background composition and especially for this chloride concentration an very satisfactory elimination was achieved [42].

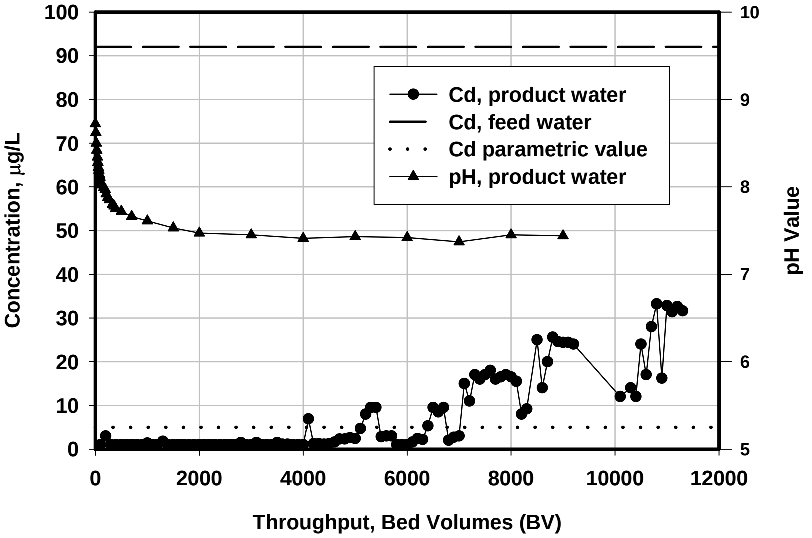

Figure 5-6: Cadmium concentration and pH value in the effluent. Resin: Duolite A7, Throughput: 20 BV/h.

In the experiment of figure 5-6 the DOC had been increased to app. 15 mg/L by means of commercially available humic acid. This concentration is much higher than that in usual raw waters. Nevertheless, DOC was decreased to about 1 - 2 mg/L, apart from eliminating cadmium.

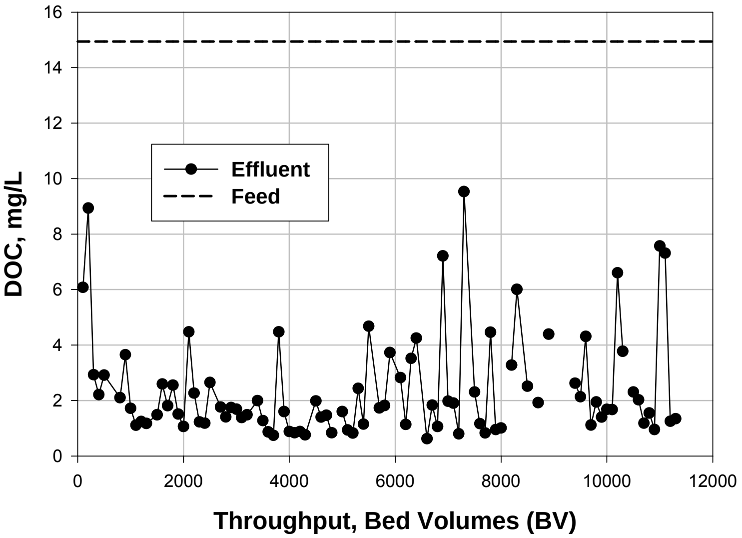

Figure 5.7: Elimination of DOC parallel to the elimination of cadmium. Resin: Duolite A7 [42].

5.2.3 Regeneration

Regenerations was carried out by means of sulfuric acid, exclusively. Regeneration of the exhausted exchanger Duolite A 7 with sulfuric acid was studied by means of resin material which had been pre-loaded by about 1,142 g/L Cd. In the first series of experiments the concentration of sulfuric acid was varied between 0.01 and 1 mol/L. The respective effluent concentrations are plotted in figure 5-8. It becomes obvious that an increase of concentration improves the efficiency. The peak concentration becomes higher and the volume of acid needed for complete elution becomes smaller. A certain disadvantage, however, might stem from the increase of temperature due to the dilution of sulfuric acid in the column.

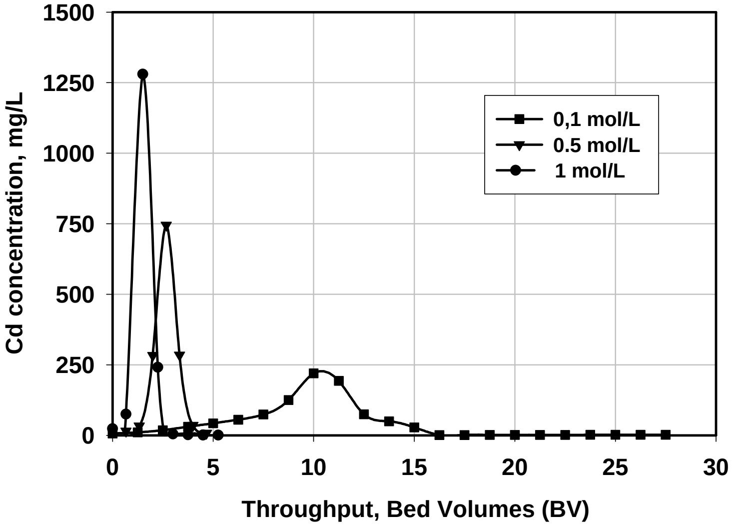

Figure 5-8: pH value and cadmium concentration in the effluent of regeneration with sulphuric acid (0.1 - 1 mol/L). Resin : DUOLITE A7, Throughput: 2.5 BV/h.

The second series comprised the study of the flow rate at a given sulfuric acid concentration. With decreasing flow rate the contact time between resin material and sulfuric acid increases. As a consequence, the elution of cadmium becomes more effective resulting in a narrower and higher concentration peak in the effluent (figure 5-9). From the results of both series a sulfuric acid concentration of 0.5 mol/L and a flow rate of 2 BV/h were selected for the further experiments.

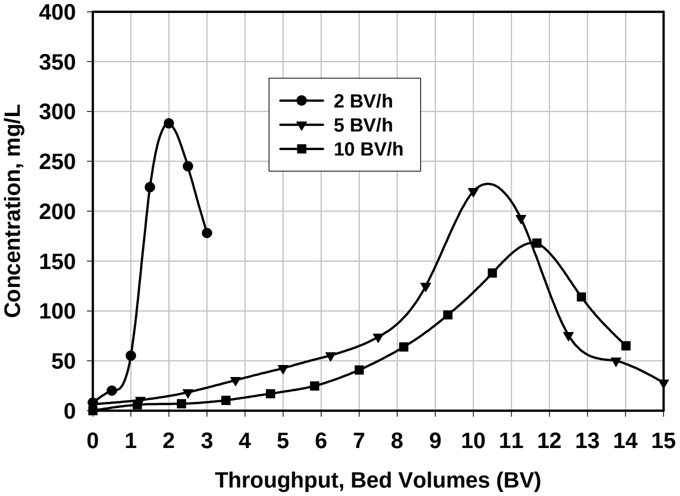

Figure 5-9: Development of Regeneration using 1 molar H_2SO_4 at different rates of filtration. Resin: Duolite A 7.

Figure 5.10 shows the development of cadmium concentration during regeneration with 1 molar H_2SO_4. As can be deduced about 4 BV of concentrated acid are required. The displacement of metal salts coincides with the development of pH which, therefore, can be used for process control. The amount of cadmium displaced is approximately equal to the amount eliminated in the service cycle.

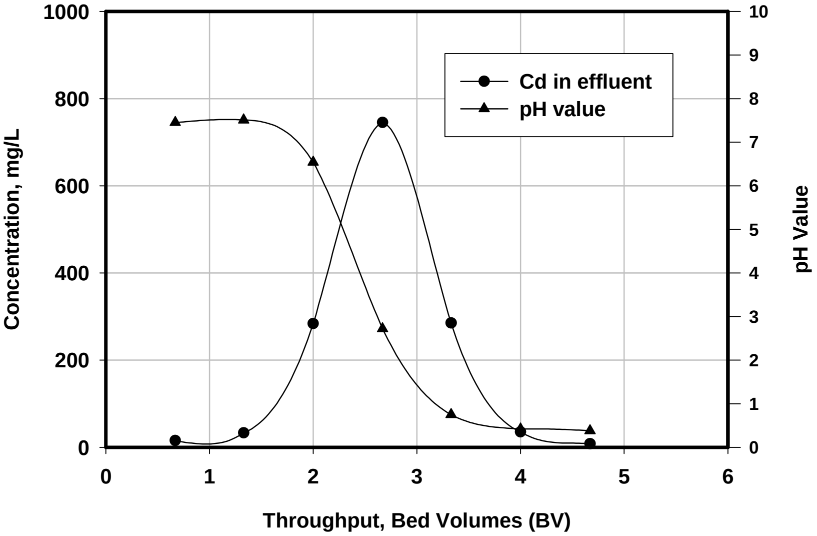

Figure 5.10: Development of Cd concentration and pH during regeneration with 1 molar H_2SO_4. Resins: Duolite A7 [42].

In a final series the re-use of spent acid containing cadmium at different levels was studied. For this purpose $Cd(NO_3)_2$ was added to the sulphuric acid solution. The concentration of sulphuric acid was adjusted to 0.5 mol/L. The development of regeneration at different initial cadmium concentrations is plotted in Figure 5-11. In all cases the elution of cadmium was complete and required about 3 BV of acid.

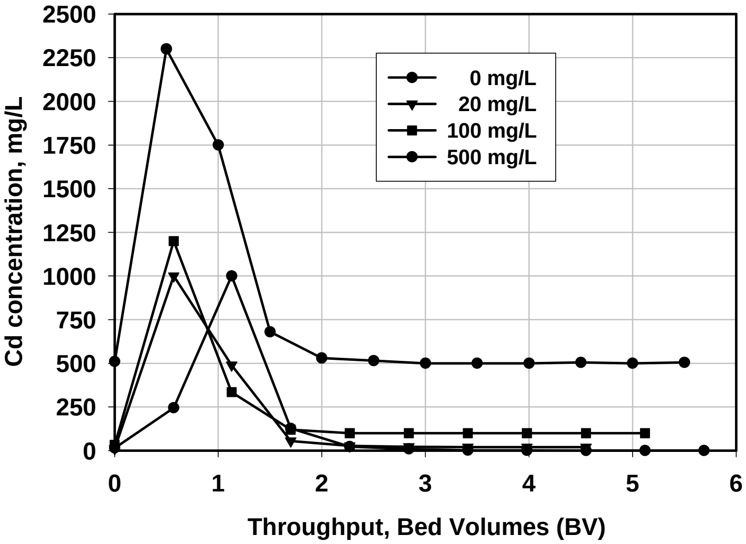

Figure 5-11: Development of cadmium concentration during regeneration with cadmium-bearing sulfuric acid.

During elution of heavy metal species by means of sulphuric acid only minor amounts of humic substances are released. The bulk part of humic substances is eluted during the second regeneration step, the treatment with NaOH (figure 5-12).

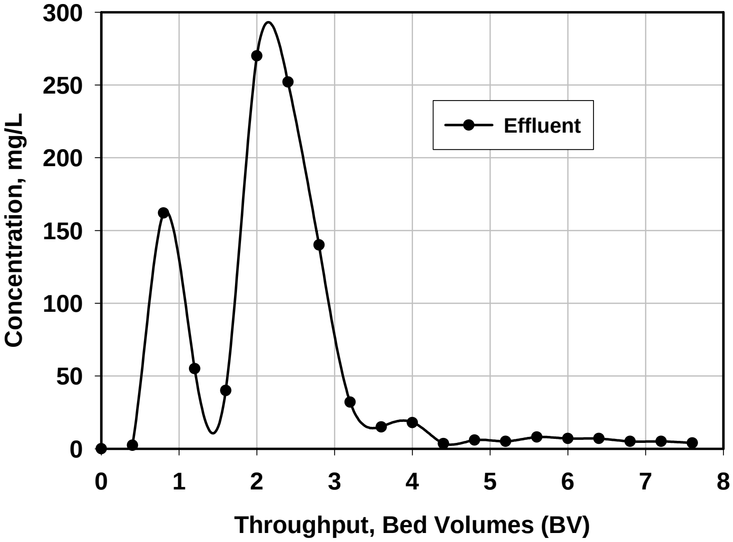

Figure 5-12: Development of DOC in the effluent of the second regeneration step with NaOH (1 mol/L). Resin : Duolite A7, Throughput: 2,5 BV/h [42].

5.3 Elimination of mercury

5.3.1 Preliminary studies

Preliminary studies with respect to mercury removal aimed at the selection of the best suitable exchanger. Experiments were carried out using spiket tap water. Corresponding to the generally small concentrations in Hg-contaminated waters the feed concentrations were between 5 and 15 µg/L.

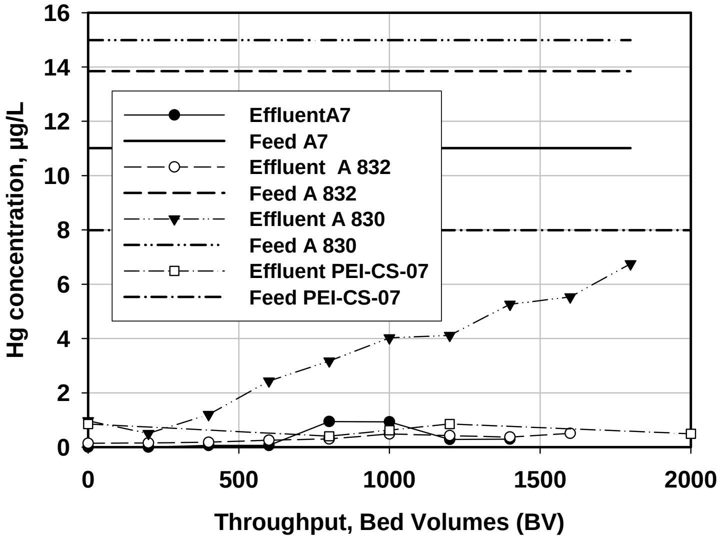

Figure 5-13: Results of screening tests using four different exchangers. Throughput: 20 BV/h.

Figure 5-13 shows the results of screening tests with four different weakly basic anion exchangers. As the results show only the exchanger Purolite A 830 seemed to be not suitable for mercury removal. Among the other resins Fuji PEI-CS-07 and Duolite A7 revealed a very good performance at small concentrations and were, therefore, selected for experiments with greater total throughputs.

5.3.2 Removal of mercury from spiked tap water

Results of respective experiments for mercury elimination from spiked tap waters at feed concentrations of 5-8 μg/L are shown in figures 5-14 and 5-15. For spiking HgCl2 was applied. The speciation of mercury is described in literature [43 - 47]. Figure 5-14 shows results from the application of the resin Fuji PEI-CS-07. Apart from few samples the effluent concentration was < 1 μg/L until the end of the experiment after a total throughput of 16,000 bed volumes.

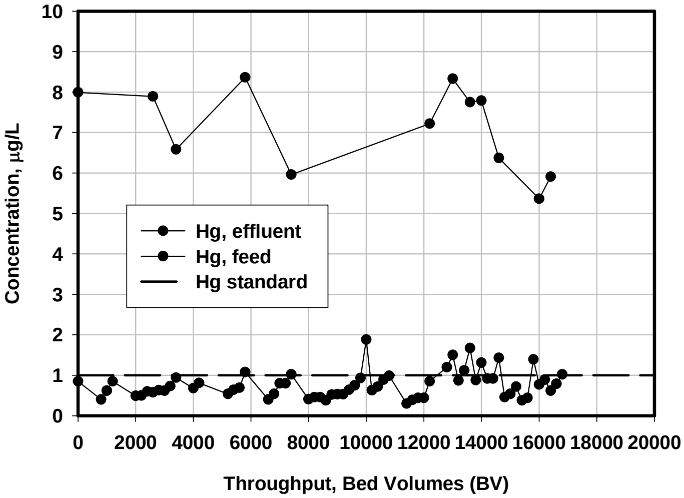

Figure 5-14: Concentration of mercury in feed and effluent. Exchanger: Fuji PEI CS 07, Throughput: 20 BV/h.

A similar result was obtained with the Chinese resin 701 using spiked tap water at a feed concentration of app. 4 µg/L and a throughput of 20 BV/h. The respective breakthrough curve is plotted in Figure 5-15.

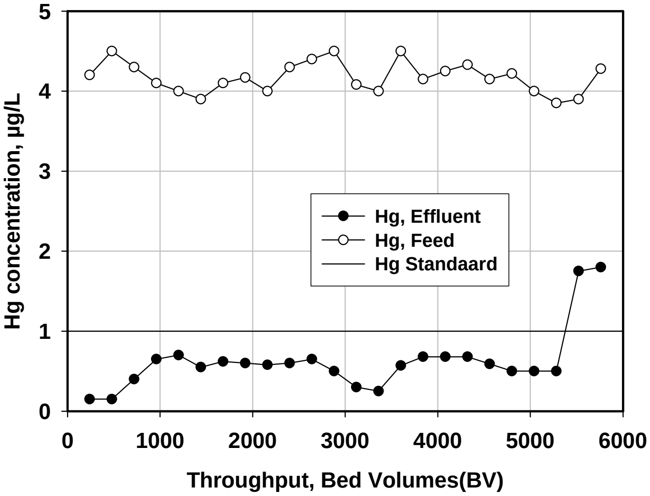

Figure 5-15: Concentration of mercury in feed and effluent. Exchanger: 701, throughput: 20 BV/h.

Although the initial performance is good the length of the service cycle with Hg concentrations below the limit of drinking water is much shorter than for the chitosan-based resin PEI-CS-07.

Duolite A7 has been tested at a relatively high feed concentration of app. 75 µg/L. the results are given in figure 5-16. The effluent concentration is above the limit for drinking water for practically the entire duration of the experiment, nevertheless concentrations between 1 and 5 µg/L can be achieved. Obviously the resin was not yet exhausted.

