

Mobility of Strategic Elements in Chilean Tailings in the Context of Secondary Mining Processes

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ABSTRACT

After a long time of dumping, tailings are characterized by hydrogeochemical reorganization processes that are reflected in weathering zones (mobilization) and accumulation zones (immobilization). These processes are connected to substantial secondary mineral formation. Accumulation zones are thereby often connected to iron phases and also have an increased content of trace elements. This knowledge is relevant for Chilean mining dumps because some of them are already affected by these long time processes.

Chilean mining companies are interested in information on the occurrence and extractability of secondary minerals and strategic elements (minor and trace elements of economic interest) from tailings. The German-Chilean project SecMinStratEl (Secondary Mining of Strategic Elements) aims to provide an understanding of the accumulation processes and will also evaluate opportunities for selective extraction. The project is actively supported by significant Chilean mining companies and universities.

Tailings considered in the study consist of granular material, which was ground during primary mining. Due to its potential content of elements of economic importance, the material is nowadays becoming an interesting resource for secondary mining. Exposed tailings suffer from weathering processes; mine waters, especially dump leachates, are enriched in some metals and trace elements which may also constitute a potential environmental hazard.

By means of specific characterization of accumulation horizons in dumps, a description of metal contents and their mobilization behavior is possible. Differentiation between the elemental contents of different layers is achieved with XRF analyses. Furthermore, a sequential extraction is performed in order to describe the partitioning of elements in mineral phases. Thus, the extractability of major, minor and trace elements can be estimated. With these findings, conclusions about extraction technologies for these elements and the environmental risk potential can be made.

Keywords: tailings, secondary mining, mine water

INTRODUCTION

Chile is the world's largest producer of copper ore. Extensive mining and processing over almost a century has left a large number of old mining legacies, which also have associated environmental issues (dust, acidic water, geotechnical instability). As metal production from processed ores was mostly directed towards copper, the tailings and heaps still contain significant amounts of other metals and minor and trace elements of economic interest. Furthermore, by today's standards old tailings are characterized by high copper contents due to earlier less efficient ore processing technology. The tailings are therefore an interesting target for secondary mining efforts.

The state-funded German-Chilean project "SecMinStratEl" (Secondary Mining of Strategic Elements) investigates minor and trace element content, distribution and extractability in Chilean tailings and the formation of secondary minerals. It aims to better understand reorganization processes due to the mobilization of the elements. Methods for the extraction of trace metals from relevant tailings will be evaluated on a conceptual level. In this context, the Institutes for Mining, Mineralogy and Mineral Processing Machines of TU Bergakademie Freiberg are cooperating with the Chilean universities Universidad de Concepción (UdeC) and Universidad de Atacama (UdA). As the project is still ongoing and deals with many different locations and tailings, only a small part of the whole investigation can be discussed here.

This article deals with one tailing of Chilean copper mining, which contains processed waste material from the copper production. The deposit has been exploited since the early 20th century, when the processing technology was much less efficient compared to today. The tailings consist of the processed material from the original ore body and its accompanying rock. Therefore, elemental contents of the mined deposits are of great interest. The tailing material originated from a porphyry copper-molybdenum deposit, which is characterized by copper sulfide minerals (bornite, digenite, chalcopyrite) and molybdenite. Furthermore, this deposit type is characterized by ore-bearing alteration zones accompanied by magnetite and rutile, as well as ilmenite and titanite (Buschmann 2014). Thus, it can be concluded, that the tailing material may contain concentrations of Au, Ag, Ti, Ga, Sn, W, Nb, In and other trace elements in addition to copper and molybdenum. Krause (2014) identified by means of XRD analysis quartz, micas (muscovite, phlogopite), chlorite, feldspars (andesine, albite, orthoclase), pyrite, and rutile to be typical minerals in the tailing material.

