

Ion Exchange by Zeolites and Peat-Based Sorption Media of Chilean Mine Water and their Potential for Secondary Mining

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Abstract Acid mine drainage (AMD) is a common phenomenon in many mines all over the world. Ion exchange is a promising option for AMD treatment and has potential to be used for secondary mining approaches. In this paper, the results of column experiments with two ion exchange materials (peat-based sorption media and zeolite-containing andesite) in relation to Chilean mine waters are presented. Both materials treat the incoming water with mean copper concentrations of 350 mg/L over 15 to 42 exchanged pore volumes. With sequential extraction, it was possible to discharge the complete amount of attached copper from the materials.

Key words Mine water, Zeolite, APTsorb, copper retention, AMD treatment, secondary mining

Introduction

Chile is one of the largest copper producers worldwide with a long history of mining. Copper production always comes along with residual materials, which are deposited in large tailings facilities. These tailings still contain amounts of copper and other elements such as zinc, cobalt, manganese or aluminium. Due to the ore processing, the residual materials are often fine grained. This enhances acid mine drainage, which results in waters with low pH values and metals contamination being discharged into the environment in large volumes. To avoid the harmful effects of these waters on surrounding surface and subsurface waters, treatment is necessary. Except for the aforementioned problems, these residual bodies can also be seen as raw materials for secondary mining opportunities, because of their significant amounts of trace and minor elements (Ussath et al. 2015).

In the last decades, the interest in ion exchangers in mining has increased, because they are a promising option for AMD treatment (Younger et al. 2002). They also enable the reclamation of the attached elements by subsequent desorption. There is a large variety of materials, which can function as ion exchangers, e.g. clay, activated carbon, resins or fly ash (Babel and Kurniawan 2003). One promising ion exchange material, which is investigated in this paper, is zeolite. Zeolites are a large mineral group of micro-porous aluminium-silicates. Due to their structure, they have high exchange capacities for different elements e.g. Cu^{2+} , Ni^{2+} , or Pb^{2+} . The pH value and particle size have a strong influence on the ion exchange capacity of zeolites, i.e. higher exchange capacities are reached at higher pH values and smaller particle sizes (Ok et al. 2007). Typical adsorption capacities for zeolite range between 1.64 and 5.10 mg/g (batch experiments) (Babel and Kurniawan 2003). Zeolites are reported to be reusable after discharging with NaNO_3 (15 g/L) (Medvidović et al. 2006). Another common ion exchanger that is discussed in this paper is a peat-based sorption media. Peat can immobilise a variety of elements by complexation and chelation due to its structure and its carboxyl, phenol and hydroxyl groups (Ho et al. 1995). Ion exchange capacities of peat have already been tested for

a wide range of elements, such as nickel, cadmium, zinc and copper (Babel and Kurniawan 2003). The exchange capacity for peat is also strongly dependent on the pH value of the surrounding solution, with an optimum between 4.5 and 7 (Brown et al. 2000). Adsorption capacities determined in batch experiments for peat range from 6.4 to 19.56 mg/g (Babel and Kurniawan 2003). According to Brown et al. (2000), 90 – 100 % of the elements attached to the peat by ion exchange can be dissolved subsequently with 0.1 M hydrochloric acid. This is especially interesting for the recovery of elements attached by ion exchange. As peat based sorption media the APTsorb from American Peat Technologies was used.