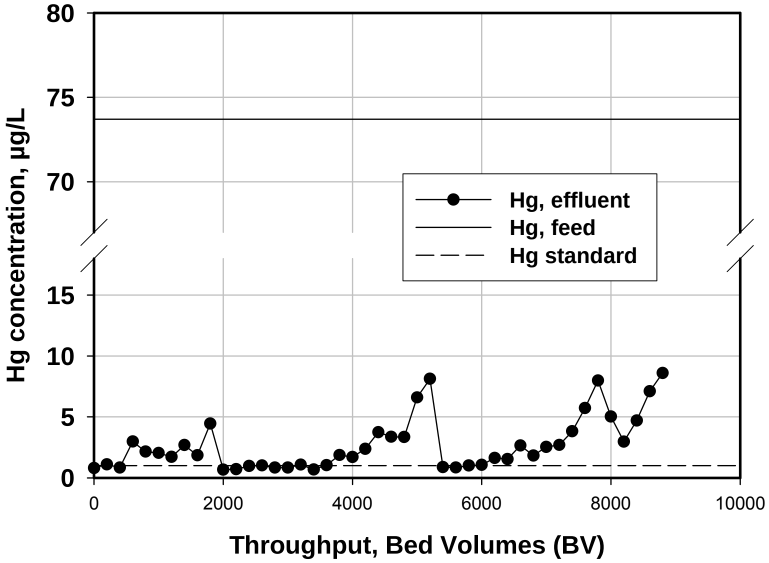

Figure 5-16: Breakthrough performance of Duolite A7 at a raw water concentration of 73.5 µg/L. Throughput: 20 BV/h.

5.3.3 Regeneration

As in the case of cadmium a complete displacement of mercury from the exchanger is achieved by means of about 5 bed volumes of sulphuric acid (0.5 mol/L). The development of regeneration is presented in figure 5-17.

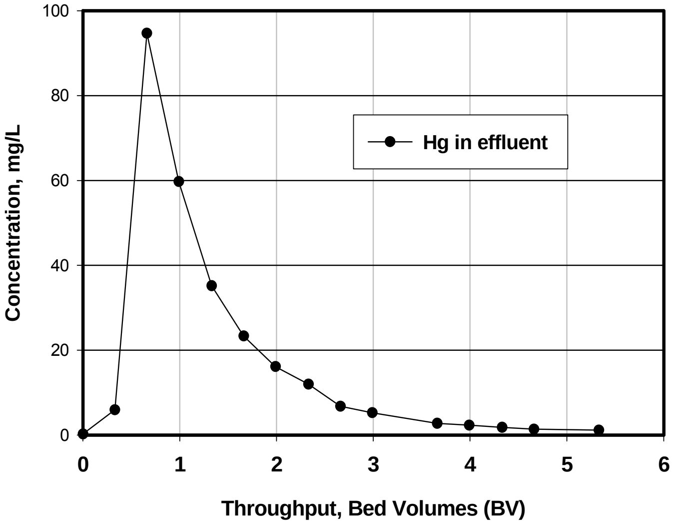

Figure 5-17: Development of regeneration. Exchanger: Duolite A7. Throughput: 2 BV/h

The development of regeneration in the case of the experiment with the Chinese resin 703 (figure 5-15) is plotted in figure 5-18 which shows mercury concentration and pH value. As can deduced from both figures there is a practically complete displacement of mercury species from the exchanger during the regeneration phase.

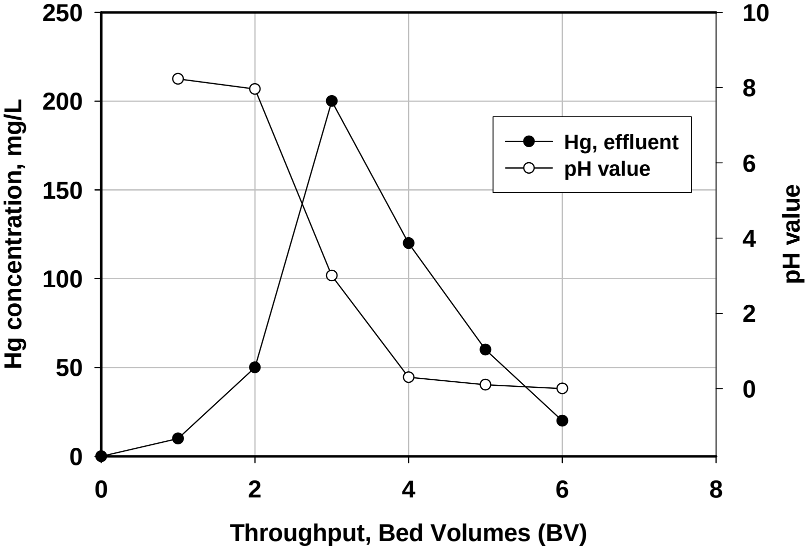

Figure 5-18: Development of Hg concentration and pH value during regeneration of the Chinese resin 703. Regenerant: H_2SO_4, 0.5 mol/L. Throughput: 2.5 BV/h.

5.3.4 Elevated mercury feed concentrations

Experiments at much greater feed concentrations (20 mg/L in de-ionised water) were carried out at INET in Beijing. The respective raw waters would not be considered as potential sources for drinking water. Nevertheless, the respective results might be of interest for remediation of ground waters contaminated with mercury. The respective results are shown in Figurre 5-19. Is is obvious that certain exchangers although without thiol or similar groups are able to adsorb mercury species very effectively.

The development of regeneration of the resin 703 by means of 0.5 molar H_2SO_4 is shown in figure 5.20. As becomes obvious a sharp peak with a very high mercury concentration is obtained. Despite of only few data it can be concluded that the mercury species are completely displaced from the exchanger.

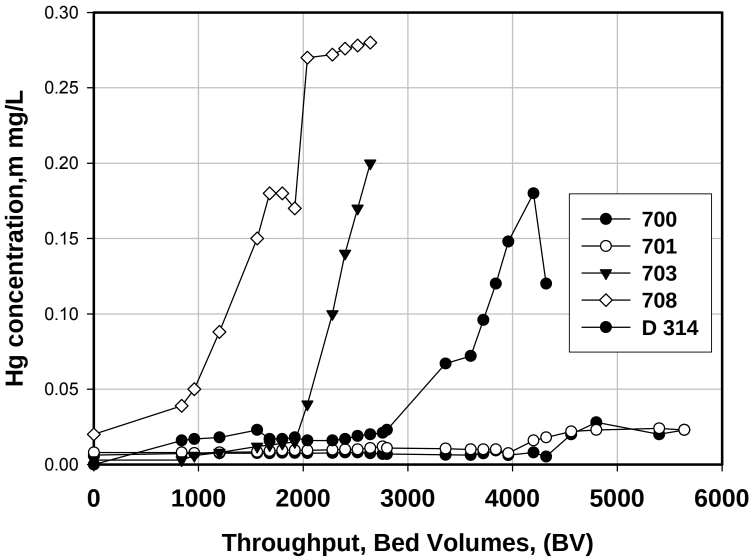

Figure 5-19: Development of Hg elimination from spiked tap water at elevated feed concentrations (20 mg/L)

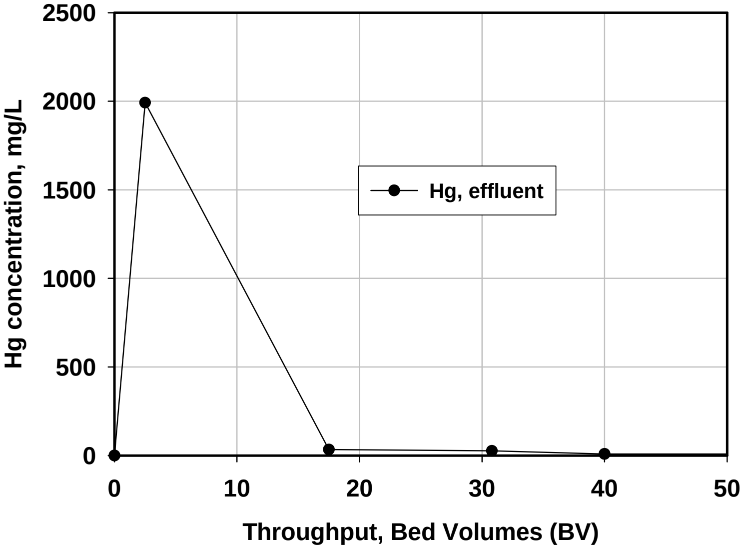

Figure 5-20: Development of regeneration of resin 703 after removal of Hg from solutions with elevated feed concentration. Regenerant: H_2SO_4, 0.5 mol/L, throughput: 2.5 BV/h.

5.4 Further metals, mixtures of several heavy metal cations

Figure 5-21 shows the development of nickel in the effluent of an experiment with a much higher feed concentration. Despite of the high feed concentration significant amounts of nickel (35 µg/L) have been found only after a total throughput of 1500 BV. Unfortunately, the rate of sorption turned out to be rather poor and could not be increased beyond 10 BV/h without significant loss of efficiency.

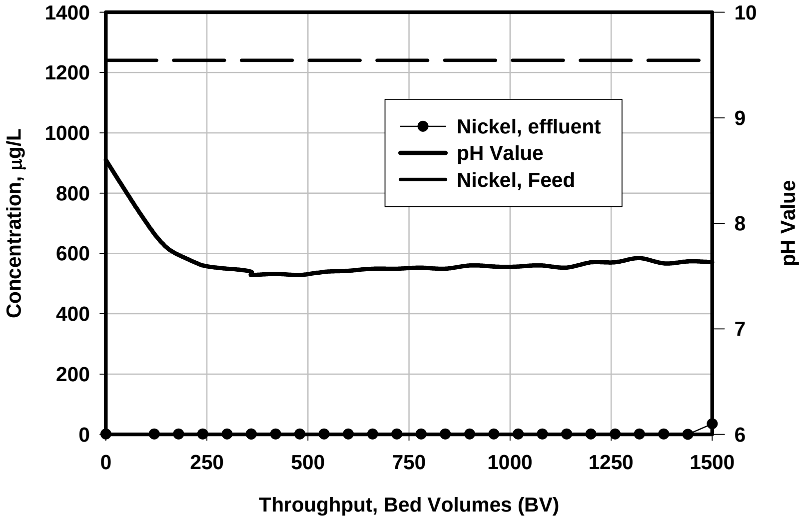

Figure 5-21: Development of nickel in the effluent of an experiment with spiked tap water. Resin: Duolite A7. Throughput: 10 BV/h [48].

Similar favourable results were obtained for the elimination of zinc from an effluent of a former mine and of lead using Duolite A7. Zinc was detectable in the product water only after a total throughput of 1850 BV. Lead was decreased from 100 µg/L to less that 5 µg/L.

Figure 5-22 shows the breakthrough performance from the combined elimination of cadmium (40 – 90 µg/L), mercury (8 – 10 µg/L) and lead (60 – 80 µg/L). For the entire duration of the experiment the concentration of mercury was below 0,5 µg/L whereas the concentrations of cadmium and lead remained below the respective limits of measurement by means of AAS (10 µg/L for lead and 1 µg/L for cadmium). These are given as bars in the diagram.

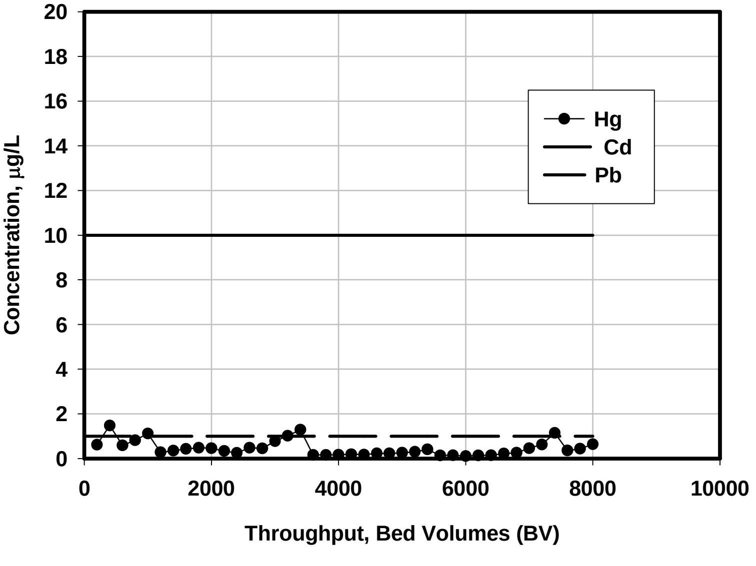

Figure 5-22: Development of the simultaneous elimination of lead, cadmium and mercury. Exchanger: Duolite A7, Throughput: 20 BV/h.

The results of this experiment reveal that and effective elimination is also possible if several heavy metals are present. Mercury removal was even better that in the experiments without other metals. This coincides well with earlier results of the simultaneous elimination of copper and nickel. In that case the copper removal was better if the exchanger had been pre-saturated with nickel.

5.5 Removal of chromium(VI)

5.5.1 Selection of suitable exchange resins

Elimination of chromium(VI) from de-ionised water was studied at INET to select suitable Chinese exchangers. The concentration of Cr (VI) in the raw water amounted to 5 mg/L, the flow rate was kept at 5 BV/h. The results of elimination of Cr (VI) were given in Table 5-1 as the thoughput in bed volumes until the limit for drinking water of 50 µg/L was exceeded.

Table 5-1: Results from the elimination of Cr(VI).

Resin	Max. Throughput, BV
SM1	4010
SM2	4090
700	<50
703	<50
701	990
D301	170
D314	<50
708	<50

In this series of tests the exchangers SM1 and SM2 with their secondary amine (45%) and quarternary amine (55%) groups revealed a larger exchange capacity than the other resins. The true weakly basic exchanger exhibited a much smaller capacity.

Results of preliminary tests with an acrylic and a styrene-DVB resin and spiked tap water at ITC-WGT gave another hint for the selection of the appropriate exchanger. The respective breakthrough curves are plotted in figure 5-23. They clearly demonstrate the superiority of the acrylic exchanger.

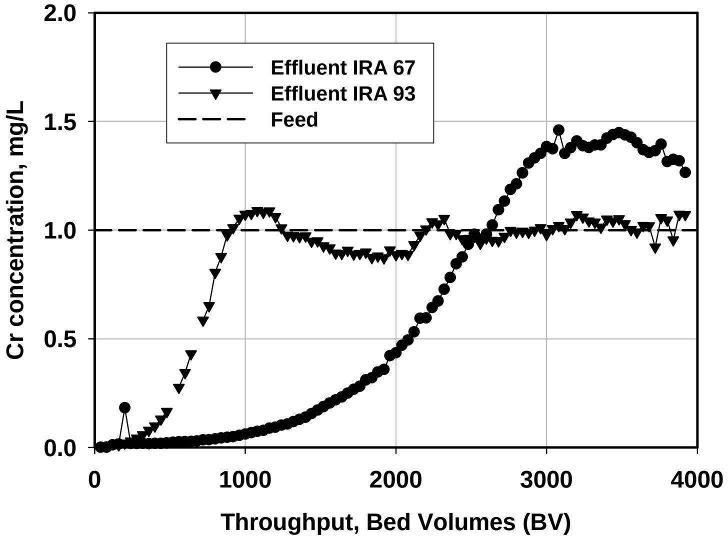

Figure 5-23: Development of chromium effluent concentrations for Amberlite IRA 67 and Amberlite IRA 93. Throughput: 10 BV/h.

5.5.2 Elimination at trace concentration levels

According to the previous results acrylic weakly basic anion exchangers can be expected to have favourable properties for the uptake of chromate ions. Figure 5-24 shows a comparison of the breakthrough performance of an acrylic and a styrene-DVB resin at trace concentration levels. (For the limit of measurement (5 µg/L), 5 µg/L were assumed.

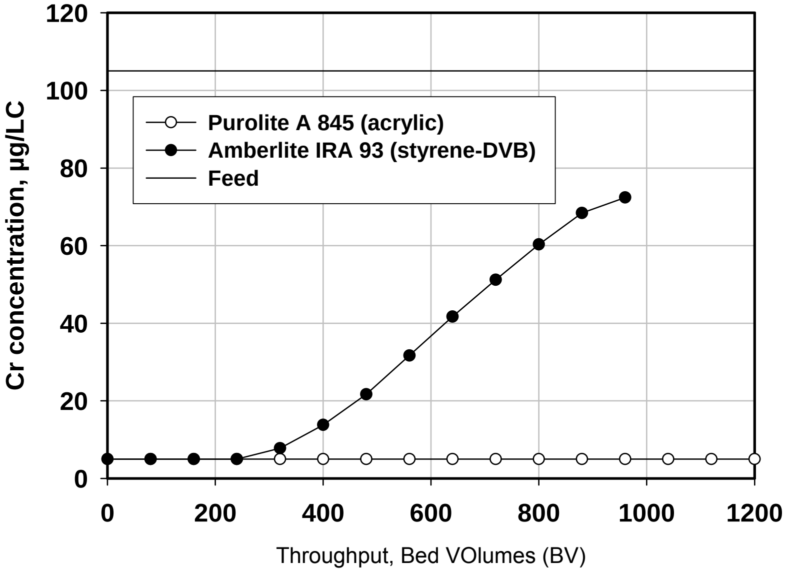

Figure 5--24: Comparison of the performance of an acrylic and a styrene-DVB resin. Throughput: 20 BV/h.

5.5.3 Influence of sulfate concentration

Despite of the preferred uptake of chromate the much higher concentration of sulfate should have some effect on the sorption of chromate. Figure 5-25 shows results of the chromate elimination by means of the exchanger Amberlite IRA 67 at three different sulphate concentrations of the feed water. Comparison of the breakthrough curves reveals the preferred uptake of chromate, which however, is affected at elevated sulphate concentrations. At feed concentrations of about 110 µg/L of chromate and 165 mg/L of sulfate the drinking water standard of chromate is exceeded after a throughput of about 700 BV.