Due to the relatively long time of deposition of the tailings, they are affected by hydrogeochemical reorganization processes that are reflected in weathering zones (mobilization) and accumulation zones (immobilization). Accumulation zones are often related to secondary mineral formation of Fe phases with an increased content of trace elements. The intention of the study is a better understanding of the formation of these enrichment zones due to mobilization and immobilization reactions.

During an on-site sampling at the tailing in Chile, aqueous and solid samples were taken. At the surface of the tailing, the authors found efflorescent mineralization. It indicates a mobilization of metals with a subsequent accumulation at the surface due to the evaporation of pore water. Therefore, seepage waters from the tailings were sampled and analyzed to determine element contents. Solid samples were collected from different layers of the tailing at different sampling points, so that accumulation zones can be distinguished. The formation of different layers could be seen visually, however, for the geochemical description of the layer material, pXRF analyses and grain-size analyses were carried out. Another approach for the characterization of mobility inside

the tailings was sequential extraction on tailing material. Integrating these measurements, conclusions about the distribution of weathering, accumulation and enrichment zones can be made. Furthermore, ideas for the selective recovery and extraction of elements of economic interest can be developed.

METHODOLOGY

General Sample Characterization and Analyses

Solid samples were collected from freshly exposed profiles at a tailing, which was exposed approximately three years earlier. Back in Germany, the samples were homogenized and dewatered. After that, they were divided for different analysis methods, e.g. sequential extraction, X-ray fluorescence analysis and grain-size analysis (derived from German standard procedure DIN 66165 with 50 g of sample).

Water samples were taken from water outflows at the base of a tailing dam. On-site, environmental parameters (pH, pE, electrical conductivity) of the waters were measured. Water samples were bottled and acidified for the analyses of element concentrations in an external laboratory (ICP-MS, Actlabs Canada).

X-Ray Fluorescence Analyses

The X-ray fluorescence (XRF) spectrometer is an instrument used for non-destructive detection of major elements and selected trace elements during the investigation of rocks, ores and soils. A portable X-ray fluorescence (pXRF) analyzer allows operating on-site for immediate analysis. Field measurements, which were carried out by means of pXRF at exposed profiles, provide an overview about the elemental distribution (of major elements) in different horizons and help characterize tailing.

For this study, a pXRF Niton XL3t980 analyzer (equipped with an Ag-Anode 50 kV X-ray tube and Silicon-Drift-Detector 8 mm spot) was used. Raw data were visualized in spectra, where x-axes represent element-specific fluorescence energies (unit keV), and y-axes quantify counts of photons (unit cps) received by the detector. Analysis is possible for most of the elements with atomic numbers ranging from 12 (magnesium) to 92 (uranium), thus, for various trace metals a semi quantitative determination is possible. Results are comparable to wet-chemical analysis, though, pXRF has higher detection limits.

It should be noted that several factors have an effect on the measurement and the data output provided by the device: surface conditions (roughness), moisture content, matrix effects and calibration for the respective solid matrices (calibration used for quantification must be appropriate to the material of the sample analyzed). For major and trace elements device-specific, standard-based correction factors for normalized, homogenized and dried samples were developed, which were determined by measuring certified reference materials (publication prepared for CANAS 2015, Grimmer et al. (2015)). Values used in this article are corrected using these factors.

Sequential Extraction

Sequential extraction is an enhanced type of leaching of granular material, which distinguishes different bonding types of elements. The same material is treated with progressively stronger leaching solutions in order to determine extractable metal concentrations of each step. Seven pH-dependent extraction steps with water, followed by saline, complexing, reducing and oxidating reactants were carried out. By that, a correlation between extracted element contents and sequentially dissolved minerals, and therefore bonding types, is possible. An evaluation of the selective extraction method provides information about the extractability and thus mobility of different major and trace elements. The project partner GFI Dresden (Kassahun, Hache) developed a sequential extraction method, which is a variation from the method of Zeien (1995) and comparable to Dold & Fontboté (2001). In each step, eluates are analyzed for pH value, redox potential, electrical conductivity, TIC, Fe(II) and elemental concentrations (ICP-MS analysis). The steps of the sequential extraction used in this project are shown in Table 1.

