

Specific Retention of Copper and Strategic Elements from Chilean Mine Water with Zeolites and Peat-Based Sorption Media

Juliane Günther¹, Maria Ussath¹, Nils Hoth¹, Carsten Drebenstedt¹

¹*Technische Universität Bergakademie Freiberg, Gustav-Zeuner-Straße 1A, 09599 Freiberg, Germany, Juliane.Guenther@student.tu-freiberg.de, Nils.Hoth@tu-freiberg.de*

Abstract

Acid mine drainage (AMD) and their high element contents is a common problem in mining. One promising possibility to remove these elements from the AMD is ion exchange. Zeolites are reported to have a high exchange capacity for cations like copper, cadmium or zinc. Furthermore, they are low cost (Babel und Kurniawan 2003). Peat-based materials such as APTsorb (American Peat Technology) also retard copper very efficiently (Eger et al 2015).

Column experiments were carried out to reproduce the conditions in the real system. In this case, original Chilean tailing material was used to generate a representative tailing water. All experiments were done for a zeolite containing rock and for APTsorb. The changes in hydrogeochemistry and element content of the water while passing the different zones were observed via respective sample ports. After the experiments, the solid filling materials were removed from the column and investigated by hXRF analyses and SEM-EDX. Furthermore, sequential extractions were performed on the reactive materials to obtain information about the mobility of elements.

In the mobilisation zone of the column, copper concentrations range up to 2 g/L. In the paper, detailed results for both reactive materials will be presented. A main conclusion is that APTsorb is more efficient in comparison to zeolite. It was able to retard nearly 100% of the released copper. Both reactive materials have a good buffer capacity. They increased the pH of the tailing water (pH=3.8) up to values between 5.5 and 7.

The investigated zeolite as well as APTsorb seem to be appropriate retention materials for Chilean mine waters. Further investigations have to be done to extend the results, determine the sorption capacity for each material and to clarify if desorption of the attached elements is possible. The main focus here is on the reprocessing of copper and strategic elements. Furthermore, the applicability for other mine waters can be tested.

Key words: Chilean mine water, Zeolite, Peat (APTsorb), copper retention

Introduction

Mining activity is often related to acid mine drainage (AMD) with discharge of mine waters contaminated by environmentally relevant metals. Therefore, it is important to remove these elements from the released waters to protect the surrounding ground and surface waters. One promising possibility for the retention of these contaminants is ion exchange. There is a large variety of materials which are well known to function as ion exchange material. One auspicious ion exchange material which will be mentioned are zeolites. They are micro porous aluminum-silicates which have a large specific area (Foo und Hameed 2011) and reported to have a high exchange capacity for cations like copper, cadmium or zinc. Furthermore, they are low cost absorbents and occur in natural deposits all over the world (Babel and Kurniawan 2003). Motsi et al. (2009) reported for zeolites a high absorption speed after 40 minutes the main part of elements was absorbed by the zeolite. An Other promising ion exchange material is peat. It has an extremely high specific area up to 200 m²/g and very good absorption capacities to various elements (Couillard 1994). Peat-based sorption materials such as APTsorb (American Peat Technology) are also reported to retard copper very efficiently (Eger et al 2015).

Chile is one of the largest producer of copper ore worldwide. Due to that and the long period of time since ore processing in Chile is done there are large amounts of legacies which causes the already

mentioned problems for the environment. Except for the environmental problems the legacies represent also a raw material body because of the enhanced metal production techniques now days. Therefore, the tailings are interesting for secondary mining approaches. Because they still contain significant amounts of minor and trace elements and metals of economic interests (Ussath et al 2015).

Column experiments are an appropriate instrument to reproduce real earth system conditions in a laboratory scale. Therefore, this experimental setup was chosen for the investigations of the absorption materials. Because they should be investigated under as realistic conditions as possible to get an impression how they can handle such complex systems and if they are an appropriate option for Chilean mine water treatment.

Sequential extraction is a type of leaching of solid material, which differentiates the mobility of elements. The same material is treated successively with stronger leaching solutions in order to determine extractable metal concentrations of each step. There are up to seven pH-dependent extraction steps incipient with water, followed by saline, complexing, reducing and oxidizing reactants were carried out. Due to that, a correlation between sequentially dissolved minerals and extracted element contents is possible. This allows inferences to the mobility's. An evaluation of the selective extraction method provides information about the extractability and thus mobility of different major and trace elements (Ussath et al 2015). These information are matter of particular interest for the evaluation of secondary mining approaches.