5.5.4 Development of effluent pH

The exchange of chromate, sulfate, and some chloride for hydroxyl ions which cannot be suppressed leads to a slight increase of pH in the effluent. Corresponding to the exchanger properties this increase is stronger for the acrylic exchanger (figure 5-26). The increase can be supressed by pre-treating the exchanger with a NaCl solution.

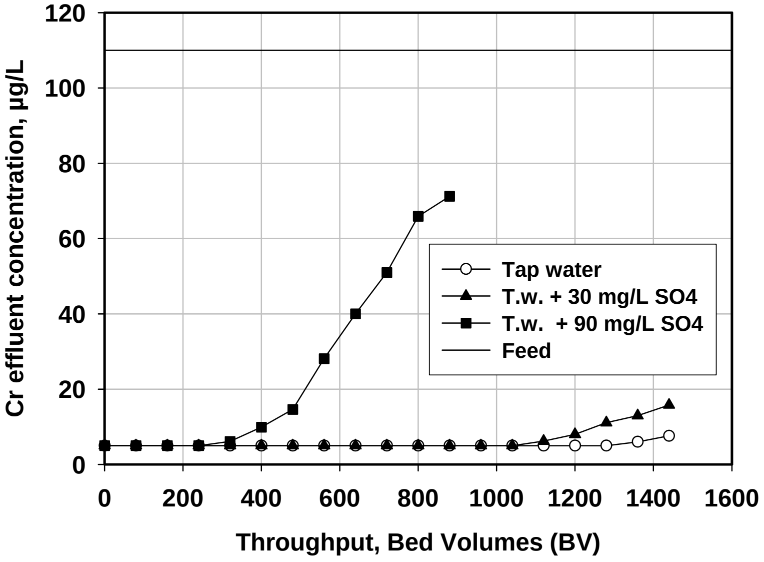

Figure 5-25: Influence of sulfate concentration on chromate sorption. Resin: Amberlite IRA 67. Throughput: 20 BV/h.

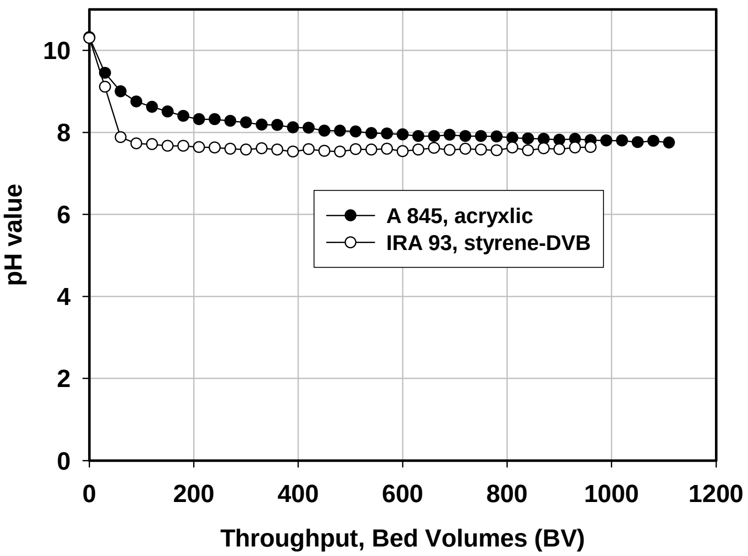

Figure 5-26: Development of pH value in the effluent. Resin: Purolite A 845.

5.5.5 Repeated service/regeneration cycles

Results from three subsequent experiments with the Chinese exchanger SM1 with its high share of strongly basic groups are shown in figure 5-27. Between the service cycles the resin had been regenerated with a mixture of 2 % NaOH and 8 % NaCl at 5 BV/h. The results of one of the regenerations are presented in figure 5-28.

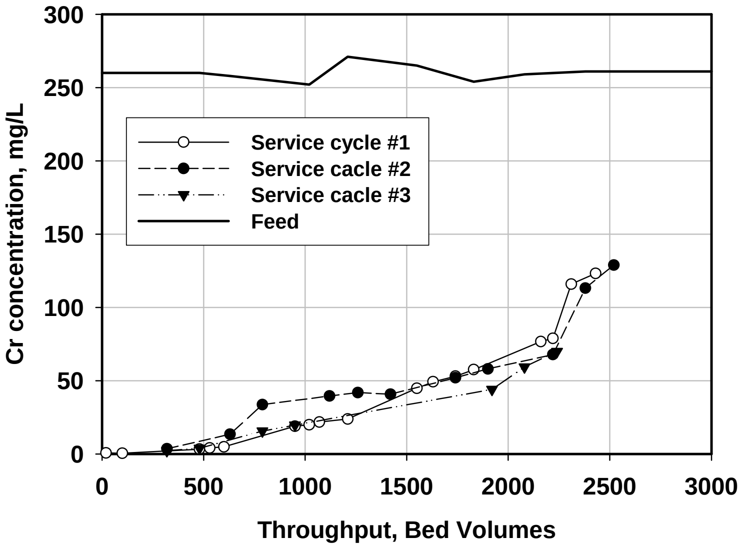

Figure 5-27: Development of chromium(VI) elimination in three subsequent service cycles. Resin: SM1. Flow rate: 20 BV/h.

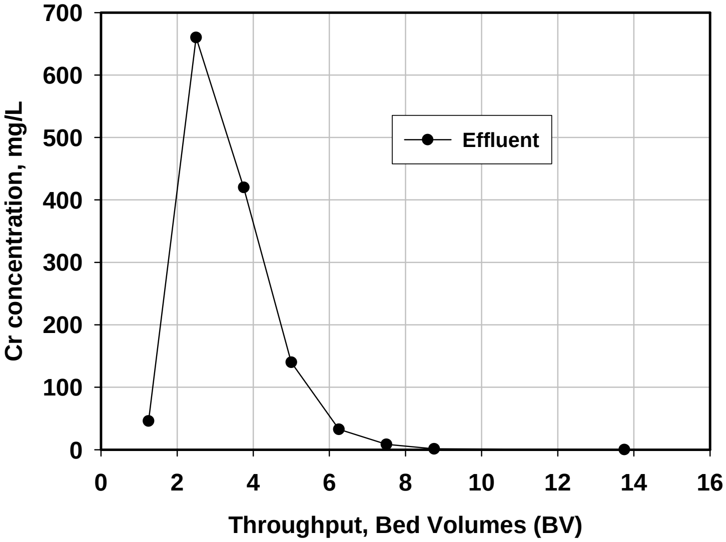

Figure 5-28: development of one regeneration. Resin: SM1. Flow rate: 5 BV/h.

5.5.6 Regeneration

a) Pure NaOH

The development of regeneration using NaOH at different concentrations is shown in figure 5-29 for the resin Purolite A 845. As can be expected an increase ofNaOH concentration leads to a sharp and high Cr peak.

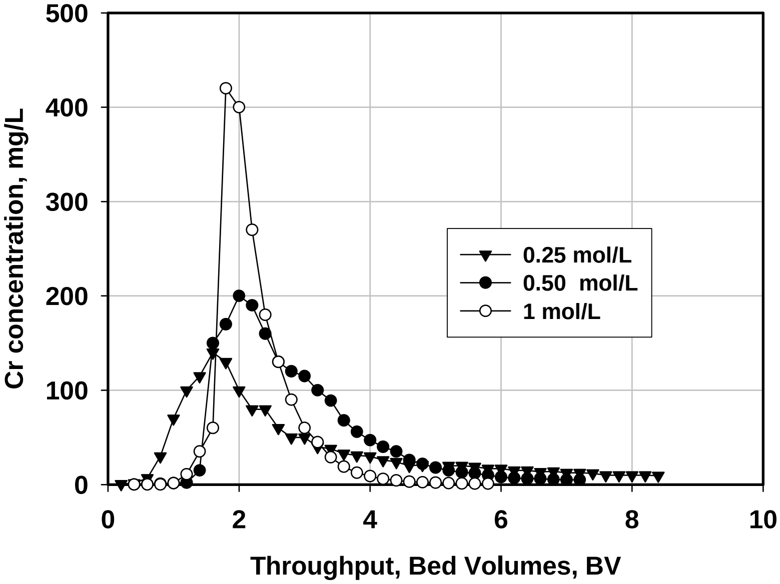

Figure 5-29: Development of Cr concentration during regeneration with pure NaOH of different concentration. Resin: Purolite A 845, throughput: 2 BV/h.

Depending on the concentration chromate is quantitatively displaced from the resin by means of 4 - 6 bed volumes of NaOH. As for the metal cations chromate is concentrated in a relatively small volume which can easily be post-treated.

b) Mixtures of NaOH and NaCl

In order to reduce the amount of the more expensive NaOH the application of mixtures of NaOH / NaCl have been tested for regeneration of the Chinese resin SM1 (45 % secondary amine and 55 % quarternary amine groups). Figure 5-30 shows the respective results which do not allow a clear judgement. The effects should mostly be due to the strongly basic properties and their non-preferred uptake of hydroxyl ions.

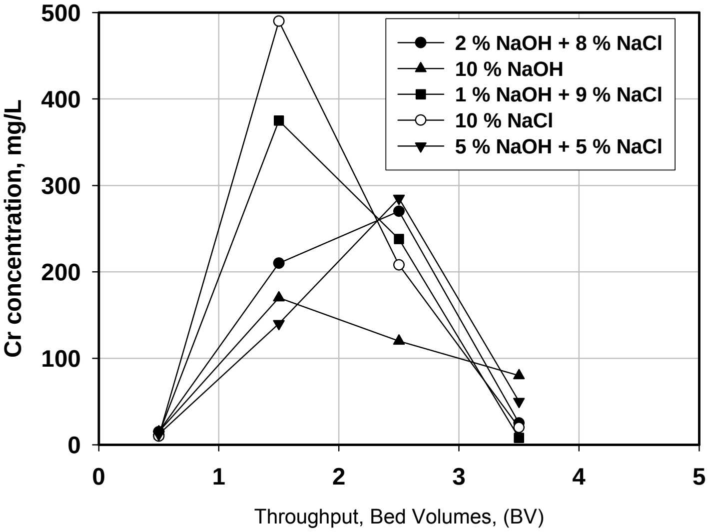

Figure 5-30: Comparison of the efficiency of different mixtures of NaOH / NaCl

c) Re-use of regenerant

The re-use of regenerant has been investigated at INET for the case of the use of a mixture of 2 % NaOH and 8 % NaCl and the exchanger 703. The re-use was simulated by adding chromate-bearing solutions to the fresh regenerant. Figure 5-31 shows the development of Cr concentration during regeneration with the simulated re-used regenerant solutions.

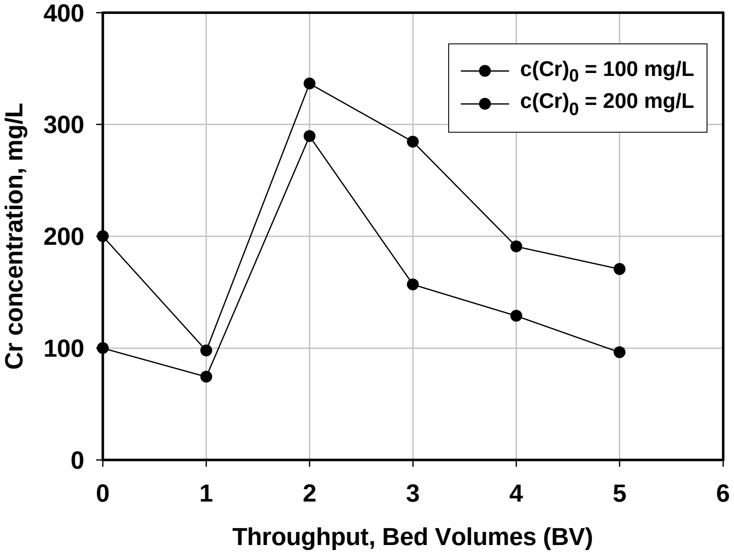

Figure 5-31: Development of Cr concentration during regeneration with Cr-bearing regenerants. Resin: 703, throughput: 5 BV/h.

The development of concentrations reveals that initially there is even an uptake of chromate from the regenerant solutions. The efficiency of chromate displacement obviously deteriorates with increasing concentration in the regenerant.

5.5.7 Elimination of DOC

As with the other weakly basic anion exchangers there is a co-adsorption of humic substances from the feed water. However, because of the properties of the acrylic matrix of the resins the affinity towards humc substances is much smaller that that of styrene-based exchangers. The results as shown in figure 5-32 demonstrate the less effective DOC elimination. As has been known from other applications of such resins in the treatment of naturalwaters the adsorption is completely reversible.

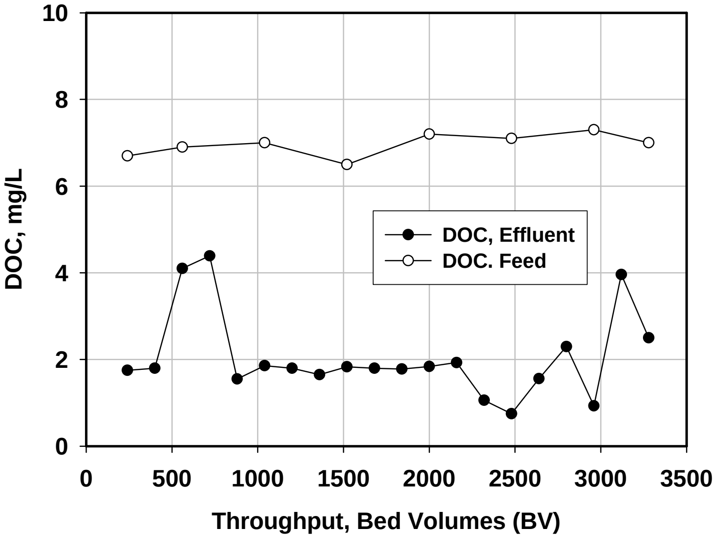

Figure 5-32: Elimination of DOC during the removal of chromate. Resin: Purolite A 845. Feed: Tap water spiked with humic acid

5.5.8 Elimination from contaminated ground water

Results of an experiment with real contaminated ground water are given in Figure 5-33. The water stemmed from the Pfinz valley close to Karlsruhe where the groundwater is contaminated with chromium because of the discharge of Cr-bearing solid waste from a former steel factory. Concentrations in the water are in the range of 100 to 200 µg/L depending on the rainfall. The sulfate concentration amounts to app. 100 mg/L.

The breakthrough curve demonstrates a very satisfactory elimination which coincides well with the results of the laboratory scale tests. During the duration of the experiment the limit for drinking water of 50 µg/L was not exceeded. Unfortunately, the experiments could not be neither extended nor repeated because of the limited amount of raw water.

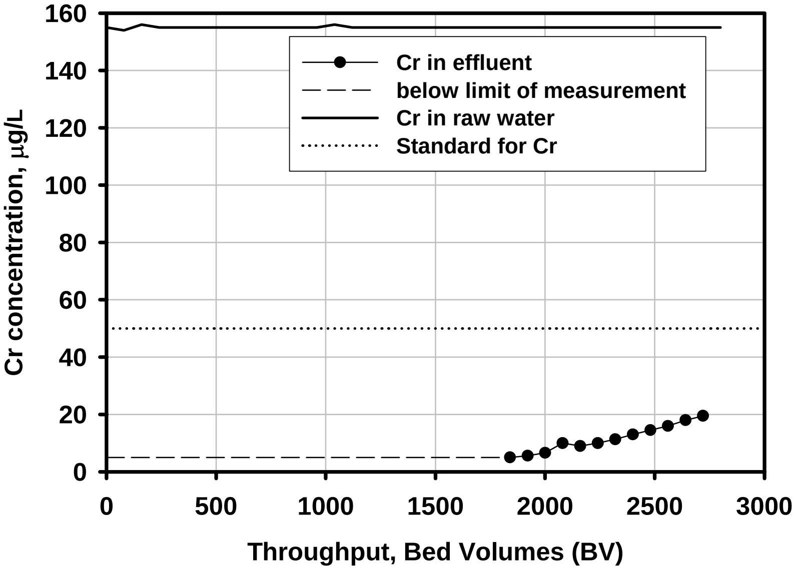

Figure 5-33: Effluent total chromium concentration (tCr) history. Feed water: contaminated ground water. Exchange resins: AMBERLITE IRA 67.

5.6 Simultaneous elimination of heavy metal salts and chromate anions

In few experiments the simultaneous sorption of heavy metal salts and chromate anions by the same resin has been studied. Figure 5-34 shows the results of an experiment with the acrylic exchanger Amberlite IRA 67 which is the preferred acrylic type for chromate removal. The development of breakthrough curves shows that chromate is as well eliminated as in the experiments with only chromate. However, the elimination of cadmium is obviously considerably better than in the case of only cadmium in the feed water.

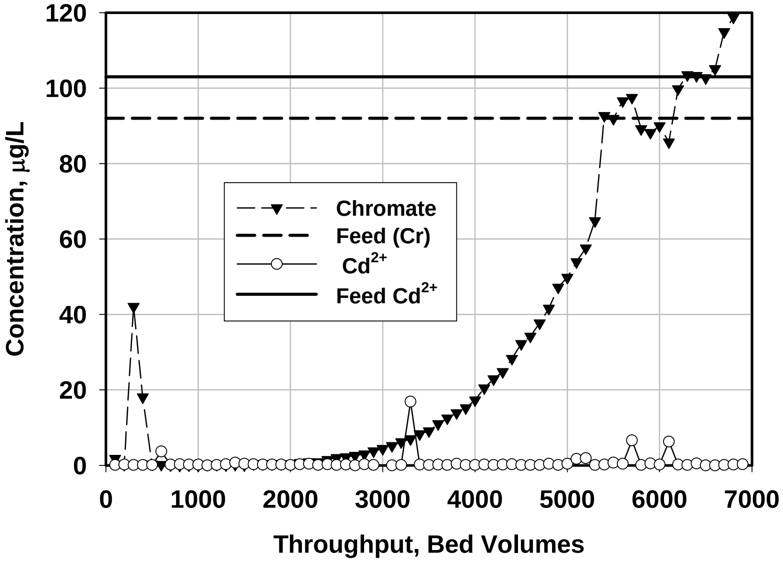

Figure 5-34: Development of the simultaneous elimination of cadmium and chromate from spiked tap water. Resin: Amberlite IRA 67. Throughput: 20 BV/h.