Table 1 Overview of extraction steps of the altered sequential extraction method (modified from Zeien (1995) and Graupner et al. (2007))

Step	Extracted phase	Leaching solution	Conditions
It	Water soluble	Ultrapure water	
II	Exchangeable	Ammonium nitrate	pH 7
IIIa	Carbonates and specific bonds	Ammonium acetate	pH 6
IIIb	Reducible	Ammonium acetate Hydroxylamine hydrochloride	pH 6
IV	Organically bound (Oxidizable)	EDTA	pH 4.6
Va	Amorphous and poorly crystallized iron and aluminium hydroxides	Ammonium Oxalate Oxalic acid	pH 3.25
Vb	Crystalline iron and aluminium hydroxides	Ammonium Oxalate Oxalic acid Ascorbic acid	pH 3.25

RESULTS AND DISCUSSION

X-Ray Fluorescence Analyses – Field measurements

Eleven profiles (spatially relatively close to each other) were registered on the tailing. An exemplary result is the distribution of the copper concentration with depth in Profile 4 (left diagram of Figure 1). In this regard, the direct field measurement (blue) is compared to the measurement of samples in the laboratory (orange). Visually and granulometrically distinguishable horizons are labeled A to G. The result of the sieve analysis, i.e. the grain-size characterization, is shown in between the two diagrams of Figure 1. The abbreviation FSa stands for fine sand, MSa for medium sand, si for silty (si2 means < 15 wt% of silt, si4 > 30 wt% of silt). Enrichment zones of copper in the lower horizon areas are clearly revealed. Horizon E, which consists of medium grained silt, shows characteristics of an enrichment horizon based on these results. However, sequential extraction results are needed to verify this conclusion – as this can also be a production/process-related phenomenon. In general, copper contents of the profiles range from 0.15 to 0.3 %, but locally reach 0.5 % and more.

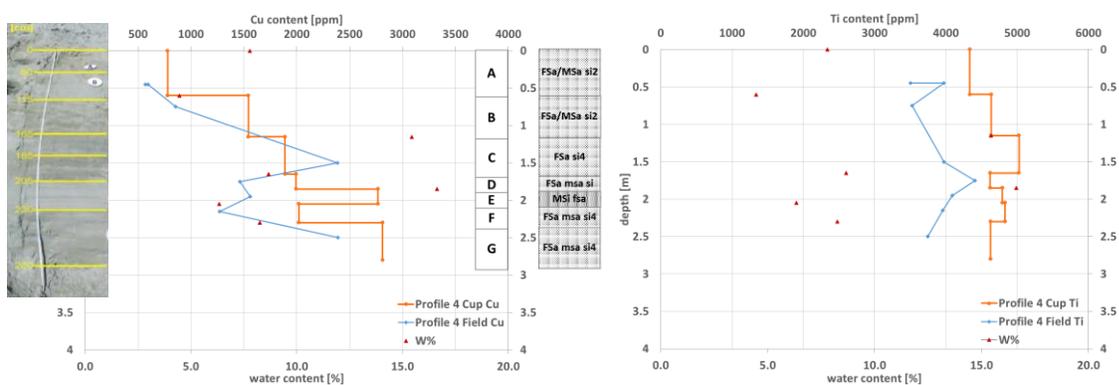


Figure 1 Copper and titanium distributions as function of the depth measured by means of pXRF; photo of profile at sampling site (left); grain size characterization of horizons (center)

These distribution diagrams were created for all profiles and major elements. In the right diagram of Figure 1, the distribution of titanium is shown. Titanium contents range within an order of magnitude of 0.5 %. This element shows less variation between the horizons than copper.

