

Investigations on Heap leaching material and potential recovery of strategic elements

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Extended Abstract

The importance of rare elements, especially for the industry sector of renewable energies is well known. Our research group collaborates with a Chilean company that leaches ore using the method of conventional heap leaching with sulfuric acid to extract copper. The dumped residuals of the leaching process have been investigated for their potential concerning the content of strategic elements. Strategic elements in this context are minor and trace elements of economic interest. One important question is whether these elements are recoverable by using simple and inexpensive processes.

Initial studies of recently dumped material were started on-site and continued later in the laboratory. The heap material is a mixture of coarse-grained to fine-grained ore chunks. With this material, pure water eluates were prepared in the field to investigate milieu parameters and element content. As expected, extremely high electrical conductivities (22.9 mS/cm) and low pH-values (down to 2.9) were measured in the solvent. Besides that, liquid phase samples were taken for ICP-MS analyses of elemental concentrations.

In the lab, sequential extraction was performed as an analytical method, providing information about the extractability and thus mobility of the different elements. Sequential extraction is an enhanced type of leaching of granular material, treating the same material with progressively stronger leaching solutions in order to determine extractable metal concentrations of each step. Furthermore, the sequential extraction method was firstly simplified and secondly modified to estimate strategic element extraction from the residual dump material. Therefore, cheap extraction agents, coming from the proximity of the mining area, were tested. In our case, the cost-effective solvents seawater and sulfuric acid were used.

The article presents the results for three different (sequential) extraction methods:

1. Complete sequential extraction (SE) of 5 g of residual material with 50 ml extracting agent (see Tab. 1 Overview of extraction steps of the altered sequential extraction method (Zeien (1995) [2] and Graupner et al. (2007) [1] modified by Kassahun, Hache) as an “analytical method”
2. Shortened sequential extraction reduced only by certain steps
3. Modified and shortened sequential extraction with special extraction agents

Shortened sequential extraction

The shortened SE consists of four steps of the “complete SE“: step I - water solubles, step II - exchangeables, step III - carbonates and the last step IV (corresponds to step Va in Tab.1) - poorly crystallized iron and aluminum hydroxides. The extractions were carried out under aerob conditions: 5 g of sample were mixed with 50 ml of extracting agent (2h in an overhead shaker).

Modified and shortened sequential extraction

The modified and shortened SE consists of four steps: step I - water solubles, step II – exchangeables, seawater instead of Ammonium nitrate, step III - carbonates and last step IV - sulfuric acid.

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
I	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 aluminum hydroxides	Ammonium Oxalate Oxalic acid	pH 3.25
Vb	Crystalline iron and aluminum hydroxides	Ammonium Oxalate Oxalic acid Ascorbic acid	pH 3.25

Summarized results of the SE method comparison:

Three different SE methods were tested on different Chilean heap and tailing materials. In general, the first (analytical) SE method is the most effective but also the most time-consuming and cost-intensive method. The effectiveness varies depending on the matrix of the original/raw material – e.g. tailing material is relatively homogeneous compared to the heap material. Depending on the (ore) deposit and the elements that should be extracted, each SE method shows a different behavior. In the case of the heap material, the release of elements shows a greater variance due to the heterogeneity of the raw material. Therefore, an accurate evaluation of the extraction results and SE method comparison is less clear in the case of heap material. However, the following results are observed for the SE method comparison with respect to the heap material:

- Step I – Water soluble: relatively high Copper contents (625 ppm); Li (40 ppm) but also REE: Ce (8 ppm), Dy, Sc, Y, La, Nd (< 3 ppm) and Sr (6 ppm)
- Step II - Exchangeable: still Cu released, but in smaller amounts (50 ppm); similar range of extracted element content in 3.5% NaCl and NH₄NO₃
- Step III – Carbonates and specific bonds: e.g. Ca, S, Si
- Step IV – (oxalate or acid step): similar range of extracted element content, acid mobilizes - as expected - some REE: Ce, Dy, Sc, Y, La, Nd and also Mo, Ti, V, Sr
- After two hours of exposure to the extraction agent, the aluminum and silicium contents are already showing the attack of the acid and the oxalate on the silicate structure (of the minerals). Iron is released from sulfidic and hydroxide phases.