Figure 5-35 shows the results obtained with the exchanger Duolite A7 which turned out to be the most favourable for heavy metal salts remoal.

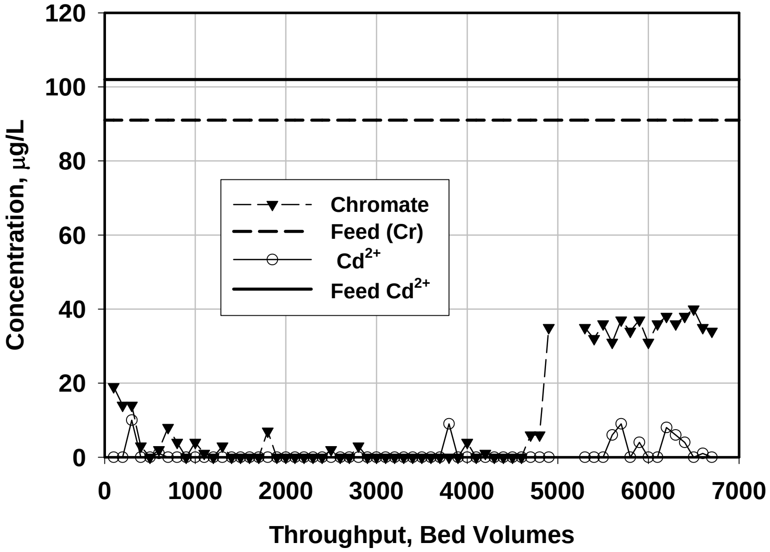

Figure 5-35: Development of the simultaneous elimination of cadmium and chromate from spiked tap water. Resin: Duolite A7. Throughput: 20 BV/h.

This result is surprising with respect to the elimination of chromate by the phenol-formaldehyde resin Duolite A7. The elimination is obviously better than that of an acrylic resin. The sorption of cadmium, however, coincides with that from the results with pure systems.

5.7 Rinsing of the columns

During the regeneration process the exchangers are always treated with NaOH to cnvert them into the free base form. After this step the remaining alkaline solution has to be rinsed out. In order to accelerate this rinsing and to achieve pH values close to that of the feed water carbon dioxide was added to the rinsing water to neutralise the remaining NaOH. Figure 5.36 shows the respective results. Three methods were compared:

- Pure tap water. The flow rate was fixed at 2-3BV/h. The pH of the pure tap water was about 7.8. <In this case more than 40 bed volumes were needed to achieve a pH < 8.0.
- tap water spiked with a certain amount of CO_2. The pH value of this rinsing water was about 5.5. Again, the flow rate was adjusted at 2-3BV/h. In this case about 25 bed volumes of tap water were needed to reach a pH < 8.

Further attempts with increased flow rates led to a faster approach to the raw water pH, however, probably only due to the decreased contact time for neutralisation.

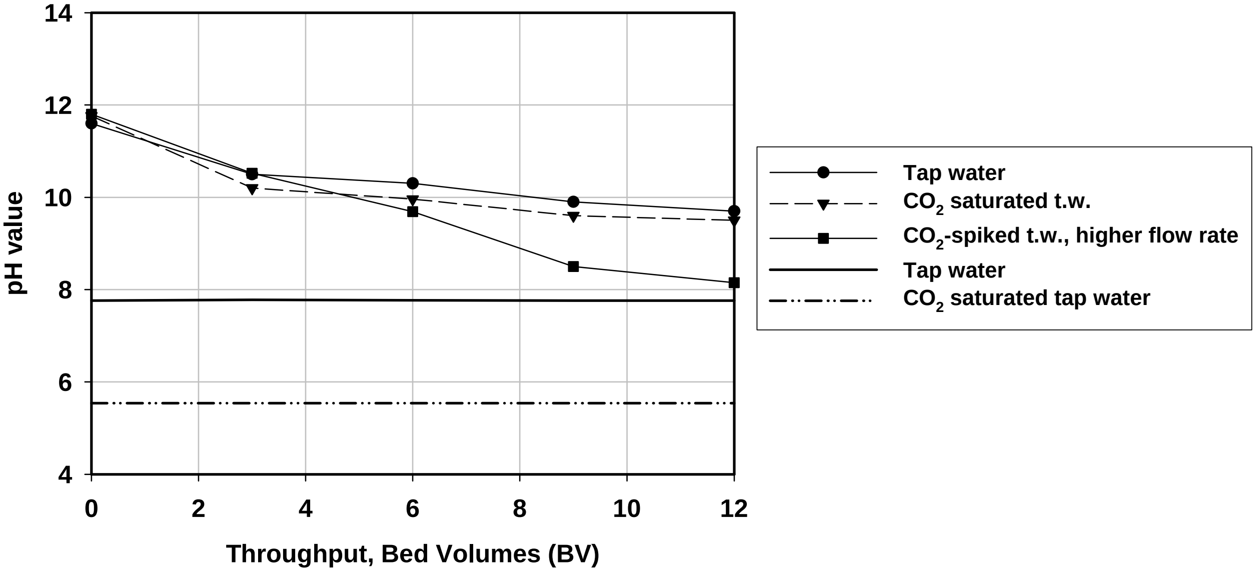

Figure 5-36: Development of pH during rinsing with tap water and CO_2-spiked tap water.

5.8. Sorption of phenol by weakly basic anion exchangers [49]

Weakly basic anion exchange resins containing amine-groups have high degree of selectivity for heavy metals, and permit separation of these ionic compounds from waters containing high levels of calcium, magnesium and sodium ions. Polluted Chinese raw waters may contain trace heavy metals such as Cd, Hg, Cr, Pb and Zn, however, other organic toxic compounds in addition . One important organic contaminant is phenol. To develop the new technology in China, therefore, the simultaneous elimination of heavy metals and phenol has been investigated.

5.8.1 Properties of phenol

Phenols (C_6H_5OH) is a compound with a molecular weight of app. 94 which ahs a sertain solubility in water. At elevated pH values the proton of the hydroxyl group can dissociate thus giving the compound the properties of a weak acid. The dissociation constant of phenol in water is 9.89.

The non-ionic and dissociated species show different adsorption behavior. The pH value of the bulk solution affects phenol speciation. Non-polar and polar resins show the ability to adsorb phenol effectively. There is an excellent adsorption of phenol molecules in acidic to lightly alkaline solutions. Hence, if adsorption is conducted at suitbale distance from the pK value a good efficiency in separation process can be achieved, but the eluting of adsorbate can be done using alkaline solutions. At pH values normally encountered in drinking water phenol is predominantly non-dissociated and can, therefore, be adsorbed by the weakly basic anion exchangers [50].

The Chinese drinking water quality standard related to phenol is 0.002 mg/L

5.8.2 Analytical

Phenol may be analysed through the measurement of the dissolved organic carbon (DOC) the Chemical Oxygen Demand (COD) or by the UV absorption at 254 nm. Results from comparative tests utilizing a series of standard concentrations of phenol solutions are shown in Fig 5-37.

With respect to these calibration results the UV absorption at 254 nm was selected for the investigations.

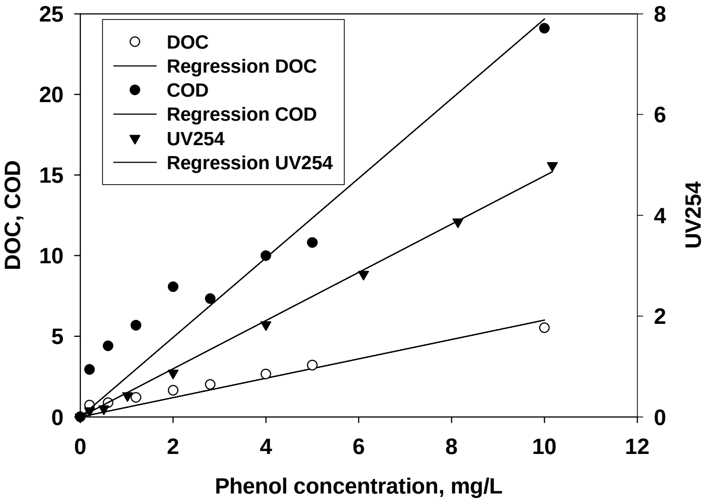

Figure 5-37: Calibration curves of phenol for DOC, COD and UV_{254} measurements.

5.8.3 Elimination of phenol

The experiments on breakthrough curves of phenol were carried by means of parallel series of columns. The feed water was demineralized water spiked with phenol (5 mg/L), the flow rate amounted to 5 BV/h. The results are summarized in Fig 5-38.

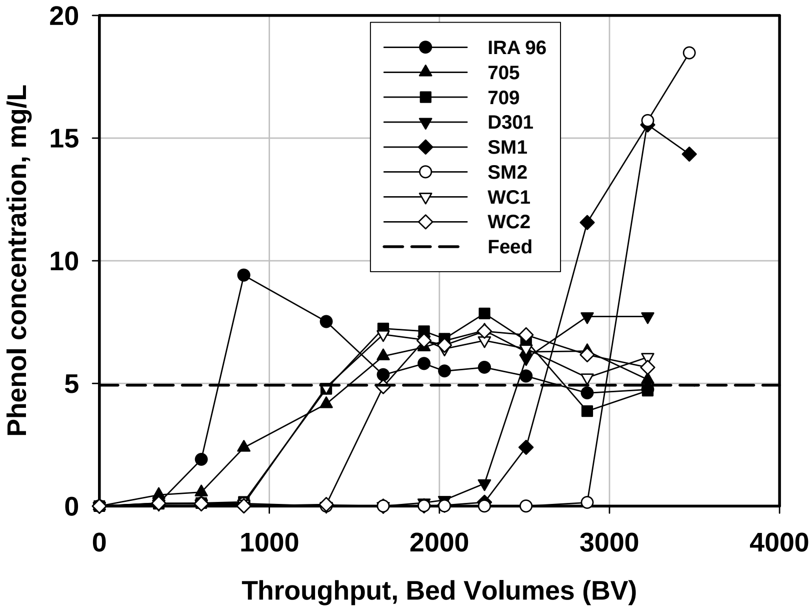

Figure 5-38: Breakthrough curves of phenol with different resins

Figure 5-38 reveals that only the exchanger SM1, SM2 and D 301 allow some uptake of phenol. These resins possess a certain share of strongly basic groups. In that cas phenol molecules dissociate because of the high pH value inside the exchanger. The pK-value of phenol at 25℃ is 9.89:

$$\overline{R-N^{+}(CH_3)_3\ OH^{-}} + C_6H_5OH \rightarrow \overline{R-N^{+}(CH_3)_3\ C_6H_5O^{-}} + H_2O \qquad (5.1)$$

In the further development of sorption phenoate anions are displaced by the preferred inorganic anions like, especially sulfate. By this means the high excess concentration occurs. Apart from the sorption due to ionic interactions there is the pure adsorption of non-dissociated molecules. This adsorption is the predominant mechanism with the other exchangers. The uptake is subject to individial exchanger properties and is higher for resins with tertiary amine groups than with secondary and primary amine groups. The sequence of preferrence is SM2 > SM1 > D301 > WC2 > WC1 > 709 > 705.

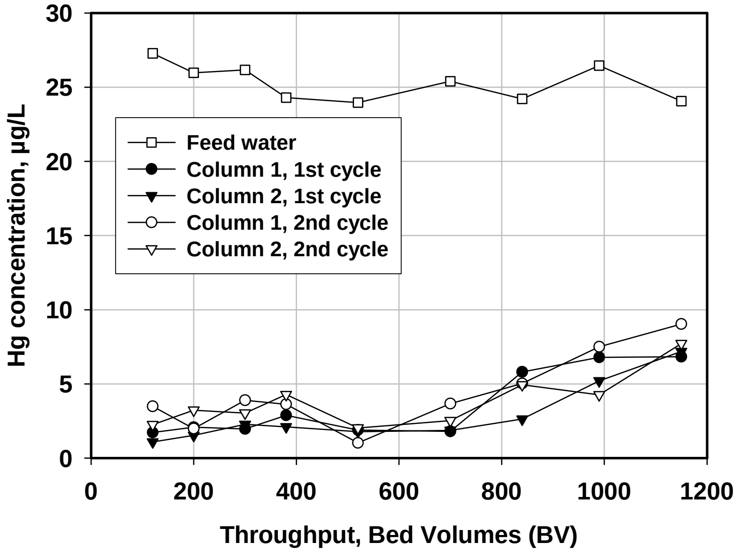

Figure 5-39: Development of mercury elimination during two experiments with two parallel columns. Exchanger: SM1.

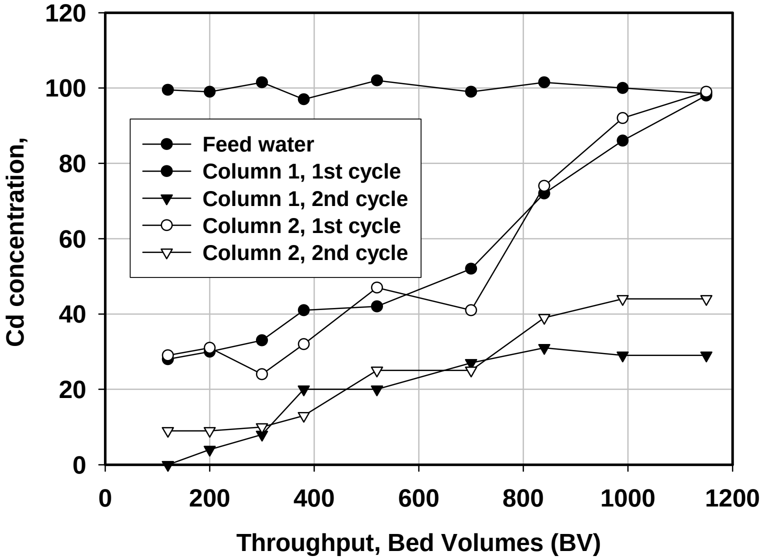

Figure 5-40: Development of cadmium elimination during two experiments with two parallel columns. Exchanger: SM1.

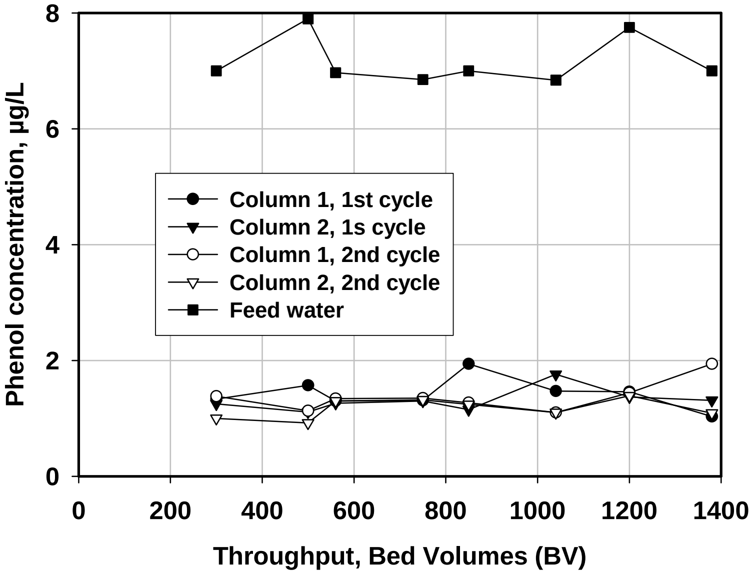

Figure 5-41: Development of phenol elimination during two experiments with two parallel columns. Exchanger: SM1.

5.8.4 Summary

Phenol concentration in effluent from available resins is listed in table 5.2. The resin materials of SM2 and SM1 exhibit the best performance with respect to the phenol removal and regeneration of spent resin.

Table 5-2: Phenol concentration in effluent from available resins

Resin type	Product water (BV)	Effluent below standard, BV	Adsorption capacity (g/L)	Regenerant (BV)	Efficiency of regeneration (%)
705	1400		4.465	45	60.07
709	1330		5.300	45	48.09
D301	2450	1670	11.330	55	84.53
SM1	2600	2030	12.082	30	97.29
SM2	2950	2510	14.280	30	97.05
WC1	1350		5.320	30	44.14
WC2	1650	200	7.329	55	50.57

The adsorption capacity of anion resins for phenol depends on the active sites at ther resin surface and, therefore, the diffusion pathways play a great role. In view of the horizontal and vertical profile of phenol of 21Å and 41.2 Å, respectively, the resins of the acrylic matrix with low cross-linking and large specific surface are more favourable for removing of phenol than SM1 and SM2.

The pH value of bulk solution also influences the adsorption capacity for phenol. Phenol is a weak acid with a pK-value of 9.89 at 25℃. Hence, the pH-value alters the speciation of phenol in solution. At pH < pK, the phenol in solution is predominantly present as non-dissociated molecules, at pH > pK, however as anions. Because of the relatively high degree of protonation of acrylic weakly basic resins phenol anions can be adsorbed by these exchangers, however, much less well by weaklier basic exchangers.