Unfortunately, results for rare earth elements analyses using complete chemical digestion are still pending at the beginning of 2015. Furthermore, deep boreholes (up to 60 m depth) were made into the tailing. They were characterized (e.g. color, granular structure) and sampled and provide an overview of the entire tailing body. From these, comparisons of oxidized and reduced deep zones and estimated element contents of the tailing can be conducted. These investigations are planned for 2015.

Grain-size analyses coupled with pXRF measurements

After sieve analyses, samples of the different fractions remain. These fractions were measured separately with the pXRF analyzer resulting in a distribution of elements depending on the fraction. For the lower horizons D to G of profile 4 the copper distribution is shown representatively in Figure 2.

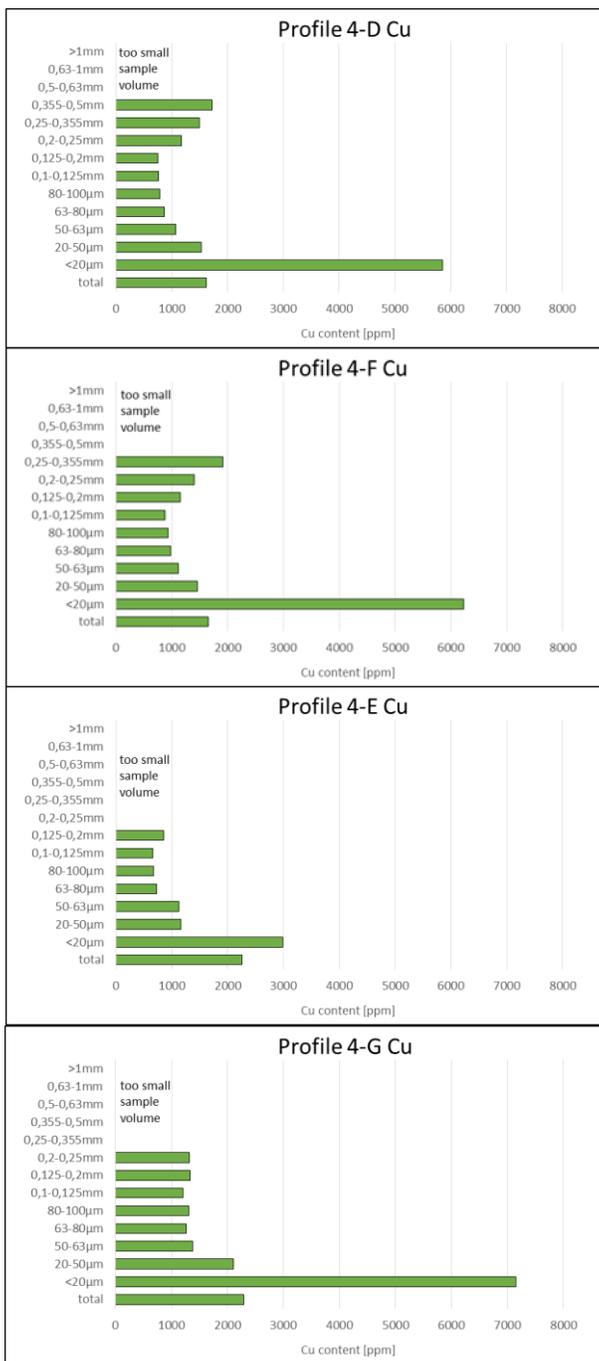


Figure 2 Grain-size dependence of copper content [ppm] measured by means of pXRF

It should be noted that the copper content in ppm refers to the respective particle size fraction whereas the masses of the fractions are not in the focus of this article. The knowledge of the fraction mass is used to estimate the fraction dependent copper contents or other elemental concentrations. In Figure 2 a higher copper content in the fractions 0.2 to 0.5 mm was identified. The highest concentrations are observed at grain sizes smaller than 50 μm .

In addition to copper, grain size dependencies were also examined for the following elements: Al, Ca, K, S, Si, Zn, V, Fe, Ti, As, Mo, and Mn. The results vary depending on the respective horizons, and show random enrichments of these elements in other fractions than $<50 \mu\text{m}$. Ongoing investigations will further elucidate these relationships.