Methods

Column experiments

Column experiments are an appropriate method to reproduce the complexity of real system conditions. Therefore, a column was divided into three main parts: mobilisation zone (Chilean tailing material), retention zone (ion exchange material) and outlet zone (quartz sand) (Figure 1). To generate a representative tailing water, the mobilisation zone of the column was filled with Chilean tailing material. Located above this, the retention zone was filled with one of the ion exchange materials (zeolite-containing Chilean andesite (Z), or APTsorb (A)). Both materials were diluted with 50 (Z) and 90 (A) weight % quartz sand respectively to provide an undisturbed flow-through. For the same reason the Chilean tailing material was also diluted with 37 weight % quartz sand. Due to the results from Günther et al. (2016), the experimental setup was slightly modified for the following tests. The first modification was the media, which flows through the columns. In the experiments presented in this paper, water from sieving tests with the Chilean tailing material was used. Hence, the copper concentrations reaching the ion exchange materials were between 1400 and 160 mg/L during the whole experiments to test the ion exchangers (zeolite-containing Chilean andesite, APTsorb) under higher inflowing copper concentrations. Changes in hydrogeochemistry and element content of the water while passing the different zones were observed via respective sample ports (Figure 1). Over the day, the pump through rate was 20 ml/h, overnight and during the weekend it was reduced to 10 ml/h.

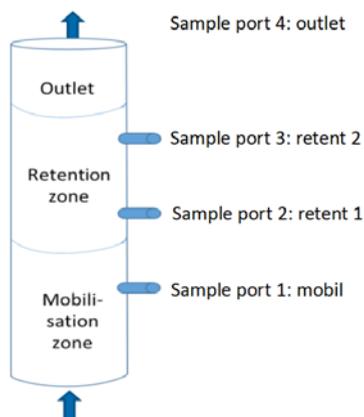


Figure 1: schematic diagram of the column experiment

Ion exchange materials

APTSorb from American Peat Technologies is a granulated reed-sedge peat. The pH value of the media itself is described with 4.9 – 5.2 and the pH values of waters treated by APTSorb should be between 4.0 and 7.5. A regeneration is not recommended and the media should be pre-wetted to allow the expansion (Product-Data-Sheet APTSorb). Zeolite-containing andesite contains approximately 18 – 21% zeolite and about 1 – 7% calcite. Other constituents are small amounts of montmorillonite (2.6%) and hematite (6.0%) (unpublished master thesis Arturo Bravo).

Handheld X-ray fluorescence spectroscopy (hXRF)

After finishing the column experiments, the solid filling materials were removed and investigated by hXRF. The aliquots were dried at 45°C. The aliquots of the APTSorb had to be milled for representative results. For the measurement, a Niton XL3t 980 hXRF device was used. Because of the different matrices of the ion exchange materials (zeolite-containing andesite and APTSorb), the data were after the measurement not corrected by device-specific correction factors to save the comparability between them.

Sequential Extraction

A sequential extraction was carried out to obtain information about the mobility of elements and to assess if a reprocessing of the attached elements after the ion exchange process is possible. The samples used were from a further column experiment with the same ion exchange materials, so the results are transferable to the column experiments presented in this paper.

An abbreviated variation from the method of Zeien (1995) was used. This methodology was developed by the project partner GFI (Kassahun, Hache) (Table 1). Extraction step I to IV were operated under nitrogen atmosphere to conserve mineral phases and bonded main and trace elements. For all eluates, the pH-value, electric conductivity, redox potential, total inorganic carbon (TIC), ferric iron and element content (by ICP-MS analysis) were determined. The samples were exposed to the leaching solutions by a solid:liquid ratio from 1:10.

Table 1: overview over the steps of the sequential extraction (modified after Zeien (1995) and Graupner et al. (2007))

Step	Extracted phase	Leaching solution	conditions
I	Water soluble	Ultra-pure water	pH 7
II	Ion exchangeable	Ammonium nitrate	pH 7
IIIa	Carbonates and specific bounded	Ammonium acetate	pH 6
IV	Organic bounded	NH ₄ EDTA	pH 4.5
Va	Amorphous and poorly crystallized iron and aluminum hydroxides	Ammonium Oxalate Oxalic acid	pH 3.25

Results and discussion

Column experiments

Due to the difficulties of the first column experiments' concerning the rapidly decreasing copper concentrations in the mobilisation zone (Günther et al. 2016); copper containing water was used as flow-through media for the following experiments, presented in this paper. The copper containing water, used as an additional source to the tailing material located in the mobilisation zone. It was an eluate from wet-sieving experiments with Chilean tailing material which has a copper concentration of 172 mg/L. By that reason, the copper concentration, which reached the retention zone, was at the beginning between 1100 and 1400 mg/L and after 2.8 and 3 exchanged pore volumes it diminishes to a mean concentration of 170 – 180 mg/L for the rest of the experiment (Figure 2, Figure 3). Except of copper, the flow-through media contains also small amounts of zinc, aluminium and manganese (7; 4 and 0.5 mg/L resp.).