Summarized results of the extracting experiments with 200 g of heap material:

For a better evaluation of that kind of extractive mining, new experiments with 200 g of residual material (instead of 5 g) were started to estimate a potential yield. The samples were taken at three different sampling sites (ES1/ES2/ES3) of the same dumping site. For each sampling site exists a shallow (0.5 meters depth) and a deep (4 meters depth) sample. The Material was separated during the water step into a fine (<1 mm) and a coarse fraction. For this extraction experiment a further simplified extraction method was applied, composed of three extraction steps: H₂O, NaCl and H₂SO₄. General results:

- Copper contents up to 1400 ppm were observed in the water soluble fraction (Fig. 1), and about 100 ppm again with NaCl extractant (see SE method comparison results)
- H₂SO₄-step: aluminum and silicium contents clearly indicate an attack on the silicates (see SE method comparison), copper release in fine fraction 300 ppm, in coarse fraction 3700 ppm, release of cerium in both fractions of about 9 ppm. Clear differences between fine and coarse fraction noticeable, release of REE in small amounts Ce, Dy, Y, La, Nd (Fig. 2) and Ti, V, Sr (Mo is probably contained but not measured)
- Comparison fine and coarse fraction: similar range of extracted element content, but Cu and Zn (and Mn and Si) significantly higher contents in the coarse fraction; for Al, Fe higher contents in the fine fraction (clays, Fe-hydroxides)
- Comparison deep and shallow samples: the element contents for extraction agents H₂O and NaCl show no significant trend, H₂SO₄ step: higher contents extracted out of the shallow samples
- Comparison sampling sites (ES1/ES2/ES3): Values previously available only for H₂O and NaCl step - significantly higher contents of location ES3 for the elements Al, Cu, Fe, Li, Mo in the water soluble fraction; NaCl step: Cu and Al content increased in orders of magnitude
- Sampling site ES1 and ES2 are located close together. ES3 is further away and at a slightly higher altitude. This may explain the difference in elemental content, whereas ES1 and ES2 seem to have the same raw material and the same weathering conditions.
- To estimate the real recovery, more investigations and extractions experiments and especially the total extraction analysis results are needed.

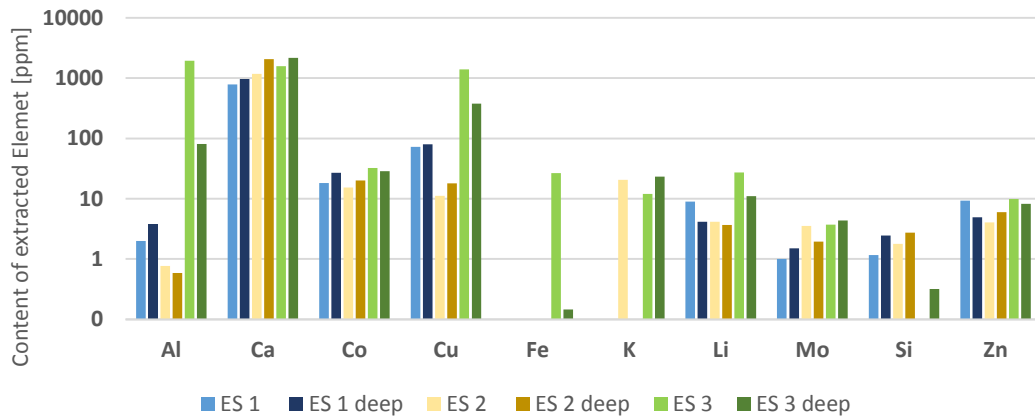


Figure 1 Extraction experiment - H₂O step: release of main elements for different heap material samples

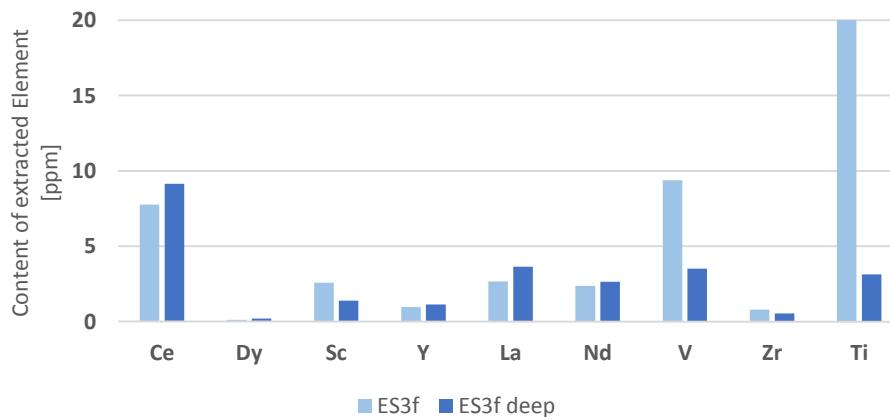


Figure 2 Extraction experiment - H₂SO₄ step: release of several REE

Derived from previous experiments, the main result is a high mobility of copper and aluminum. There is evidence to suggest that aluminosilicates have been attacked long-term (heap leaching takes about 60 days) and there is a release of strategic elements and rare earth elements in connection to that. These were also detected in the residual liquid phase of the first extraction step (pure water). For example Y, La, Nd, Ce and some Dy, Gd, Sc were detected. In the further extraction steps also Dy, Sc can be found.

Key words: heap leaching, strategic elements, sequential extraction

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