Sequential Extraction

Evaluations of eluate analyses show varying characteristics of the extraction behavior of major and trace elements. A differentiation between a high and a low percentage of extracted element content has to be made. A low percentage means that after step Vb the bigger part of the element content still is bound to the remaining solid (especially sulfides, silicates). The pXRF measurements provide an estimation of the total element content in the original tailing material for the comparison with the extracted content. Another differentiation can be made between easily soluble/extractable elements, which are detected in the eluates from steps I, II and III and more strongly bound elements from the steps IV, Va and Vb.

Copper

Copper was the objective of primary mining processes. However, due to the evolution in ore processing technologies, the remaining copper content in the older tailings is nowadays of interest for secondary mining.

Figure 3a shows the results of the sequential extraction for copper. In comparison to total copper contents determined by XRF, copper is completely extracted by the leaching steps. Furthermore, except of layer A, which has experienced weathering processes, more than 75 % of copper is extracted from the tailing material within the leaching steps I, II, IIIa or IIIb. These results show the great mobility of copper in the sampled tailing.

(a)

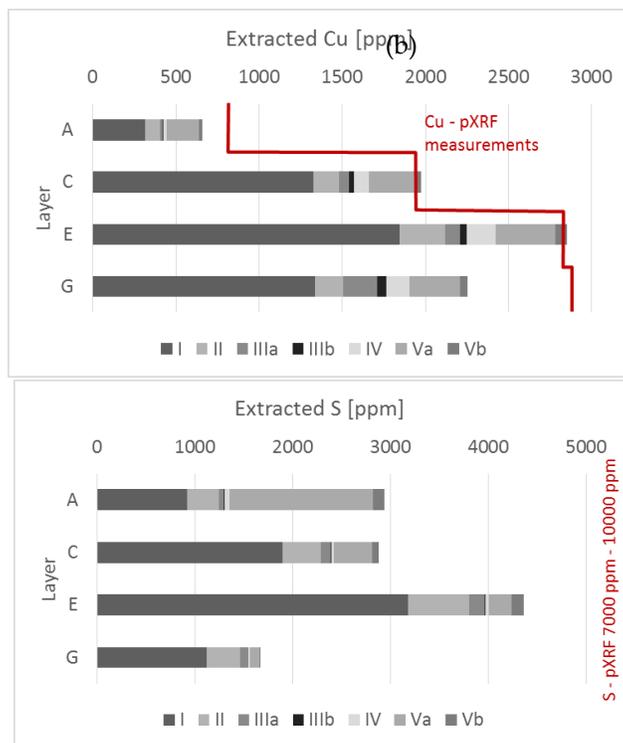


Figure 3 Extractable copper (a) and sulfur (b) during sequential extraction

More than half of the available copper can be recovered by a simple water extraction (step I). Solubility and thus removal of copper was also detectable as a loss of mass during wet sieving analyses. Copper complexes such as copper sulfate are very soluble and highly mobile. Thus, relocation to the depth (with seepage water) or due to evaporation and capillary action to the surface can lead to efflorescences. In this context, the formation of chalcantite was observed in coarse tailing material with low moisture contents.

The remaining copper content is almost completely recoverable by means of ammonium oxalate as the extracting solution, i.e. during sequential extraction step Va (Table 1). This extractant dissolves amorphous and poorly crystallized iron and aluminum oxides.

Sulfur

Based on the assumption, that sulfur occurs mostly as (copper) sulfate inside the tailing, the sequential extraction of sulfur was examined. Figure 3b presents these results and furthermore shows the total sulfur amounts determined by pXRF (7000 – 10000 ppm). In contrast to copper, sulfur has not been extracted completely within the sequential leaching, as can be seen in comparison to the pXRF value. Extracted phases of sulfur are sulfates (step I), but also sulfur adhered to iron hydroxides (steps Va and Vb).