Methods

Column experiment

Column experiments were carried out to reproduce the conditions in the real system. In this case, Chilean tailing material was used to generate a representative tailing water. To investigate the reactive materials, the column was divided into three zones. The lowest zone represents the mobilisation zone and is filled with the original Chilean tailing material. To reach better flow through it was mixed with 37 % mass of pure quartz sand (inert dilution material). Above that, is the reactive “retention zone” located which consists of one of the ion exchange materials. Both materials were diluted by 50 % mass of pure quartz sand. The third zone was filled with quartz sand and characterises the outlet. All experiments were done for a Chilean rock which contains approximately 15-20 % of zeolite and for APTsorb. Changes in hydrogeochemistry and element content of the water while passing the different zones were observed via respective sample ports. To get information about the composition of the generated mining water the first sample port was located in the upper third of the mobilisation zone. The retention zone was monitored by two sampling ports one at the beginning and the other at the end of the zone. Ultrapure water was pumped through the column from the bottom to the top with speed of 20 ml/h. According to that takes the exchange of one pore volume 7.5 h with an effective pore volume of 10 %. All water samples were analysed by photometry in matters of their copper und sulphate concentrations. After the experiments, the solid filling materials were removed from the column and stored at -20°C.

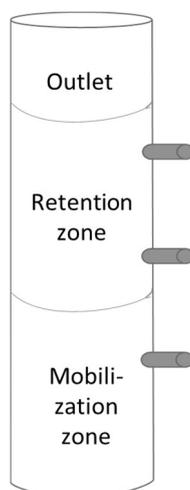


Figure 1: schematic diagram of the column experiment

Sequential Extraction

To get information about the mobility of the retarded elements on the ion exchange materials a sequential extraction was done. An abbreviated variation from the method of Zeien (1995) was used, developed by the project partner GFI (Kassahun, Hache). In

Table 1 the steps used in the sequential extraction are shown. For all steps a solid:liquid ratio from 1:10 was used. To conserve the mineral phases and bonded main and trace elements, step I to IV were done under nitrogen atmosphere. For each step the eluates were analysed for pH, electric conductivity, redox potential, total inorganic carbon (TIC), ferric iron and element content (by ICP-MS analysis).

Table 1: overview of 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 experiment

Former own investigations on the tailing materials have already shown a high mobility of copper. This can be confirmed by the current experiments. In the mobilisation zone of the columns, copper concentrations range up to 2 g/L during the first 24 h (17 h without and 7 h of pumping with a pump rate of 20 ml/h). But it also decrease very fast. For example after two days only 0.1 g/L copper was measured in the mobilisation zone of the APTsorb column. In figure 2 is the pH-development of each column zone for both reactive materials (APTsorb and zeolite) shown. Due to that it can be estimated that the Chilean tailing material used in the mobilisation zone behaves in both columns similar and is homogenous. Both reactive materials have a good buffer capacity. APTsorb were able to increase the pH-value of the tailing water over the whole time of testing in a range between 5.5 and 6. In comparison to that is the zeolite able to increase pH of the water up to a pH-value of 7.5 but not constantly over the complete time (see fig. 2). After one exchanged pore volume the buffer performance decrease and settle down to a pH of 5.5. This high buffering of the zeolite at the beginning of the test may related to contained calcite.

Both materials have a good retention potential (fig. 3) but APTsorb is more effective than the zeolite. The first two cm of APTsorb in the column retard the copper completely over the whole period of time. As in figure 3 shown does the first centimeters of the APTsorb (A retent 1) retard already the complete incoming copper. The zeolite accomplished the complete copper retention only up to three pore volumes and then decrease constantly. But a breakthrough in the outlet cannot be observed. The first time when copper can be detected in the outlet was in the last sample of the experiment after 5.5 pore volumes. But it has to be considered that in the experiments no pure zeolite was used. The zeolite content was estimated of 15-20 %. In comparison to APTsorb is the content of reactive material in case of the zeolite much lower. This can be one reason for these considerably differences between APTsorb and the zeolite. APTsorb has also a much higher adsorption capacity for copper than zeolite. Babel and Kurniawan 2003 reported for typical zeolites adsorption capacities between 1.64 and 5.10 mg/g (batch experiments) in comparison to that, have peat capacities from 6.4 to 19.56 mg/g (batch experiments). According to our results of the column experiments the adsorption capacities for copper can appraised for APTsorb on 286 mg/g and for zeolite between 120 and 160 mg/g (depending on assumed zeolite content). These obvious difference between the literature value and the experimentally observed value might be explained by possible precipitation and filter mechanisms which are only occur in column experiments.