5.9 Conclusions from the laboratory scale filter experiments

5.9.1 Heavy metal salts

The experiments withr espect to the elimination of heavy metal cations, especially of cadmium and mercury (or their respective salts) have demonstrated:

- Weakly basic anion exchangers allow an efficient elimination of cadmium and mercury salts. The effluent concentrations could be decreased below the standards for drinking water, even at feed concentrations only slightly above these standards. The filter throughput until the standards are exceeded are in the range of several thousand bed volumes.
- Initially, the effluent pH is above that of the feed water. This can be suppressed by a pretreatment with NaCl solution during the final rinsing of the column.
- It seems that phenol-formaldehyde-based resins have optimum properties for removal of all kinds of heavy metals cations. A few other anion exchangers exhibit similar properties.
- Because of the slow kinetics of uptake the linear velocity in a filter is limited. For the short filters used in the investigations (< 25 cm bed height) the contactt ime should not be less than 3 min. At a throughput of 20 bed volumes per hour this corresponds to a linear velocity of 5 m/h. At greater bed heights the throughput can be increased.
- The presence of further metal cations increases the efficiency of uptake of the more preferred metal species.
- Regeneration requires about 5 BV of 0.5 molar sulfuric acid in the first step. The spent acid can be re-used after concentration to the same proton concentration without any loss of efficiency. Pert of the organic matter is desorbed in the first step.
- In the second step, 5 BV of 0.5 1oBy this means the exchangers are neutralised (re-converted to the free base form). Furthermore, the organic matter adsorbed is desorbed.
- The final rinsing requires about 20 BV of water, preferrably spiked with carbon dioxide to neutralise NaOH and to accelerate the rinsing.

5.9.2 Chromate elimination

The filter experiments with respect to the elimination of crhomate species have shown:

- Chromate can be selectively eliminated by weakly basic anion exchangers in the free base form.
- Because of the mechanism being an ion exchange anion exchangers with higher pK values (i.e. resins based on acylic acid) have to be applied. Styrene-based exchangers exhibit less favourable properties.

- There is a competitive uptake of sulfate anions. However, below a total concentration of about 100 mg/L sulfate the interference is negligible.
- Chromate anions and heavy metal cations can be sorbed in parallel. Despite of the different sorption mechanisms, the performance equals that of pure systems.
- Regeneration requires about 5 BV of NaOH. Its concentration should be between 2 and 4%. Addition of NaCl may improve the efficiency.

5.9.3 Further results

- The elimination of heavy metal salts and of chromate anions is always combined with a substantial decrease of the content of dissolved organic matter.
- The elimination is more efficient with styrene-based exchangers than with acrylic ones.
- There seems to be no irreversible sorption on the exchangers. Part of the organic substance is eluted during the treatment with sulfuric acid. The major part is displaced by the neutralisation / regeneration using NaOH.
- Phenol which is important in the case of the Chinese raw waters and be co-eliminated together with heavy metals. Because of the dissociation of phenol this elimination is more effective with resins with as considerable share of strongly basic functional groups.

6. Modeling of the breakthrough performance

6.1 Description of sorption equilibria

For description of the multicomponent equilibrium the surface complexation theory has been applied which was presented in several publications [27, 29, 30, 51 - 57). For a multicomponent system with k exchangeable components the theoretical treatment leads to a set of k-1 coupled equilibrium relationships:

$$\log Q_{j+1}^{j} \equiv \log \frac{q_j \, c_{j+1}^{w_{j+1}}}{q_{j+1} \, c_j^{w_j}} = \log K_{j+1}^{j} + m(j, j+1) \sum_{m=j+1}^{k} y_m \qquad (6.1)$$

with the generalised separation factors Q being

$$Q_{j+1}^{j} = \frac{q_j \, c_{j+1}^{w_{j+1}}}{q_{j+1} \, c_j^{w_j}} \qquad (6.2)$$

and the abbreviation

$$m(j, j+1) = \frac{z_R}{\ln 10} \cdot \frac{q_{max} \cdot F^2}{A_0 \cdot C(j, j+1) \cdot R \cdot T} \qquad (6.3)$$

In a system without chemical reactions in the liquid phase there are k unknown equilibrium concentrations and k unknown equilibrium loadings. To calculate these 2k quantities further relationships are needed:

- Electroneutrality conditions for the liquid and exchanger phases:

$$\sum_k x_k = 1 \qquad (6.4)$$

$$\sum_k y_k = 1 \qquad (6.5)$$

- Mass balances for each component

$$V_L \, c_0 \, (x_{0,j} - x_j) + m_{exch} \, (y_{0,j} - y_j) = 0 \qquad (6.6)$$

As a total a system of 2k+1 (nonlinear) relationships results from which either one mass balance or one condition of electroneutrality can be omitted.

In systems with additional chemical equilibria in the liquid phase further species are involved which, however, are excluded from ion exchange. Thus, the number of unknown quantities increases depending on the individual system. To achieve a solution further relationships have to be considered:

- the respective liquid-phase equilibria (dissociation or complex formation),
- mass balances for the further species species.

In addition the balances for exchangeable species have to be extended in an appropriate way. As has been shown, again a system of nonlinear relationships can be generated which allows the calculation of the concentration of all components and the loading of all exchangeable components.

The non-linear systems of equations can be linearised using the Newton-Kantorowitch method. The resulting linear system is solved by means of the Gauss elimination method.

6.2 Differential mass balance approach

6.2.1 Mathematical relationships

The general mass balance for a differential filter section is

$$\varepsilon \frac{\partial c_i}{\partial t} + v_F \frac{\partial c_i}{\partial z} + (1-\varepsilon)\frac{\partial \overline{c}_i^{av}}{\partial t} = 0 \tag{6.7}$$

with axial dispersion being neglected. This equation has to be solved with respect to the initial and boundary conditions:

Initial:

$t = 0$: $c_i(t,z=0) = 0$ (6.8)

$t \geq 0$: $c_i(t,z=0) = c_{i,0}$ (6.9)

Boundary:

$t > 0,\ z = 0:\ c_i = c_{i,0}$ (6.10)

The change in the average exchanger loading is subject to external or internal mass transfer. To facilitate the calculations especially for multicomponent systems linear driving force approaches have been used. For predominant film diffusion control the change in the loading is given by

$$J_i = \beta_f \left(c_i^{bulk} - c_i^*\right) \tag{6.11}$$

For particle diffusion control it is assumed that the driving force is proportional to the difference between the surface and average loading:

$$\overline{J_i} = \beta_p \left(\overline{c_i^*} - \overline{c_i^{av}}\right) \tag{6.12}$$

Differential mass balance and exchange kinetics can be calculated separately for each component. The individual concentrations and exchanger loadings at the exchanger / liquid interphase are linked by the exchange equilibrium conditions:

$$x_i^* = f(y_i^*),\ i=1,n \tag{6.13}$$

$$y_i^* = f(x_i^*),\ i=1,n \tag{6.14}$$

For numerical solutions the differentials have to be replaced by quotients of differences.

6.2.2. Derivation of kinetic parameters

The mass transfer coefficients β_f and β_s were determined from the height of a theoretical plate HETP$_i$. Assuming a constant dimensionless distribution coefficient

$$K_{D,i} = \rho_{exch}\, q_{max} / c_0 \tag{6.15}$$

HETP and the mass transfer coefficients are linked by [58]

$$\mathrm{HETP}_i = \frac{2v_F}{\beta_{S,i}}\frac{K_{D,i}}{(K_{D,i}+\varepsilon)^2} + \frac{2v_F}{\beta_{L,i}}\frac{K_{D,i}^2}{(K_{D,i}+\varepsilon)^2} \tag{6.16}$$

HETP_i is, therefore, a superposition of two relationships for each film and particle diffusion. By means of the true solution-phase velocity $v_f = v_F/\varepsilon$ the relationships for pure film diffusion and pure exchanger-phase diffusion result:

$$\mathrm{HETP}_{L,i} = \frac{2v_f}{\varepsilon\beta_{L,i}}\frac{\left(\rho_{exch}\frac{q_{max}}{c_0}\right)^2}{\left(1+\frac{\rho_{exch}\,q_{max}}{\varepsilon c_0}\right)^2} \tag{6.17}$$

$$\mathrm{HETP}_{S,i} = \frac{2v_f}{\varepsilon\beta_{S,i}}\frac{\rho_{exch}\frac{q_{max}}{c_0}}{\left(1+\frac{\rho_{exch}\,q_{max}}{\varepsilon c_0}\right)^2} \tag{6.18}$$

By means of these relationships the required effective transport coefficients $\beta_{L,i}$ and $\beta_{S,i}$ can be determined from simple binary filter experiments. In the evaluation it has to be assumed that either film or particle diffusion is rate-controlling. The combined case cannot be solved without further considerations. Using the approach with the differential mass balance the number of theoretical plates, either $\mathrm{HETP}_{L,i}$ or $\mathrm{HETP}_{S,i}$ is varied until an optimum agreement with the experimental breakthrough curve is obtained.

6.3. Prediction of the column performance

For the prediction the computer program DIEX_FD has been used. This program had been developed by Dr. A. I. Kalinitchev (Russian Academy of Sciences, Institute of Physical Chemistry, Moscow) in the framework of a DFG-supported cooperation project with the Institute of Technical Chemistry, of Forschungszentrum Karlsruhe [59, 60].

Figure 6-1 shows an example of such a prediction for the elimination of cadmium from tap water. The parameters needed for the calculation are summarised below.

1) Valencies:

Z(Me) = 2

Z(Me) = 2

Z(Cd) = 2

Z(Re) = 2

2) Surface complexation parameters:

log K(Me,Me) = 0.000

log K(Me,Cd) = 0.000

log K(Cd,Re) = 2.400

m(Me,Me) = 1.0000

m(Me,Cd) = 1.0000

m(Cd,Re) = 98.0000

(The computer program can consider up to three competein metal ions. In the case of non-existing componentes their lok K values are put to zero).

3) HETP Values:

HETP(Me,Re) = 1.3000 cm

HETP(Me,Re) = 1.3000 cm

HETP(Cd,Re) = 1.3000 cm

4) Column parameters:

Capacity	a= 0.015 eq/L
Porosity	ε = 0.4000
Linear Velocity:	vF = 23.3000 cm/min
Length of column:	L = 28.0000 cm
Diameter of colum:	D = 2.8000 cm
Flowrate:	Q = 95.6468 mL/min
Bed Volume:	BV = 172.4106 mL
Kappa:	κ = 1.5000
Total conc.:	c0 = 0.0000 eq/L

5) Input concentration times [min]:

Time1 = 0.00

Time2 = 1.00

Time3 = 90000.00

Time4 = 90001.00

6) Printing parameters for output on screen [min]:

Begin: T0 = 0.00

Period: TP = 10.00

7) Printing parameters for output on files [min]:

Begin Tout = 0.00

Period DTout = 10.00

Bed Vol.Step = 100.00

8) Input concentrations,mmol/L:

C_{in}(Me) = 0.0000

C_{in}(Me) = 0.0000

C_{in}(Cd) = 0.0009

C_{in}(Re) = 0.0000

9) Initial loading of column [eq/L]:

q_{in}(Me) = 0.0000

q_{in}(Me) = 0.0000

q_{in}(Cd) = 0.0000

q_{in}(Re) = 0.0150

10) Dimensionless Input concentrations [-]:

X_{in}(Me) = 0.0000

X_{in}(Me) = 0.0000

X_{in}(Cd) = 1.0000

X_{in}(Re) = 0.0000

11) Initial dimensionless loading of column [-]:

Y_{in}(Me) = 0.0000

Y_{in}(Me) = 0.0000

Y_{in}(Cd) = 0.0000

Y_{in}(Re) = 1.0000

12) Iteration progress parameters:

Time increment:	Tau calculated = 0.00000122 min
Time increment:	Tau selected = 0.00100000 min
Number of Length increments:	N = 60
Length increment calculated:	h = 0.475 cm

13) Mass transfer coefficients (film diffusion control assumed:

β(Me,Re) = 23.893613 1/min

β (Me,Re) = 23.893613 1/min

β (Cd,Re) = 23.893613 1/min

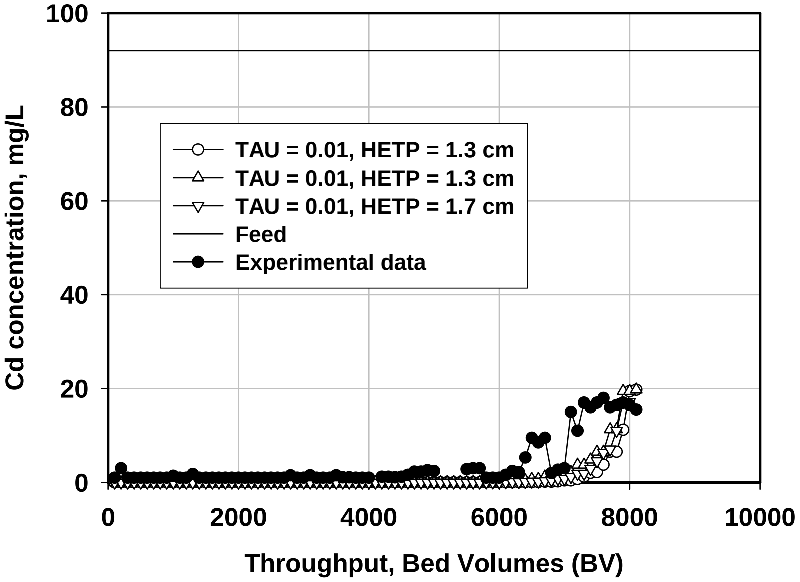

Figure 6-1: Comparison between experimental data and predicted column breakthrough performance. Resin: Duolite A7, Throughput: 20 BV/h [28].

6.4 Conclusions

The mathematical simulation of the filter performance is based on the solution of the differential filter balance. In addition an approach from chromatography is applied to describe the kinetics of sorption. Together with equilibrium constants and resin properties the prediction of the column performance becomes possible.

The results have demonstrated that the numerical calculation can be suitable for the prediction of the column performance of laboratory scale columns. Its applicability to other cases and especially to technical filters, however, still needs to be demonstrated.

7. Release of organics by anion exchangers

Ion exchangers and polymers which are applied for food and drinking water treatment are subject to certain restrictions with respect to the monomers and to the release of organics during service [61]. The respective conditions are summarised in regulations such as the German DIN 54411 [62].

The Western weakly basic anion exchangers applied in the investigations of this project have been tested by their manufacturers and can be applied to the treatment of food and drinking water. However, there is no information about the performance of the resins of Chinese production. It was, therefore, one of the objectives of the project to carry out the respective leaching tests. These test were carried out according to the German DIN 54411 ("Umpumpverfahren").

For the tests the resins were pretreated in the following way:

- 2 L of 2% NaOH solution passing the resin bed in 1 h.
- 3 L of distilled water washing the resin bed in 1.5 h.
- 3L of 1% HCl passing the bed in 2 h.
- 6 L of distilled water washing the resin bed in 3 h.
- Repeating the first step .
- Repeating the second step .

The parameters of the test series were:

Volume of ion exchangers:	350mL
Volume of circulated water:	3500mL
Flow rate:	6L/h
Temperature of water:	20-25 Centigrade
Circulation time:	168h (= 7 days)

The test develops as follows:

- Test of the installation with deionised water without resin as given above, determination of a "blank value",
- Repetition if the DOC values measured are belo the limit of measurement until reproducible values are obtained
- Filling in of the resin material, recirculation of the water across the resin filter, measurement of DOC after 168 hours.

At the end of the 168 hours pumping the DOC in the circulated solution was measured by means of the KMnO4 method. The results of toxicity test are listed in table 7-1.

Table 7-1: DOC values of the resin tests, mg/L

Resin	Distilled water	Blank value	After 168 hours	∆DOC
SM1*	1.05	1.24	9.81	8.57
	1.2	1.56	3.07	1.51
703	1.40	1.87	2.54	0.67
701	1.42	2.00	4.16	2.16
D314	1.43	1.76	2.40	0.64
WM1	1.08	1.30	4.30	3.00
IRA-96RF	1.38	1.79	4.30	2.51

Corresponding to the German standards a polymeric adsorbent or exchange resin is suitable for food treatment if the increase of DOC in 168 hours is below 1 mg/L. In the light of this regulation only the exchangers 703 and D314 can be applied for drinking water treatment.

Most ion exchangers are normally applied in industrial water treatment. For application in drinking water treatment they have to be pre-treated to elute the shar of non-polymerised monomers and other impurities from the production. The effect of such kind of pre-treatment becomes obvious from the two experiments with the exchanger SM1. In the second test the amount of organics eluted was considerably smaller.

8. Pilot tests for elimination of heavy metals

8.1 General

According to the objectives of the project a pilot plant was to be assembled and operated at different sites in China to demonstrate the process and to obtain data about the economics of this kind of treatment. Several sites were checked in different cities. Finally, the following sites and objectives of treatment were selected:

- Shenyang, for elimination of chromate from ground water
- Haikou, for elimination of mercury from surface water,
- Huludao, for elimination of copper and mercury from ground water.

The locations in China can be seen from the following maps.

The experiments comprised the service and regeneration cycles and the respective waste water treatment.