The water, which reaches the retention zone, has a typical pH value of AMD waters, from 3.5 to 4. By means of the ion exchange materials (zeolite-containing andesite or APTsorb) located in the retention zone, this pH value is increased. The initial pH of the zeolite-containing andesite is 8.5. This is attributed to the calcite content. During the experiment, this pH value could not be maintained, but the pH of the inflowing, generated tailing water was still increased up to pH 6 – 6.5 (Figure 2). This was true, even when copper was already detected in the outlet, which indicates an exhaustion of ion exchange capacity. Hence, the pH value cannot be used as indicator for decreasing ion exchange performance in case of the zeolite-containing andesite. Compared to that, the ion exchange capacity of APTsorb seems to correlate with the development of the pH value and can be used as an indicator (Figure 3). The initial pH value of the APTsorb was 5.8, which is considerably lower than the zeolite-containing andesite. If ion exchange occurs, APTsorb increases the pH of the incoming, generated tailing water up to pH values between 5.5 and 6. When the ion exchange decreases the pH value decreases immediately as well. So in case of the APTsorb, an increase of the pH value only occurs as long as ion exchange happens.

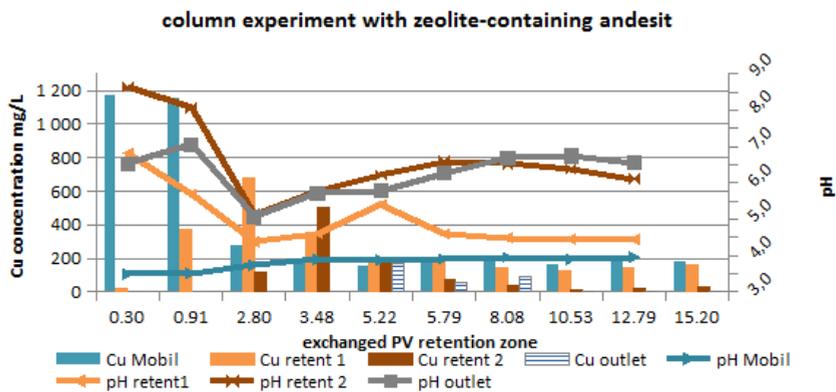


Figure 2: pH development and copper concentration for each column zone for the column experiment with the zeolite-containing andesite as reactive material in the retention zone vs. exchanged pore volumes (PV) of the zone

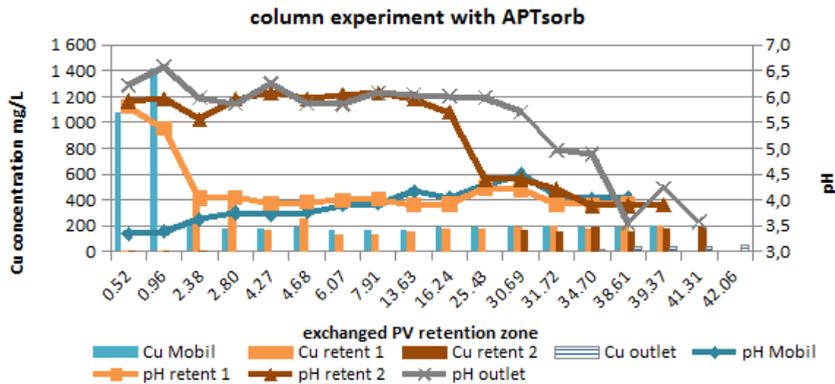


Figure 3: pH development and copper concentration for each column zone for the column experiment with APTsorb as reactive material in the retention zone vs. exchanged pore volumes (PV) of the zone