The comparison of figure 2 and 3 show some similarities between copper retention and buffering. In case of the zeolite the buffer capacity decreases temporally delayed when the retention decline. When no retention can be observed the pH commute to a constant value. APTsorb indicates an analogue behavior.

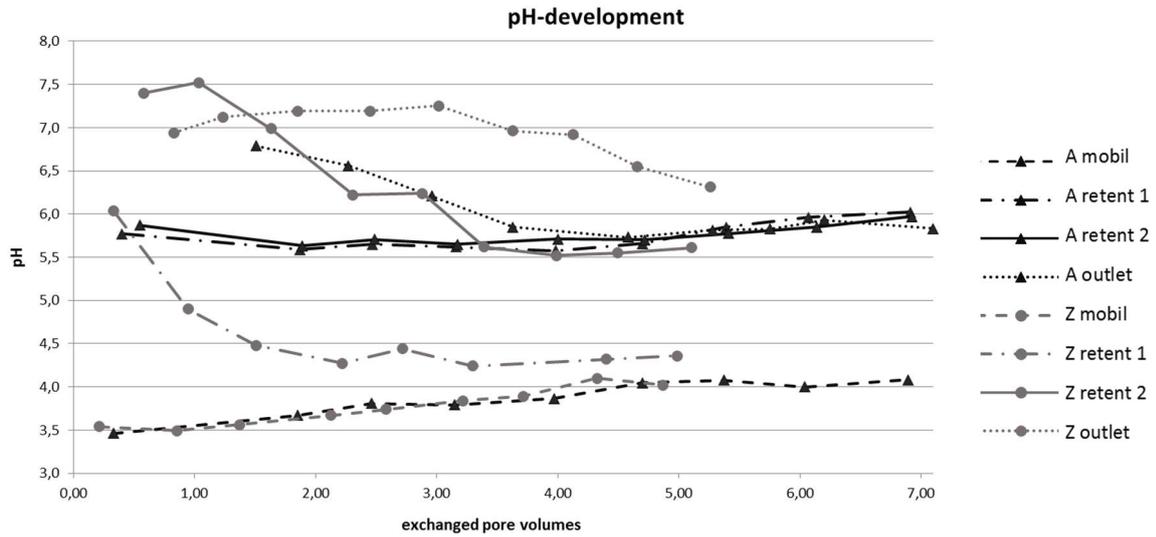


Figure 2: Development of the pH-values in each column zone as a function of exchanged pore volumes. ▲ Column A (retention material: APTsoorb). ● Column Z (retention material: zeolite); mobil (mobilisation zone), retent 1 (retention zone first sample port), retent 2 (retention zone second sample port)

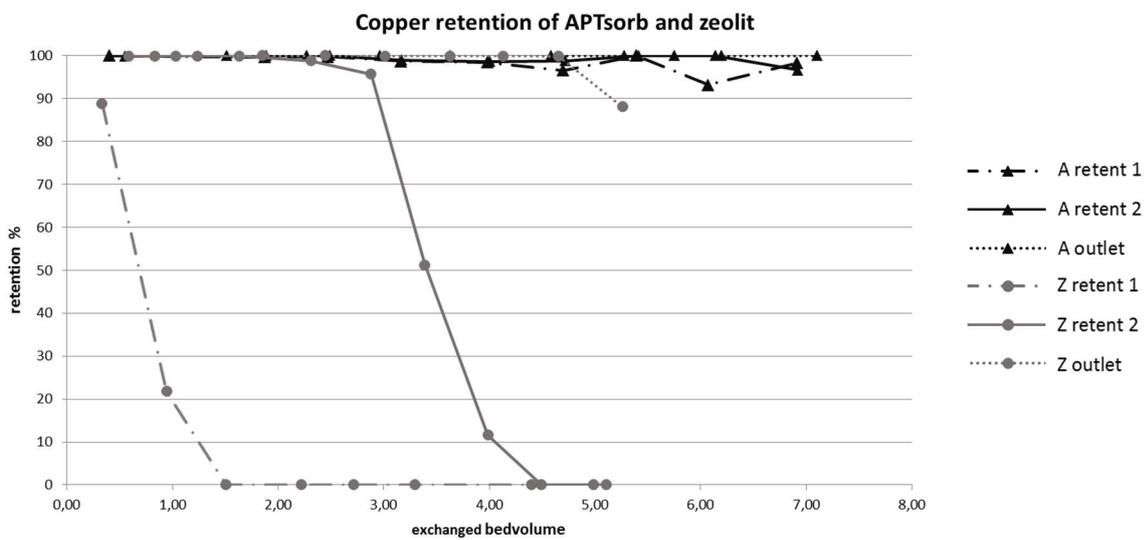


Figure 3: Copper retention in % for zeolite and APTsoorb. ▲ Column A (retention material: APTsoorb). ● Column Z (retention material: zeolite); retent 1 (retention zone first sample port), retent 2 (retention zone second sample port)