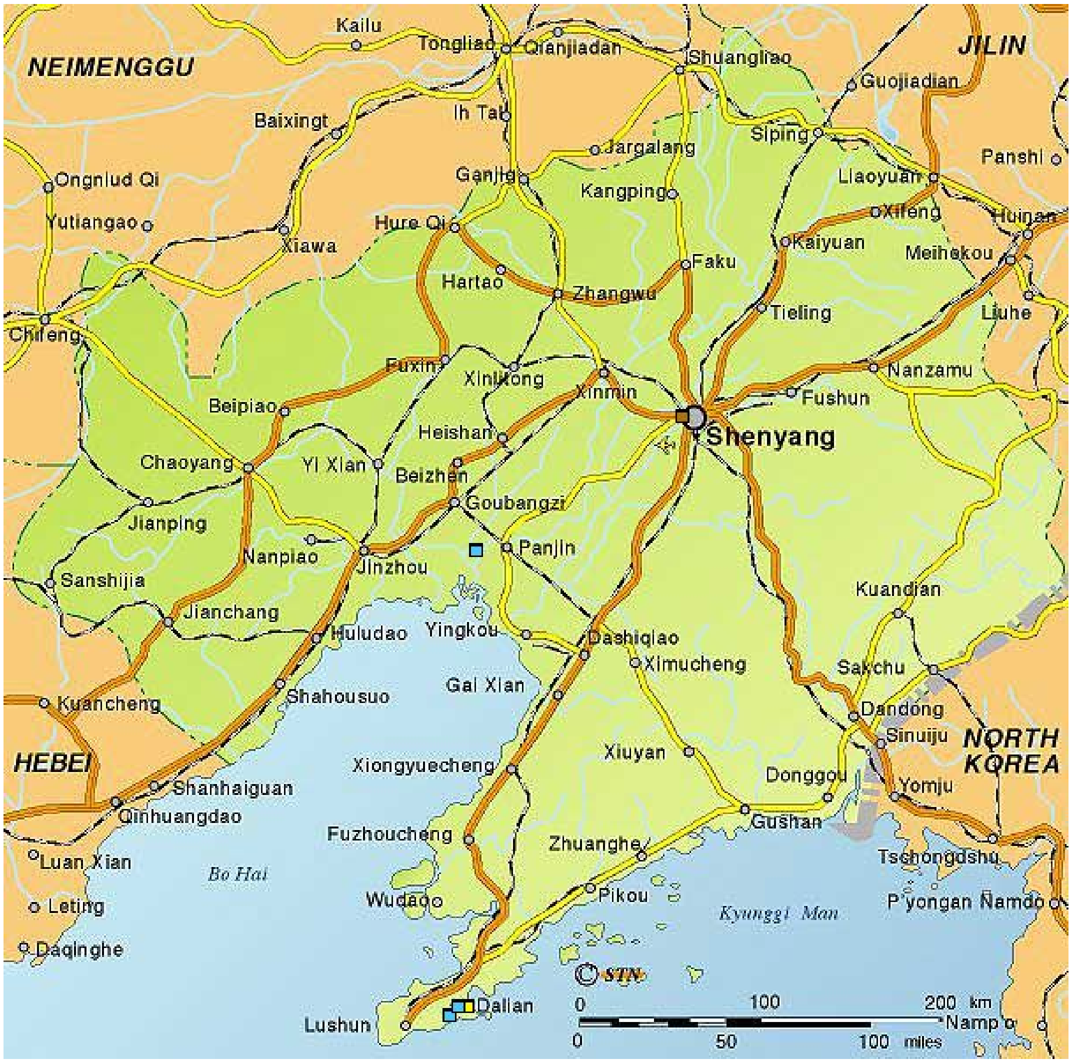

Figure 8-1: Map of Lianoning province with Shenyang (capital) and Huludao [63].

Figure 8-2: Map of Hainan Province with Haikou (capital) [63].

8.2 Pilot plant

Design and construction of the pilot plant were based on the results of the laboratory investigations carried out at Forschungszentrum Karlsruhe and at the Institute of Nuclear Energy Technology in China. Figure 8-3 shows the scheme of this plant.

The installation consisted of two ion exchanger filters which operated in parallel. Each filter had a diameter of 0.25 m (= 0.049 m^2 cross sectional area) and was filled with 75 L of exchanger material. Accordingly the bed height amounted to app. 1.5 m. During the service cycle the raw water passed the filters in downstream direction at a flow rate of 20 BV/h. Regeneration was carried out in counterflow at flow rates of 1 - 2.5 BV/h. To simplify the experiments the entire plant was operated manually.

Details about the construction of the plant are listed in table 8-1.

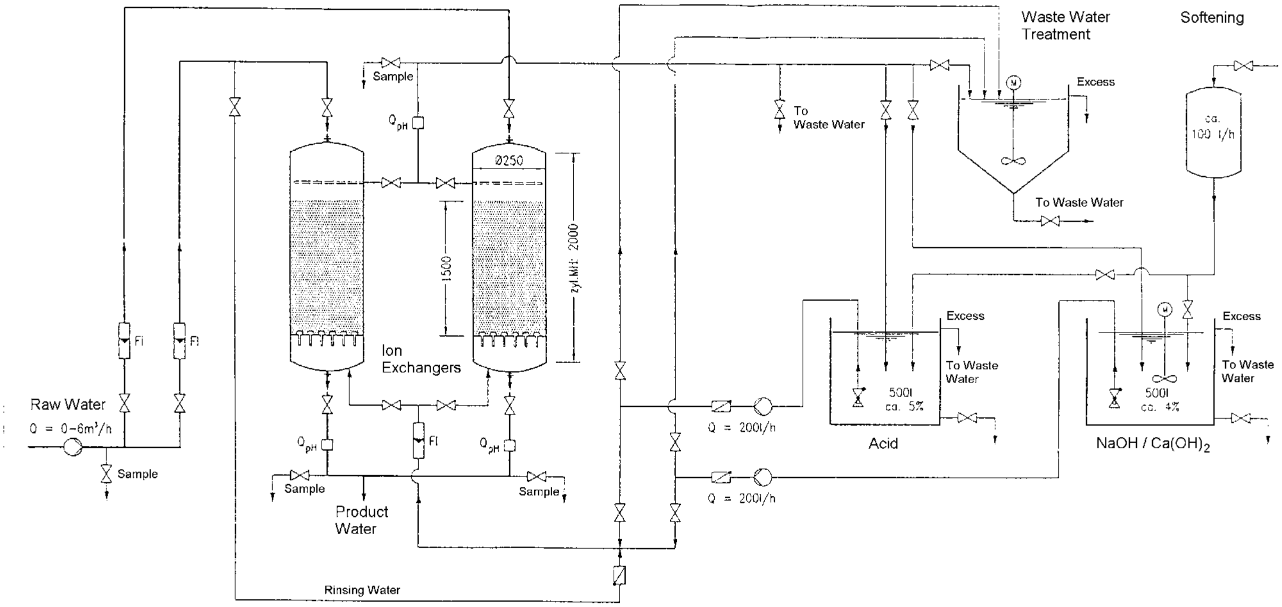

Figure 8-3: Scheme of pilot plant

Table 8-1: Components of the pilot plant

Component	Quantity	Dimensions
Cylindrical filter with nozzles	2	D = 250 mm, cylindrical height: 2 m
Waste water treatment vessel	1	500 L
Storage vessels for H_2SO_4 and NaOH	2	500 L
Softener	1	--
Sand filter	1	D=800, F=0.5m², H= 2.5m

The exchangers applied were:

- Duolite A7, Rohm and Haas Company
- Purolite A 847, Purolite International Company

For the selection it was important that both exchanger resins are allowed for food and drinking water treatment.

The exchanger plant and the additional vessels without the sand filter were stored in a 20 feet container.

8.3 Results of the demonstration campaign

8.3.1 Elimination of chromate at Shenyang

a) Resin Purolite A 847, service cycles

At the first site In Shenyang the plant operated between July 25 and September 15, 2001. The task of the treatment consisted in the elimination of chromate from a contaminated ground water available on the campus of Shenyang Airplane Corp (SAC). The plant was operated by a master student of INET, Tsinghua University. All the analyses were made by the Shenyang Institute of Environmental Science. The composition of the raw water was analysed several times. The results are summarised in table 3-2.

Table 8-2: Raw water composition during the experiments at Shenyang (values in mg/L).

Date	Cr	NO_3^-	SO_4^{2-}	Cl^-	Fe	Mn	Ca	Mg	Na	Cu	Zn	HCO_3^-	UV254
7.27	0.091	8.28	54.96	29	0	0.006	46	10	15.50			1.466	
7.31	0.090												0.0166
8.4	0.095												
8.7	0.100			30	0	0	44	12	16.2		0		
8.10	0.100												
8.14	0.101	8.44	55.28	30	0	0	44	14	14.1		0		0.0108
8.21	0.089												
9.3	0.099												
9.12	0.100												

As becomes obvious from the list the ground water has a comparatively low total salinity, however, chromate concentrations of about 100 µg/L.

For the experiments both exchangers were tested although Duolite A7 had not been tested for chromate removal in the laboratory experiments. Figure 8-4 shows the result of one experiment with Purolite A 847.

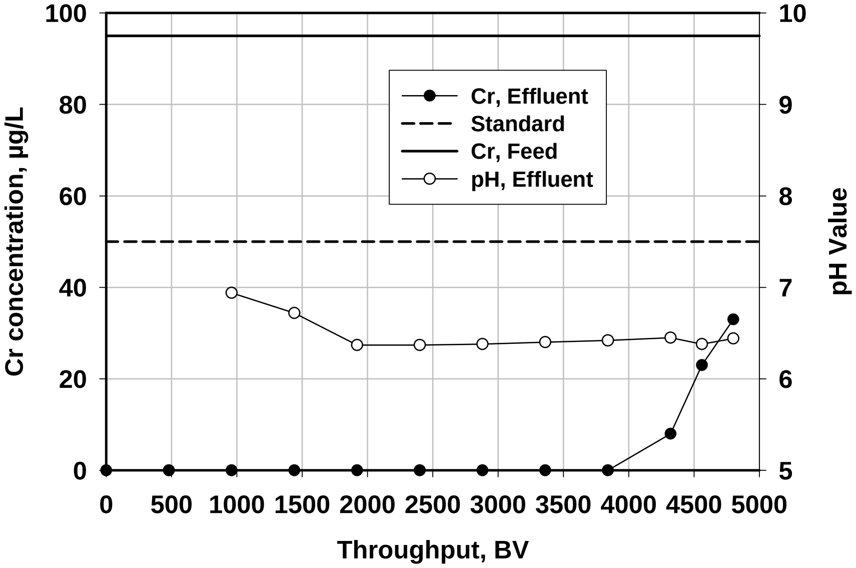

Figure 8-4: Breakthrough curve of experiment #1 with the fresh exchanger Purolite A 847.

Originally it was estimated that one service cycle should last for one week. However, it turned out that the performance of the resin was considerably better. The development shows that chromate was completely eliminated during a total throughput of 1900 bed volumes. At the end of the experiment after passing 4800 bed volumes (i.e. after 10 days) the effluent concentration was still below the limit for drinking water.

For the first regeneration a 1% NaOH solution was applied (details are given in Table 8-2). The development of the second service cycle is plotted on Figure 8-5. Obviously the regeneration with only 1% NaOH did not lead to a satisfactory desplacement of chromate.anions. Corresponding to the strong preference of chromate, the initial effluent concentration is again below the limit of measurement. However, the breakthrough occurs much earlier and the standard for drinking water was exceeded after a total throughput of only 1800 bed volumes. The concentration history shows a chromatographic displacement of chromate species, probably due to the uptake of the less preferred sulfate ions which, however, have a much higher concentration in the feed.

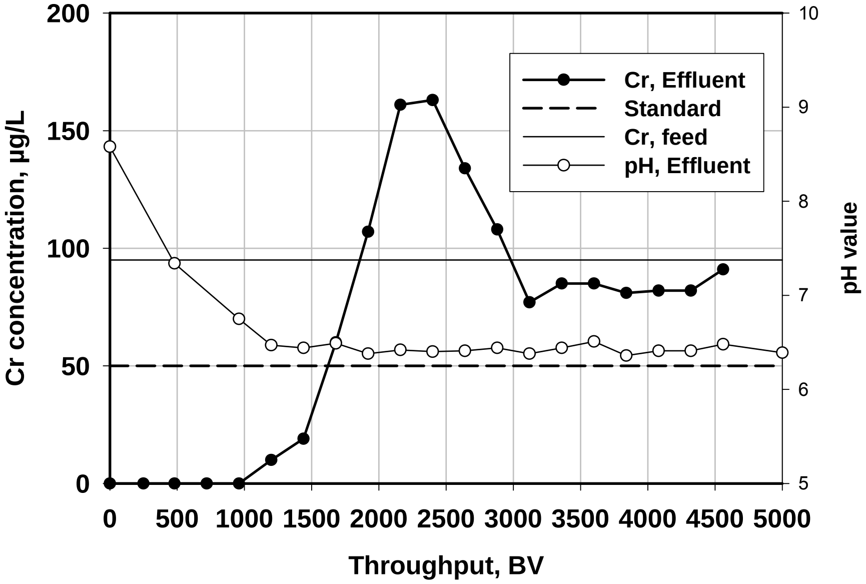

Figure 8-5: Breakthrough curve of experiment #2 with Purolite A 847.

After the second service cycle regeneration was carried out using 2% NaOH. The development of the third service cycle is plotted in figure 8-6.

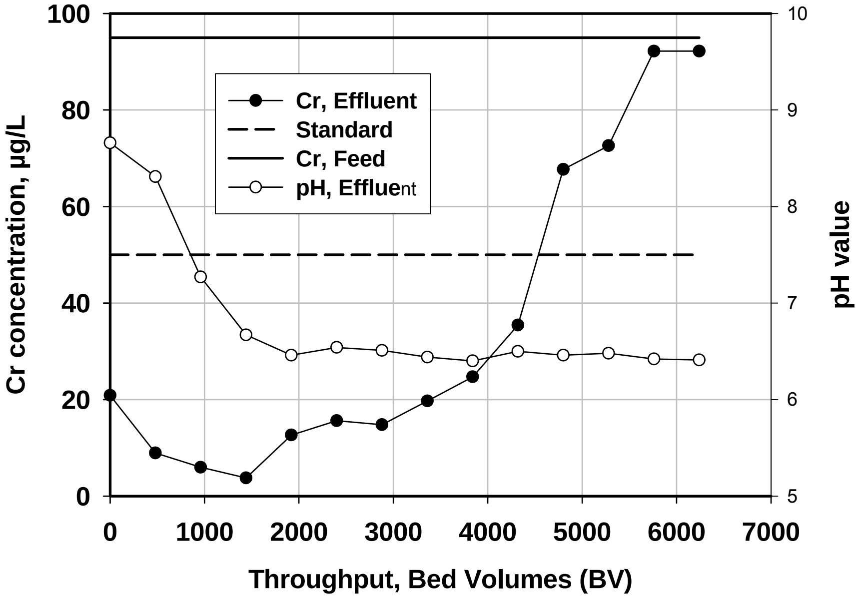

Figure 8-6: Breakthrough curve of experiment #3 with Purolite A 847.

The results reveal that the efficiency of regeneration had been strongly improved. The chromium(VI) standard for drinking water was exceeded only after a throughput of about 4750 BV. Unlike in the preceding experiments there is a considerable initial leakage of chromate. The reasons could not be found.

For further investigations of the regeneration efficiency a 4% NaOH solution was used for the third regeneration. Results of the fourth service cycle are plotted in figure 8-7. As can be seen, there is again an initial leakage of chromate and an the standard for drinking water is exceeded after about 4000 bed volumes.

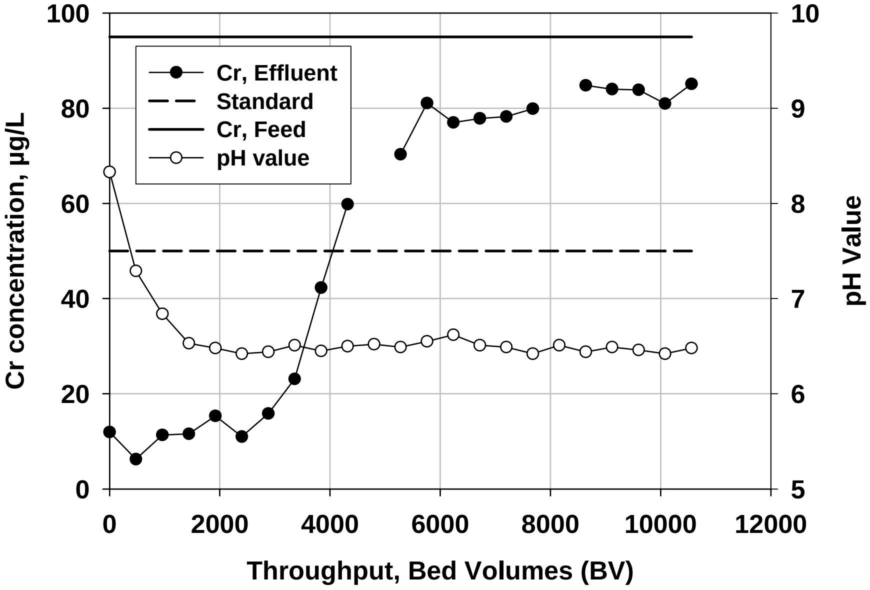

Figure 8-7: Breakthrough performance of experiment #4 with Purolite A 847.

b) Resin Purolite A 847, regeneration and rinsing

Regeneration was carried out by means of NaOH solutions of different concentration and at different flow rates / contact times. The conditions of the three regenerations are summarised in table 8-3.

Table 8-3: Conditions of regeneration and rinsing

Regeneration #	1	2	3
Concertration of NaOH	1%	2%	4%
Flow rate of regeneration, (BV/hr)	2.5	1.5	1
Time, (hr)	4	4	3
Spent regenerant, (L)	700	400	200
Flow rate of backwashing, (BV/hr)	5	5	10
Time, (hr)	4	4	3
Spent rinsing water, (L)	1400	1400	2100

Rinsing was carried out using raw water to wash out the remaining NaOH. The development of pH in the rinsing water at different throughput rates is plotted in figure 9-8. No addition of carbon dioxide gas was tried as in the laboratory trials. The results reveal that the higher flow rate does not necessarily lead to a better elution of NaOH.

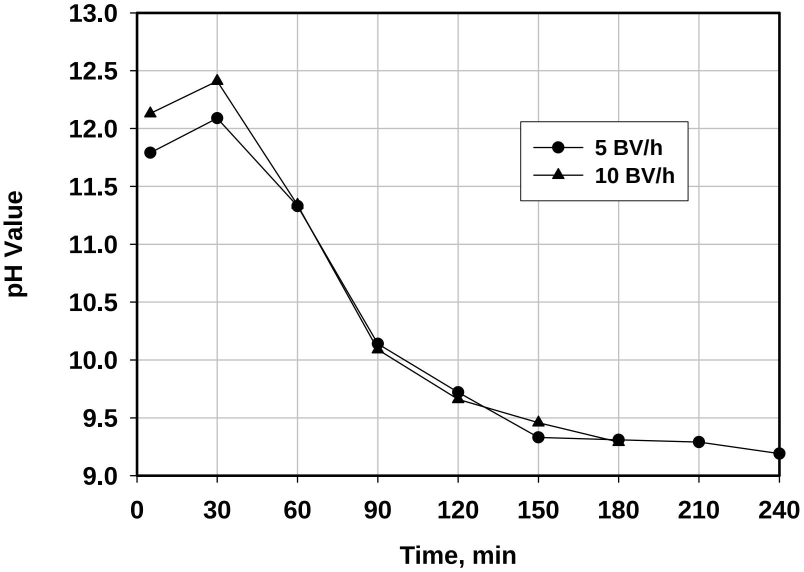

Figure 8-8: Development of rinsing at two different flow rates.

c) Waste water treatment

The post treatment of the chromate-bearing spent regenerant was as follows:

- Reduction of chromate by means of Na_2SO_3,
- Precipitation of $Cr(OH)_3$ by adding of $Ca(OH)_2$.