Arsenic

The behavior of arsenic shows the importance of considering the mobility of some elements. Arsenic levels up to 100 ppm are detected in tailing samples by pXRF. According to the findings from the sequential extraction, arsenic is barely dissolved until step Va (ammonium oxalate). This

means arsenic is difficult to mobilize, which is also confirmed by the analysis of tailing water outlets.

Other elements

In case of strategic elements, such as yttrium, cerium and vanadium, mobilization starts with extraction step IV (organically bound, oxidizable), which means they can be mobilized by EDTA. Molybdenum is partly dissolved during extraction steps IIIa, IIIb and IV, i.e. it is soluble with an acetic buffer. Therefore, these elements are more difficult to extract from the tailing compared to copper and they are less mobile.

Water Samples

Water samples were analyzed with ICP-MS in order to characterize mobile fractions, which were dissolved inside the tailing and transported with the seepage water. Due to dissolution processes within the tailing, specific elements are mobilized. It is assumed, that outflowing tailing waters mainly contain easily extractable elements. One example for that is arsenic, which is difficult to extract and in fact was not to be found in outflowing tailing waters.

Table 2 lists measured ranges of element concentrations of copper and selected light and heavy rare earth elements: cerium, dysprosium, gadolinium, lanthanum, neodymium, samarium and yttrium. Maximum copper concentrations of 888 mg/l are an indication for significant solubility and high mobility. In the second row, maximum concentrations measured in a pond at the base of the tailing are included. These values show the high potential capacity for element mobility within the tailing. Evaporation as a cause of enrichment has to be taken into account, as samples were taken during the summer. Nevertheless, the pond water accumulations show also a significant amount of rare earth elements, which originate from the tailing material.

Table 2 Overview of ICP-MS analysis results for copper and selected rare earth elements (contents in µg/l)

element	Cu	Ce	Dy	Gd	La	Nd	Sm	Y
Outflow waters - range	100000 - 350000	20 - 50	11 - 19	8 - 17	6 - 20	19 - 62	7 - 17	70 - 118
pond water	888000	275	75	53	90	183	48	510

CONCLUSION

During the first part of the investigation, eleven profiles at a tailing of a Chilean copper mine are characterized. Investigated tailing shows a formation of horizons, which are due to a variety of processes. The geochemical composition (e.g. copper content) of the horizons is initially influenced by the original ore body and by primary recovery processes or attributes such as coarseness, flotation fluids and their chemical properties, hydraulic dumping of the processed waste material, and exposure time among others. Apart from that, hydrogeochemical reorganization processes cause mobilization and immobilization of elements and also the formation of distinct horizons. It is possible to get a general idea of the horizontal zonation of the tailing and the approximate

elemental contents of the respective horizons by means of pXRF measurements. However, the tailing composition is not yet fully understood, especially in terms of mineralogy.

Understanding of hydrologic processes and especially the generation and location of accumulation zones inside the tailing is important. For instance, Dold & Fontboté (2001) described cases, “where evaporation exceeds precipitation, the water-flow direction may change to upwards migration via capillary forces. [...] Supersaturation controls the precipitation of mainly water-soluble secondary sulfates (e.g. bonattite, chalcantite) and leads to partly strong enrichment at the top of the tailings”. Distributions of the fine granular materials are important, e.g. copper shows enrichments in the fine material (< 50 µm). Based on the sequential extraction results the following recommendations for secondary copper production from tailing sites can be made: in the case of hydraulic mining, water is not only a transport medium, but also an extracting agent and should be completely collected, as already done with seepage waters of several copper tailings in Chile. Otherwise the majority of the copper content will be lost.

Future investigations will deal with the development of simplified extracting methods for leaching as a secondary mining solution. Furthermore, immobilization horizons will be characterized mineralogically in order to provide a basis for selective mining. For that, more detailed examination of the potential of minor and trace elements in the tailing samples will be conducted.

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).

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