Sequential extraction

To get some information's about the strength of the element attachment to the sorption media and if they can be desorbed from materials afterwards a sequential extraction was done. Due to that the materials can be assessed if they are suitable for secondary mining approaches. Both retention materials bond the copper strong enough that it could not be desorbed by ultra-pure water from the ion exchange material in significant values. In figure 4 is the copper release from both sorption medias for each extraction step shown. For the zeolite the sequential extraction show that the copper is bonded by a variety of binding types but mainly to the ion exchanger (ammonium nitrate solution) and carbonate fraction (ammonium

acetate solution). Due to the results the strength of bonding seems to be a function of contact time in case of the zeolite. The zeolite sample from Port 1 is near the mobilization zone and so exposed to the copper for a longer time than the material from the second Port. According to that the copper attached stronger to the zeolite with increasing contact time as in the figure 4 shown. In the ion exchangeable fraction released the zeolite from the second port higher copper amounts. For the stronger bonded carbonate fraction a reverse behaviour was observed. This assumption is supported by the results from the desorption behavior for the ammonium EDTA solution and the oxalate buffer. Both solutions release more copper from the zeolite of the first sample port than of the second. Due to these results the zeolite seems to be appropriate for secondary mining approaches because the main part of the released copper in the experiment was with quite cheap and unproblematic solutions.

In case of the APTsorb the results from the column experiment can be confirmed because there was no significant copper release from the material of the second sample port. As expected most of the copper attached to the APTsorb could be desorbed by the ammonium EDTA solution (see fig. 4) which represents the organic bounded fraction. The oxalate buffer was also able to release large amounts of copper. But for ammonium nitrate and acetate the copper amounts were very low. For the reclamation approach of attached elements to the ion exchange material, the APTsorb seems not to be the best possibility because ammonium EDTA is quite pricey and so the economic yield would be too low. One possibility is to look for a cheaper extraction solution as an alternative for ammonium EDTA.