To the spent regenerant from the experiment with Purolite A 847 (volume: 200 L) 150 g Na_2SO_3 was added corresponding to 120% of the content of Cr(VI). The mixture was stirred for about three hours to reduce Cr(VI) to Cr(III). $Cr(OH)_3$ was then precipitated by adding 10 g/L $Ca(OH)_2$ until a pH value of 9 was achieved. After 12 hours of sedimentation the supernatant liquid was discharged into the municipal sewage system. The remaining sludge was punped into an intermediate vessel of 50 L volume. From this vessel it is pumped into a chamber press in which the sludge is dewatered at 15 bar pressure. The remaining filter cake with 25 % dry substance was added to the other sludges of left at Shenyang Airplane Corp. for further disposal

For Duolite A7 the quantities of $NaSO_3$ and $Ca(OH)_2$ amounted to 750 g and 20 g/L

The results of four experiments with Purolite A 847 are summarized in the following table 8-3.

Table 8-4: Results of experiments with Purolite A 847

Service Cycle	Breakthrough (BV)	Parameter values in Regeneration	Efficiency of Regeneration (%)
1	5000	1%NaOH, 4h	72.24
2	2800	2%NAOH, 3h	87.03
3	4400	4%NaOH, 2h	92.94
4	3900	2%NaOH, 3h	77.56

The summary of results shows that the best regeneration efficiency is obtained with 4% NaOH and sufficiently long contact time.

d) Resin Duolite A7

Corresponding to the results of the laboratory experiments the field of application of the exchanger Duolite A7 was to be the elimination of divalent cations. There was no experience about the performance of this phenol-formaldehyde resin with respect to the removal of chromate. Because one column had been filled with Duolite A 7 this resin was also tested for chromate removal. The results of the experiment are plotted in figure 8-9.

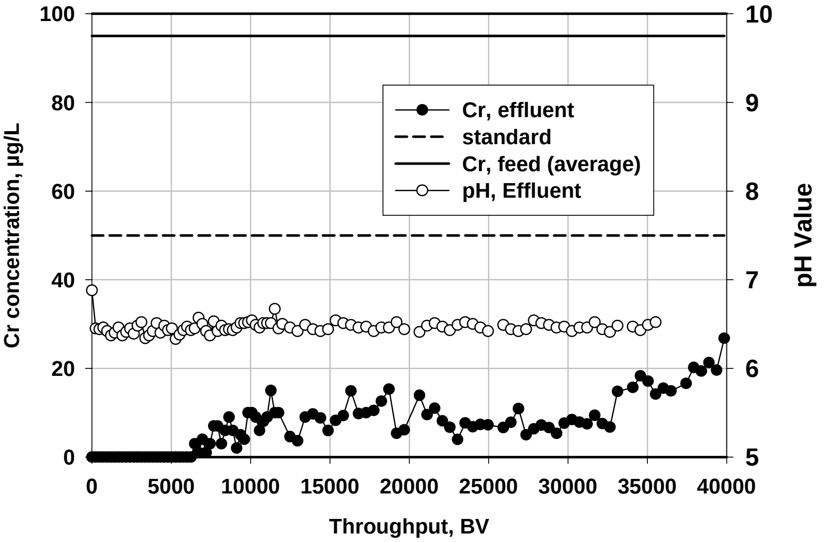

Figure 8-9: Breakthrough performance of the exchanger Duolite A7.

Compared to the performance of the acrylic resin Purolite A 847 the (first) service cycle was much longer. The experiment had to be stopped after a total throughput of about 40,000 bed volumes (= 2,000 hours = 83 days) when not even the standard for drinking water had been reached. The extraordinary performance cannot be explained only by ion exchange. It seems possible that the exchanger material was oxidised by the chromate species which in turn were converted to trivalent chromium species which precipitate as $Cr(OH)_3$. Because of the end of the experiments at Shenyang no regeneration could be carried out to verify this hypothesis.

To confirm the results and to investigate the kind regeneration required, laboratory scale experiments were carried out at Forschungszentrum Karlsruhe using spiked tap water with about 100 µg/L chromium as Cr(VI). The results confirmed the result obtained with the pilot plant. This laboratory scale experiment also showed that $Cr(OH)_3$ precipitates on the exchanger. Therefore, sulfuric acid was applied in a first step to dissolve chromium hxdroxide and to displace it from the column. In a second step NaOH was applied to remove chromate species and to neutralise the exchanger. By this means all of the chromium species could be removed from the exchanger. A subsequent second service cycle with about the same spiked raw water showed a rather poor chromate elimination with leakages above the drinking water standard. It could, therefore, be concluded that the chromate adsorbed indeed oxidised the functional groups of the exchanger. Obviously, a re-use of the material after chromate uptake and regeneration is not possible.

e) Concentration profiles in the exchanger column

During two experiments with Purolite A 847 samples were taken from the sampling valves at the column to elucidate the breakthrough waves inside of the column. The results are plotted in figure 8-10.

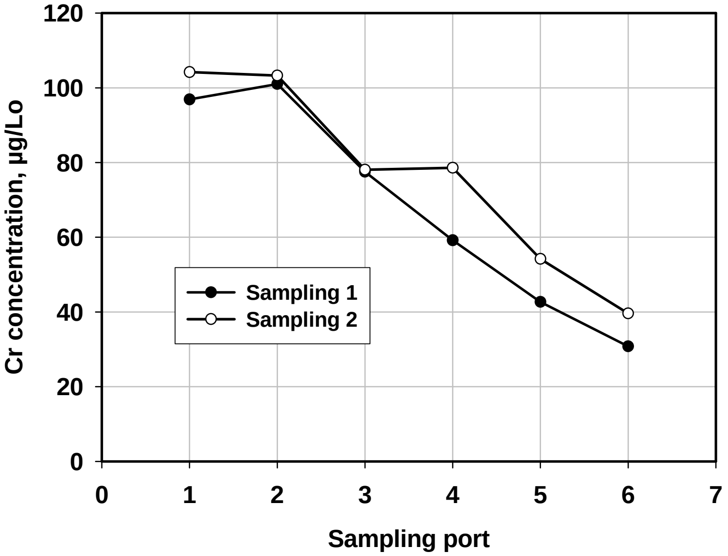

Figure 8-10: Concentration profiles in the Duolite A7 column

f) Elimination of organic matter

One of the properties of weakly basic anion exchangers is the fact that they adsorb organic matter. This has already been demonstrated in the laboratory scale experiments. TO demonstrate the same phenomenon with the pilot scale the UV absorption at 254 nm was measured in samples of the raw water and of the effluents of both columns. Although this parameter is mainly an indicator for aromatic compounds the results in figure 8-11 show that there is some considerable reduction in the content of organic matter in the water. The decrease amounts to 30 - 40 %.

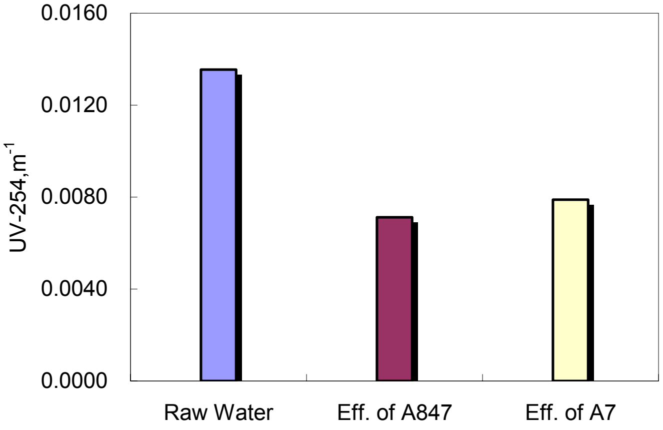

Figure 8-11: UV absorbence at 254 nm of raw water and effluents of the two exchanger columns.

g) Background composition of raw and product waters

Corresponding to the properties of weakly basic anion exchangers in the free base form there should be no elimination of cations and a negligible reduction of the concentration fo ions from the background composition of the water. Figure 8-12 shows the concentrations of the main constituents of raw water and the effluents of both resins.

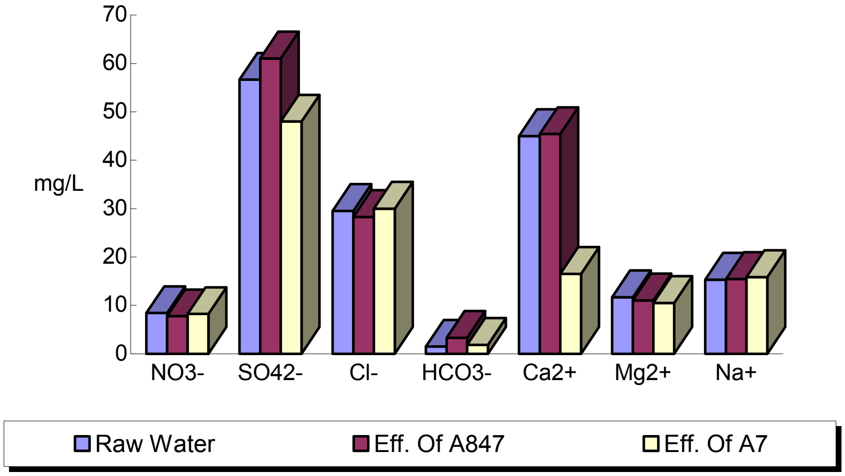

Figure 8-12: Concentrations of the main constituents in raw water and effluents.

As can be deduced from figure 8-12 there is practically no change in the background composition with both types of exchangers. The decrease of calcium concentration with Duolite A7 should be due to some mistake.

h) Conclusions about the removal of chromate

Elimination of traces of chromate anions with the acrylic weakly basic anion exchanger Purolite A 847 in the pilot scale confirmed the results of the laboratory scale experiments in an excellent way. At equal regeneration conditions using 4% NaOH solution a reproducible chromate elimination could be achieved. In addition, the content of natural organic matter could be reduced by about 40 %. Measurements of the effluent concentrations revealed that there was indeed no change in the inorganic background composition of the water. The consumption of water for regeneration and rinsing was comparatively small and the final solid waste could be reduced to a very small volume.

Surprisingly, the elimination by means of the phenol-formaldehyde-based exchanger Duolite A7 war by far more effective. However, this was obviously due to an oxidation of the exchanger and conversion of chromate to $Cr(OH)_3$ on the exchanger as the elimination was not reproducible after regeneration.

As a consequence, acrylic weakly basic anion exchanger in the free base form are the best suitable anion exchangers for direct selective elimination of chromate from contaminated ground waters.

8.3.2 Elimination of mercury at Haikou

The second site of operation was Haikou on Hainan island. Objective of the experiments was the selective elimination of mercury from a the water of a barrier lake. The water contains around 1.7 µg/L Hg and, therefore, cannot be used for watering in agriculture. The local situation did not allow to run the pilot plant directly at the lake. Therefore, the experiments were carried out at the local water work and lake water was transported to the plant by means of trucks. Because of the limited amount of water available only one column could be operated. Table 8-5 summarises the composition of the raw water.

Table 8-5: Raw water composition at Haikou

Date	**Hg (µg/L)**	**NO_3^- (mg/L)**	**SO_4^{2-} (mg/L)**	**Cl^- (mg/L)**	**Fe (mg/L)**	**Mn (mg/L)**	**Ca (mg/L)**	**Mg (mg/L)**	**Na (mg/L)**	**HCO_3(mg/L)**	**COD(mg/L)**
27.12.2002	1 - 3	4	16	9	0.56	0.052	7.5	5.1	6.6	No data	10.71

For the experiments the same exchanger materials as in Shenyang had to be used, no replacement by fresh material was possible. As a consequence, the exchanger Duolite A7 had to be applied in the state after the high loading with chromate, only partly regenerated and with oxidised functional groups. Therefore its performance was much worse than in the laboratory scale experiments.

a) Experiments with Duolite A7

The pilot experiments in Hainan started on 24th.Dec, 2001. However, due to the inadequate regeneration at Shenyang, the initial effluent concentration of Hg exceeded 1ug/l. In addition, on December 26 and 27, 2001, there were problems with the power supply of the water works. Therefore, the operation of resin column was stopped on December 29 and put into regeneration. After treating with sulphuric acid and NaOH, operation of the column started on January 4, 2002.
Data about the first service cycle are summarized in table 8-6.

Table 8-6: Data about the first service cycle with Duolite A7

Date (BV)	Feed Hg concentration (µg/L)	Effluent Hg concentration (µg/L)	pH of feed water	pH of effluent
30.12 (480 BV)	1.69	0.37	6.30	6.50
31.12 (960 BV)	1.47	0.37	6.28	6.47
01.01 (1440 BV)	1.99	0.44	6.34	6.80
02.01	Problems with pump.			
03.01	Problems with pump.			
04.01 (1920 BV)	2.17	0.46	6.37	6.49
05.01 (2400 BV)	1.69	0.42	6.32	6.55
06.01 (2880 BV)	1.81	0.44	6.30	6.56
07.01 (3360 BV)	1.97	0.67	6.29	6.59
08.01 (3840 BV)	1.64	0.89	6.27	6.50
09.01 (4320 BV)	1.95	1.14	6.25	6.52
10.01	Regeneration			
11.01	Regeneration			

The table shows the oscillations of the feed Hg concentration in Experiment #1. Similar oscillations probably occurred during the other experiments, however, there are no analytical data. Therefore, an average feed concentration is assumed in the figures.

Data about the second service cycle are summarised in tTable 8-7.

Table 8-7: Data about the second service cycle with Duolite A7

Date (BV)	Influent concentration of Hg (ug/L)	effluent concentration of Hg (ug/L)	pH of feed water	pH of effluent
12.01 (480 BV)	1.52	0.48	6.26	8.12
13.01 (960 BV)	1.89	0.44	6.30	7.26
14.01 (1440 BV)	1.94	0.47	6.31	7.26
15.01 (1920 BV)	1.93	0.45	6.30	6.74

Figures 8-13 and 8-14 show the results of the two experiments with Duolite A 7. They reveal that the standard for mercury is exceeded already after a throughput of only 4000 - 5000 bed volumes.

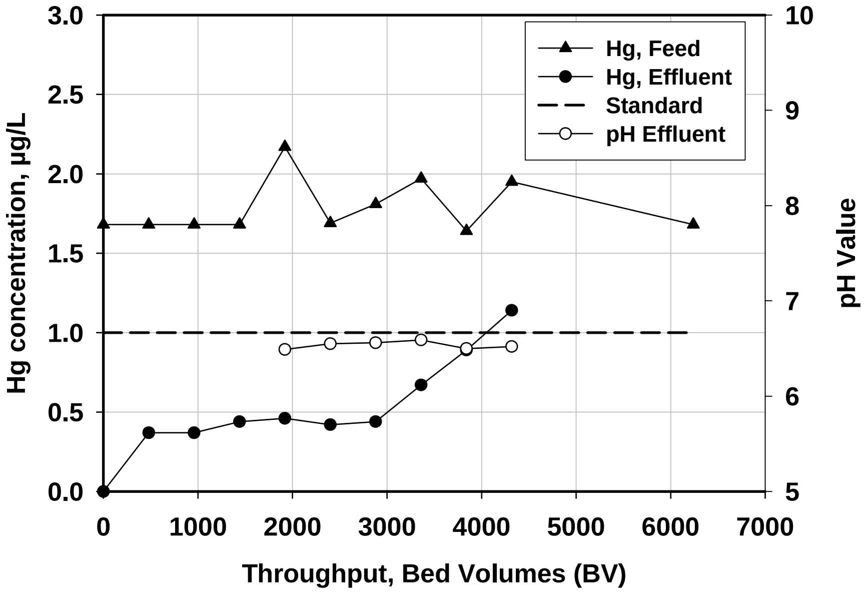

Figure 8-13: Results of first experiment with the exchanger Duolite A7.

b) Exchanger Purolite A 847

The experiment with the exchanger Purolite A 847 led to a much better result. The feed concentration from the same feed water of this experiment was similar to that of the other two experiments. Again the average concentration of Hg in the raw water was obtained by the calculation based on the analyses results during the whole pilot experiment period. Figure 8-15 shows the results. The mercury standard was exceeded only after a throughput of about 15000 bed volumes.