Both ion exchange materials show a good copper retention. Nevertheless, APTsorb is considerably more efficient than the zeolite-containing andesite. The zeolite-containing andesite could remove the complete incoming copper up to 5.2 exchanged pore volumes (Figure 2). Afterwards, the copper retention surprisingly increases again. One explanation for this might be the extremely high copper concentration right in the beginning of the experiment. So, it seems that the zeolite had some difficulties with high copper concentrations or at least the contact time was too small for this amount of copper. The ion exchange capacity of the zeolite may therefore not be completely exploited, unfortunately. Another point is the low zeolite concentration within the andesite. It was estimated at about 15 – 20 weight % and additionally, the material was diluted by 50 weight % quartz sand. Hence, the concentration of reactive zeolite in the retention zone was about 7 to 10 weight %. However, the APTsorb was used with approximately the same concentration (10 weight %) in the retention zone and was distinctly more effective than the zeolite. It could remove the incoming copper from the mobilisation zone completely up to 14 exchanged pore volumes and was also able to deal with the very high copper concentrations in the beginning of the experiment.

Sequential extraction

From both materials, 100% of the copper attached during the column experiment could be released by sequential extraction with some differences between the materials. Based on the results, the zeolite appears to bond the copper mainly on the ion exchangeable, as well as on the carbonates and specifically bounded fraction, because the main part of the copper was desorbed by ammonium nitrate and acetate solution (Table 2). Hence, the zeolite-containing andesite has a quite high potential for secondary mining approaches, due to the easy mobilization of copper with relatively cheap and uncomplicated solutions (ammonium nitrate and -acetate). It shall be tested if they can be replaced by other eluents. One opportunity is NaNO_3 solution (15 g/L) in order to discharge the attached elements and reuse the material for following ion exchange cycles (Medvidović et al. 2006). If the zeolite

containing andesite used in the presented experiments is suitable for reuse the influence of the contained carbonates on ion exchange has to be clarified. In contrast to that stands the APTsorb. It bonds the adsorbed elements quite strongly to the organic fraction as the results show (Table 2). The main part of the adsorbed copper can only be released by EDTA solution (sequential extraction step IV). This is not suitable for secondary mining approaches because EDTA is fairly expensive. By that reason, other extraction solutions should be tested. One option is HCl. Brown et al. (2000) reported that 90 – 100% of copper attached to the peat could be desorbed with a 0.1 M HCl solution. This could be a cheaper alternative to the expensive EDTA solution to unload the APTsorb. Since a reuse of APTsorb is not recommended by the company American Peat Technology, the advantage of the higher copper retention can be compensated by the reuse of the zeolite-containing andesite.

Table 2: results of the sequential extraction of copper dissolution for both materials zeolite and APTsorb for each sequential extraction step (I – Va)

Sample	I		II		IIIa		IV		Va	
	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
Zeolite	0.0	0.0	620.2	76.6	217.4	26.9	55.2	6.8	19.9	2.5
APTsorb	13.3	0.8	21.3	1.3	93.6	5.9	1166.2	72.9	382.9	23.9

Conclusions

Both ion exchange materials were tested under challenging conditions with high incoming copper concentrations and a mixture of different elements compared to most of the mentioned studies, which often consider only one element. Despite this, the zeolite-containing andesite and APTsorb show very good ion exchange capacities for copper. However, the APTsorb was considerably more effective in copper retention than the zeolite. Concerning the secondary mining potential, the zeolite-containing andesite seems to have advantages. Attached elements can be mobilised easier from the zeolite than from the APTsorb. In case of the zeolite, the regeneration solutions are considerably cheaper than the EDTA solution required for APTsorb. Nevertheless, the complete amount of copper attached to the ion exchange material in the column experiments can be dissolved by sequential extraction. To simplify the release of elements, the alternative solutions NaNO₃ and HCl should be tested in future. Especially for the zeolite-containing andesite, it would be interesting if a reuse is possible after regeneration and if there is an effect on the ion exchange capacity for following cycles.

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