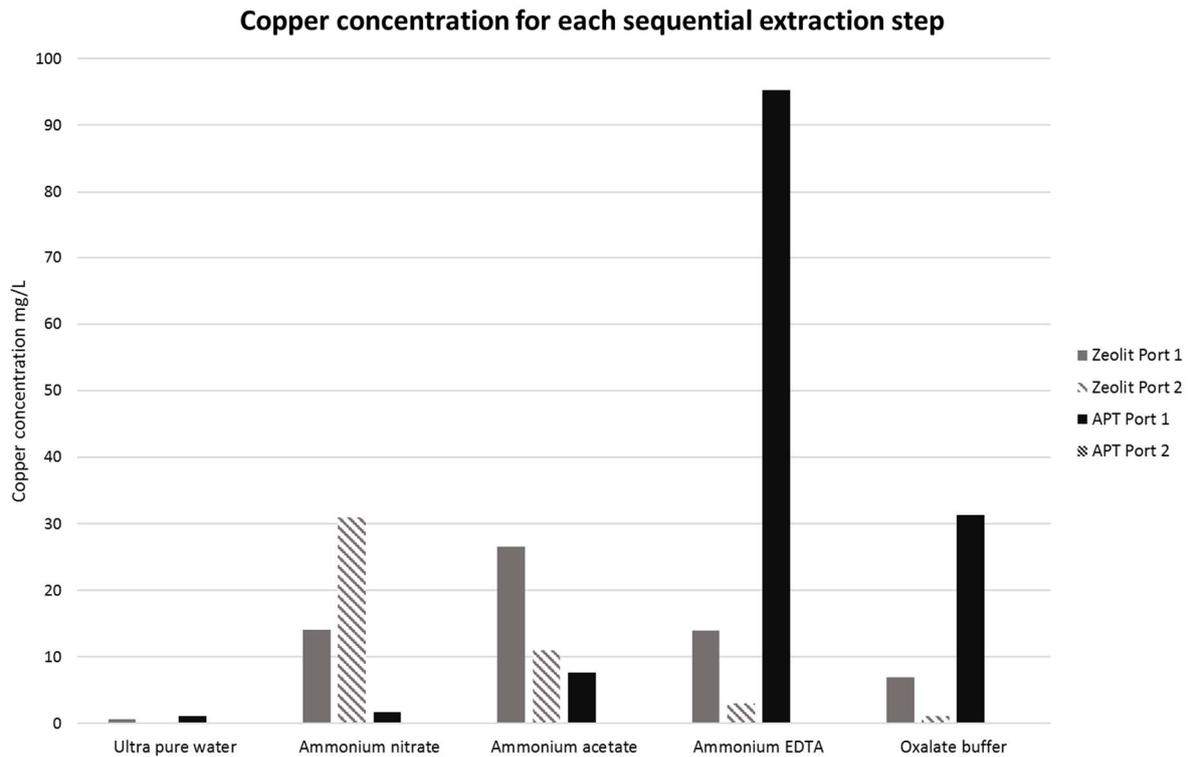


Figure 4: distribution of the copper release from the loaded sorption materials (zeolite and APTsorb) subjected to the extraction solutions.

Conclusion

The investigated zeolite as well as the APTsorb seems to be appropriate retention materials for Chilean mine waters. Both were able to increase the pH-values of the incoming tailing water up to environmental unproblematic values and retard large amounts of copper and other contained elements. Additionally, the developed experimental setup for the column experiment worked out well. Nevertheless, further investigations have to be done to extend the results and determine the sorption capacity for each material. Furthermore, the applicability for other mine waters can be tested.

In case of the secondary mining approach the main focus is on the reprocessing of copper and strategic elements. Therefore, the zeolite seems to be more suitable than the APTsorb because of the relatively pricy extraction solution needed for the APTsorb which would reduce the economic profit. With further investigations other extraction solutions or techniques should be tested.

Acknowledgements

The project SecMinStratEl is funded by the German Federal Ministry of Education and Research (BMBF) as a part of the CLIENT-program “International Partnerships for Sustainable Technologies and Services for Climate Protection and the Environment” (grant no. (FKZ) 033R118A). The authors also thank American Peat Technologies for providing the APTsorb.

References

- Babel, S.; Kurniawan, T. A. (2003): Low-cost adsorbents for heavy metals uptake from contaminated water. A review. In: *Journal of Hazardous Materials* 97 (1-3), S. 219–243.
- Couillard, D. (1994): The use of peat in wastewater treatment. In: *Water Research* 28 (6), S. 1261–1274.
- Eger, P.; Jones, P.; Green, D. (2015): Solving Mine Water Problems with Peat-based Sorption Media. – In: *Agreeing on solutions for more sustainable mine water management – Proceedings of the 10th ICARD & IMWA Annual Conference.* – electronic document (paper 139); Santiago, Chile (GECAMIN).
- Foo, K. Y.; Hameed, B. H. (2011): The environmental applications of activated carbon/zeolite composite materials. In: *Advances in Colloid and Interface Science* 162 (1-2), S. 22–28.
- Graupner, T.; Kassahun, A.; Rammlmair, D.; Meima, J.A.; Kock, D.; Furche, M.; Fiege, A.; Schippers, A.; Melcher, F. (2007) Formation of sequences of cemented layers and hardpans within sulfide-bearing mine tailings (mine district Freiberg, Germany), *Applied Geochemistry*, vol. 22, p. 2486-2508
- Motsi, T.; Rowson, N. A.; Simmons, M.J.H. (2009): Adsorption of heavy metals from acid mine drainage by natural zeolite. In: *International Journal of Mineral Processing* 92 (1-2), S. 42–48
- Ussath, M.; Wendler, C.; Hoth, N.; Kelm, U.; Haubrich, F.; Hache, M.; Heide, G.; Grimmer M.; Drebenstedt, C. (2015): Mobility of Strategic Elements in Chilean Tailings in the Context of Secondary Mining Processes – In: *Agreeing on solutions for more sustainable mine water management – Proceedings of the 10th ICARD & IMWA Annual Conference;* Santiago, Chile (GECAMIN).
- Zeien, H. (1995) *Chemische Extraktion zur Bestimmung der Bindungsformen von Schwermetallen in Böden*, Inaugural-Dissertation Rheinische Friedrich-Wilhelms-Universität Bonn, Institute for Pedology, Bonner Abhandlungen, 17