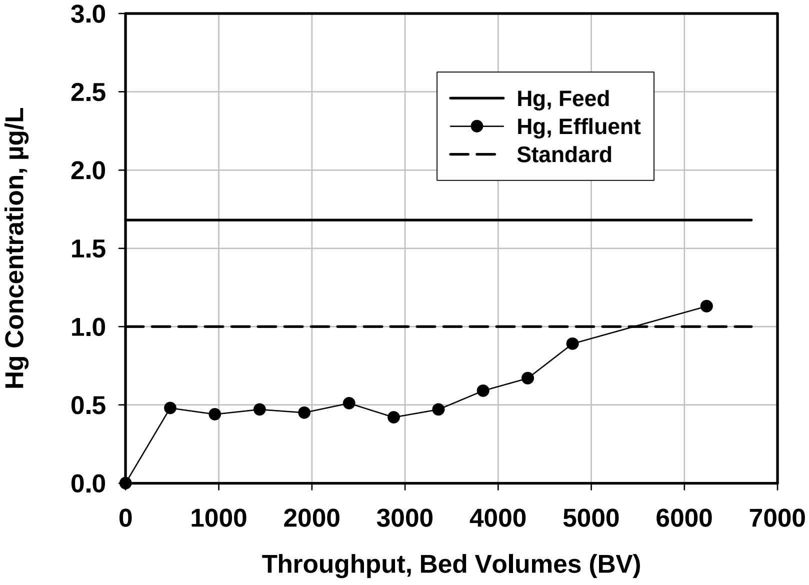

Figure 8-14: Results of the second experiment with the exchanger Duolite A7

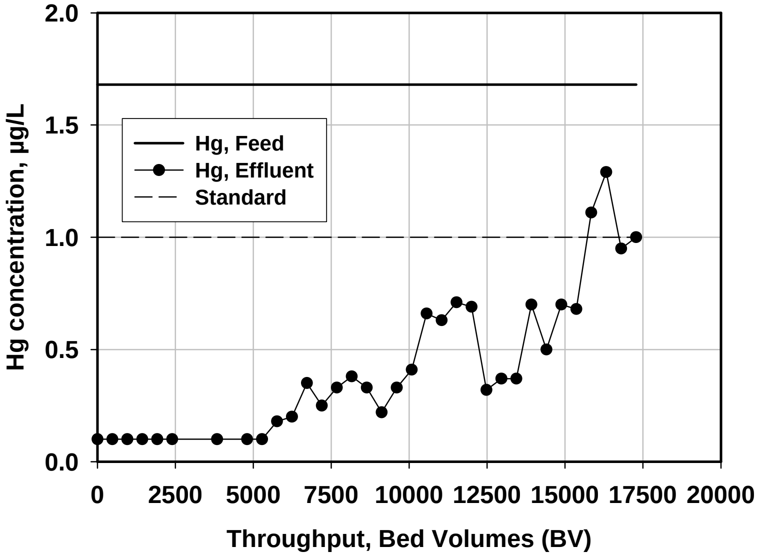

Figure 8-15: Results of the experiment with Purolite A 847.

c) Regeneration

Regeneration was carried out by means of 5 bed volumes of 0.5 molar H_2SO_4 and 5 bed volumes of 1.0 molar NaOH, followed by a rinsing step with 10 bed volumes of water. The post-treatment of the acid waste water comprised:

- Addition of $Ca(OH)_2$ to increase the pH
- Co-precipitation of mercury species after adsorption onto solid $Ca(OH)_2$.

The hydroxides were dewatered by means of a filter press and put to a landfill deposit.

d) Conclusions about the removal of mercury

The results of the pilot scale elimination of mercury present in the low trace level revealed that both exchangers allow a very efficient removal at very long service cycles. The efficiency of Duolite A7 was certainly negatively affected by the oxidation during the preceding demonstration campaign at Shenyang.

Regeneration again required only few bed volumes of H_2SO_4 and NaOH plus some Ca(OH)2 for neutralisation and solidification of the mercury displaced from the exchanger. Again the final volume of solids to be disposed was small.

8.3.3 Experiments at Huludao

The third site for the experiments was Huludao where the pilot plant operated at the campus of the Liaoning Bohai Shipyard. Huludao and it surroundings are an industrial area with many metallurgical installations and production units. Because of these activities the groundwater is contaminated by discharged waste water. The raw water of the experiments contained copper up to 10 µg/L and mercury up to 0.3 µg/L. Detailed information about the further raw water composition was not available. The experiments started on August 21, 2002 and lasted for three months. The plant was again operated by a master degree student of INET. All samples were transported to Beijing and analysed at INET.

The experiments were again carried out with both exchangers. However, the damaged Duolite A7 had been replaced by fresh resin. Because of considerable problems with pumps and other parts of the equipment the results of only one experiment are available.

a) Exchanger Duolite A 847

Results from elimination of copper in experiment #1 with Purolite A 847 are plotted in figure 8-16.

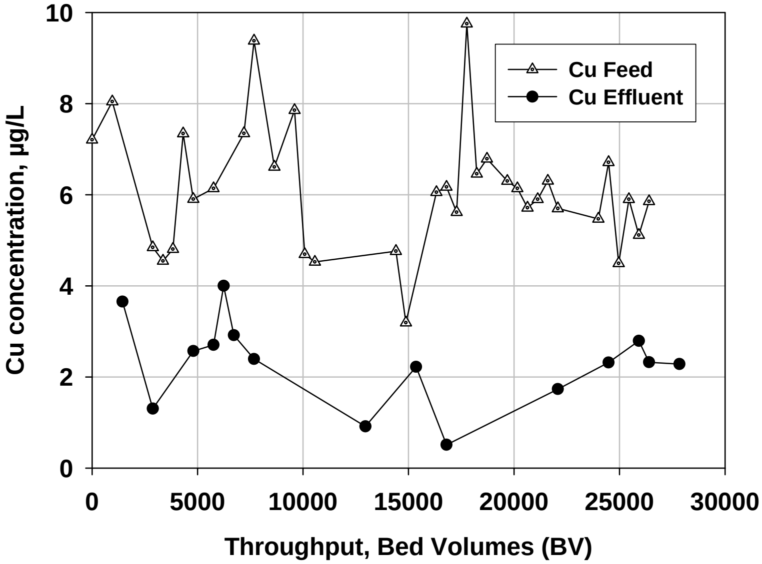

Figure 8-16: Development of copper concentrations in the experiment with Purolite A 847

The development shows that the effluent concentrations amount to about the EU recommended parameter value for copper in drinking water. Because of the oscillations of the feed concentration a clear breakthrough cannot be observed.

Figure 8-17 shows the development of the concentration of mercury in the feed and effluent for the same experiment. Although not above the standard for drinking water, there is still a considerable elimination of mercury species even at these very small concentrations.

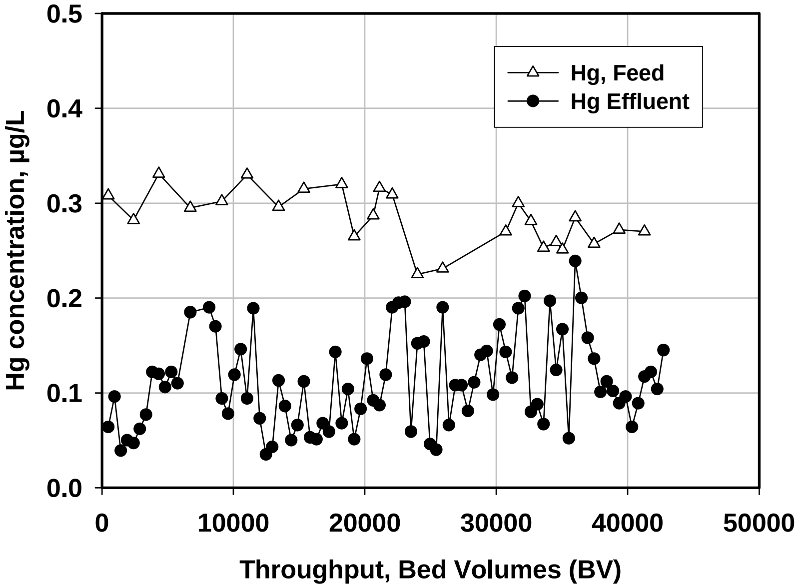

Figure 8-17: Development of the elimination of mercury by means of the exchanger Purolite A 847.

For the entire duration of the experiment, i.e. up to a total throughput of 43000 bed volumes the mercury concentration was decreased to 30 - 50 % of the feed concentration.

b) Exchanger Duolite A7

Results of the elimination of copper by means of the exchanger Duolite A7 are plotted in figure 8-18.

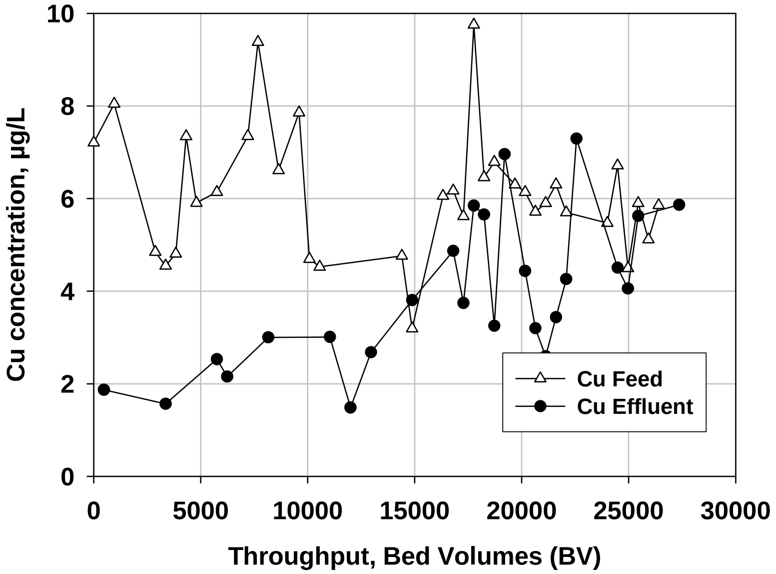

Figure 8-18: Development of the elimination of copper by means of the exchanger Duolite A 7.

The results of the elimination of mercury, again during the same experiment are plotted in figure 8-19.

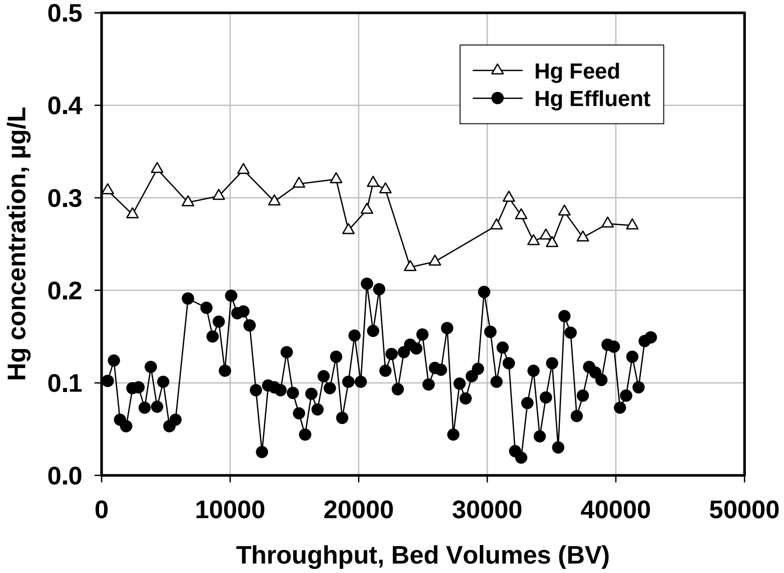

Figure 8-19: Development of the elimination of mercury by means of the exchanger Duolite A7.

c) Regeneration

As in the preceding experiment regeneration was carried out using 5 bed volumes of 0.5 molar H_2SO_4 followed by a neutralisation step using 4 % NaOH.

The spent acid and NaOH solutions were mixed for mutual neutralisation. From this mixture the heavy metals were precipitated by adding 10 g/L $Ca(OH)_2$. As in the other experiments the supernatant water obtained after 12 hours settling was discharged into the municipal sewage system. The sludge was de-watered by means of a filter press yielding filter cakes of 25 x 25 cm of 2 - 4 cm thickness. This final solid went to landfill disposal together with the much larger solid waste from the factory.

8.4 Economic evaluation

The economic evaluation of the results of the demonstration campaign are presented in section 10 in the framework of the design of a technical installation of a municipal water supply.

8.5 Conclusions

It was the objective of the pilot scale experiments to demonstrate the application of weakly basic anion exchangers for removal of traces of heavy metals from surface and ground waters in China which might serve as raw waters of the drinking water supply. For this purpose a pilot plant was operated at three different sites and with three different objectives. For the experiments two commercially available exchangers from Rohm and Haas and Purolite International companies were applied. Both exchangers are allowed for the treatment of food and drinking water.

The results can be summarised as follows:

- The concentration of chromium(VI) can be decreased by means of a acrylic weakly basic exchanger from about 100 µg/L to less than the standard for drinking water for a throughput of about 4000 bed volumes between two regenerations. The elimination is favoured by sulfate concentrations below 50 mg/L. Application of a phenol-formaldehyde resins leads to a much better performance. Unfortunately, this kind of resin is not sufficiently stable against the oxidative properties of chromate anions.
- Mercury concentrations can be decreased from 2 µg/L to less than 1 µg/L by means of an acrylic weakly basic resin at a total throughput of at least 15000 bed volumes between two regenerations. The performance of the phenol-formaldehyde resin should be better, however, could not be investigated because of the pre-oxidation by chromate in the preceding experiment.
- Copper concentrations of up to 10 mg/L can be decreased to less than 2 mg/L for throughputs of up to 30000 bed volumes by means of the acrylic weakly basic exchanger.
- Economic considerations about the ratio of volumes treated during the service cycles and needed for regeneration lead to a product yield of more than 99 %.
- The demonstration campaign has shown that very long service cycles are feasible for all applications studied. Taking into account the relatively small volumes for regeneration and rinsing a high efficiency of the treatment with a high yield of product water > 99.5 % becomes possible.

9. Design and estimation of operating cost of a full-scale plant

9.1 Design

Based on the results of the laboratory and pilot scale experiments the design of a full scale plant can be made. The estimations are based on the following assumptions:

- A maximum throughput of 2,500 m³/h,
- a specific throughput of 20 BV/h,
- a total of 4000 BV between two regenerations.

The composition of the raw water should be similar to those in the pilot scale experiments. For this design the exchange resins Purolite A 847 has been selected, e specially because it is being manufactured in China and, therefore, available at relatively low cost. Furthermore, this exchanger is allowed for the treatment of food and drinking water.

With respect to maximum and specific throughputs a cross sectional area of 83.13 m² is required. Five filter solumns have been selected from which always four are in service while one filter is regenerated or aout of service for maintenance. As a consequence the entire Throughput has to be treated by four filters only. To meet these conditions the design given in table 9-1 has been selected.

Table 9-1: Data about selected filters

Number of filters	Diameter, m	Cross sectional area, m²	Bed height m	Cylindrical filter m	Volume of packed bed, m³
5	5	19.625	1.60	2.8	31.25

With five filters the total exchanger volume amounts to 156.25 m³.

Regeneration of one filter 5 BV of 4% H_2SO_4 and 5 BV of 4% NaOH, both at throughput rates of 1 BV/h (31.25 m³/h). Furthermore, rinsing required 10 BV of water at a throughput rate of 10 BV/h., therefore, 5 x 156.15 m³/h. For neutralisation of acid and NaOH a buffer tank with a total volume of 625 m³ is needed. The upper part of this tank should by cylindrical, the lower part has to be conical if the heavy metals have to be reduced and precipitated as hydroxides. The solids precipitated should be pumped to a filter press and be de-watered to a total solids content of 25%.

9.2 Estimation of operating cost

At a service cycle length of 4000 BV between two regenerations of one filter the plant outlined above produces a total fo 125,000 m³ of product water in each filter. Based on the prices in Germany of the chemicals needed operating cost are generated which are summarised below.

a) NaOH

Amount:	5 BV = 156.25 m³ (4%)
Specific cost:	€ 69.--/100 kg
Total cost:	€ 4,500.--

b) H_2SO_4

Amount: 5 BV = 156.25 m^3 (4%)
Specific cost: € 37.--/100 kg (96%)
Total cost: € 2,370.--

c) Rinsing

Amount: 10 BV = 312.5 m^3

The consumption of energy corresponds to the pressure loss resulting from pumping the chemicals across the packed bed.

d) Energy

Pressure loss (estimated): 1 bar
Energy consumption: 0.1 kWh/m^3
Specific energy cost: 0.15 €/kWh
Energy cost: 0.015 €/m^3

As has been demonstrated by the pilot scale experiments, the chromate elimination does not need the regeneration step with H_2SO_4. As a consequence, the total operating cost would be in the range of € 0.055/m^3.

In the case of mercury elimination the length of a filter between two regenerations increases to about 16,000 BV, however, acid and NaOH cycles are needed for regeneration. Taking into account the specific cost deduced above, the specific operating cost of mercury removal would be in the range € 0.018/m^3. Based on the results of mercury removal in the laboratory scale it can be estimated that the service cycle length of the exchanger Duolite A7 exceeds 20,000 BV between two regenerations. Therefore, the respective specific cost should be still smaller.

The elimination of copper and mercury cannot be used for such calculations because both feed concentrations are already below the standards for drinking water.

10. Summary

The results of the entire research projects can be summarised as follows:

- The basic sorption principles applied allow a a selective removal of heavy metal species. The feasibility of removal of mercury, cadmium, and other metal cations as well as of chromate anions by means of suitable commercially available ion exchangers has been demonstrated in the laboratory scale and and in the pilot scale in on-site experiments. The process concept allows a parallel elimination of heavy metal cations and oxy-anions. The standards of the drinking water regulations can easily be achieved. The background composition with the main inorganic components remains unchanged.
- The laboratory scale experiments have demonstrated that long service cycles can be achieved. These results could be well confirmed by the pilot scale experiments with real waters.
- The sorption of metal species is accompanied by a reversible adsorption of humic substances which leads to a further improvement of the drinking water quality. No negative effect on the removal of heavy metals could be observed during the experiments.
- Regeneration requires relatively small volumes of sulfuric acid / NaOH or only NaOH. Therefore, a very favourable ratio of product / process water is achieved. Spent acid regenerant solutions may be re-used for further cycles after re-concentration. The post-treatment of the spent regenerant solutions is similar to that of conventional processes.
- The equilibrium of sorption of of heavy metals which are present as a variety of species can be calculated using methods from the competitive adsorption of organic substances onto activated carbon. The breakthrough performance of filters can be predicted by means of a scientific approach. The suitability has been demonstrated for the elimination of cadmium salts.
- Economic evaluation of the pilot scale results show that the operating cost for technical application might be in the range of 0.05 € /m³ for chromate removal and 0.2 €/m³ for mercury removal.

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