Reagents and fractions impact on sulphide ore heap bioleaching at Smolník mine

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Abstract. Mine Smolník is one of the oldest sulphide ore mines in Europe and it is also an important part of bioleaching development. This paper follows previous attempts to extract residual metals from nearby heaps via variations in bioleaching reagents with regard to recent findings and needs in the related industry. Furthermore, economic and process relations between reagents and chosen heap fractions were also investigated in this case study.

1. Introduction

The hydrometallurgy is a well-known technique for metal extraction and recovery. There is a rich evidence of exploiting ore bodies via hydrometallurgy since middle ages all around the world. Various techniques were developed to recover metals from enriched mine waters including copper cementation on scrap iron considered as the oldest [1,2]. Hydrometallurgy has become emerging topic in past decades due to its low energy consumption as the increasing demand for metals caused by global human population growth necessarily led to marginal ore bodies exploitation [2,3]. Nowadays it is clear that phenomenon causing metal dissolution is caused either by an inorganic chemical reaction and biochemical activity of autochthonic microorganisms with varying influence depending on the conditions.

Sulphide mine Smolník located in Slovakia has been exploited for over six centuries and the ore mining continued until 1990 and the mine was flooded in 1994. During its existence, hydrometallurgical principals were applied as the meteoric (rain) water was directed into mine tailings and collected for further processing. To enhance this process acid mine waters (AMD) have been pumped onto tailings, however, no significant difference has been achieved [1,4,5,6].

This paper follows previous attempts to exploit residual metals (Cu) dispersed in mine tailings. The main aim of this study is to evaluate the influence of tailings fractions and different solvents to establish the most advantageous correlation between fraction and solvent under condition present in mine Smolník. In general, leaching kinetics is affected by the particle size of the material that is leached and generally, a smaller particle size gives faster leaching kinetics since finer particles have a larger surface area. That means that a smaller particle size has a greater influence on a leaching process that is diffusion controlled [6]. However, disintegration is a highly energy-intensive process, thus the economic correlation between time and metal recovery is an important aspect of low-grade resources processing.
2. Materials and methods
Leaching took place in aerated 5L PET containers during 49 days. Samples for AAS spectrometry
were taken every 7 days and pH was also measured.

2.1. Samples
Tailing samples have been taken randomly from heaps cumulated nearby mine Smolnik. Samples were
grounded in a vibratory mill and homogenized via quartation. Homogenized samples were sieved into
3 fractions: <1 mm, 1-6 mm, 6-20 mm.

In order to compare different leaching solvents containing various microbial consortia contributing to
bioleaching yield four solvents for each fraction were prepared:
- Pure bacterial culture (Solution: AT+AF). Consortium of Acidithiobacillus thiooxidans +
  Acidithiobacillus ferrooxidans was incubated for 8 days in 9K solution.
- Autochthonic microbial consortium AMD water from mine Smolnik (Solution: DK1).
- Autochthonic consortium (Solution: DK2). Consortium was incubated from precipitated
  sulfate salts found on the heap via dissolving of 1g of this material in 50 ml of water.
- Water acidified by H2SO4 (Solution: K).

In total 12 (3 fractions x 4 solvents) aerated reactors were simultaneously used for this experiment.

Prior to pH adjustment by 2M H2SO4, Reactors were filled with water so that total volume in all 12
reactors was 3L as presented in table 1.

| Table 1. Experimental conditions for exploited heaps bioleaching. |
|---------------------------------------------------------------|
| Fraction                        | 0-1 mm | 1-6 mm | 6-20 mm |
| Tailings sample                  |        |        |         |
| Inoculum AT+AF (50:50)           | 25g    | 50g    | 100g    |
| Inoculum DK2                     | 50 ml  | 50 ml  | 50 ml   |
| Inoculum DK1                     | 50 ml  | 50 ml  | 50 ml   |
| pH                              | 1.5L   | 1.5L   | 1.5L    |
| Total volume                     |        |        | 3L       |

Temperature 20°C was maintained during the experiment. Tap water was used in this experiment in
order to avoid hypotonic environment caused by demineralized water and also to simulate in situ
process conditions.

3. Results and discussion
Results of Cu recovery from different size fractions of exploited heap under different solvent
conditions are presented in figure 1-3. During the whole experiment, pH in all 12 reactors did not
exceed 2.4 and remained stable.

As presented in figure 1 metal recovery from tailings sample fraction 0-1mm took place according
to preconditions that presence of adapted bacterial cultures present in solutions contributed to the
higher metal recovery. However, the impact on the metal recovery of autochthonic bacterial consortia
wasn't significant and the extraction process was similar to inorganic leaching in an acidified water
sample (K).

Results of the metal recovery from tailings sample fraction within the range 1-6 mm presented in
figure 2 are similar to results mentioned above. Bigger fractions slowed the diffusion controlled
process of leaching as expected but after 30 days of leaching achieved similar recovery results as in
figure 1. Comparing figure 1, figure 2 and figure 3 representing tailings samples within the range 0-20
mm the significant contribution of biochemical leaching to overall recovery process arises. Acidified
water (K) and pure culture solvents (AT+AF) had a very similar process, however, autochthonic
cultures originating from AMD (DK1) and precipitated sulphates from Smolnik achieved higher recovery rates. In total DK1 culture achieved the highest metal recovery rates in all examined fractions [6,7].

Figure 1. Recovery of Cu into solution from particles 0-1 mm.

Figure 2. Recovery of Cu into solution from particles 1-6 mm.
The positive influence of adapted bacterial cultures on metal recovery is observed. The most interesting is the correlation between fraction size and biochemical leaching. In other words, the contribution of biochemical leaching to overall leaching process is rising with the higher granularity of the sample within the examined range. It appears that bioleaching of the exploited tailings in mine Smolnik requires determination of specific surface area that needs to be considered in potential further exploitation and the principals of the diffusion controlled process doesn't fully describe contributions of biochemical activity of autochthonic microorganisms [8-11].

4. Conclusion
In conclusion, it appears that contribution rate between inorganic leaching and biochemical leaching to overall metal recovery process depends on the specific surface area. Within the examined range of exploited tailings samples, contribution of biochemical leaching is rising with the increasing particle size.

While leaching the finest sample fraction the kinetics of metal mobilization into solution via chemical and via bio-chemical leaching had a similar process. Difference between biochemical (DK1, DK2) and chemical (K) metal recovery values did not exceed 4%. Interestingly, as the particle size was rising the leaching process differences arisen in-between all applied leaching conditions. The results are clear that the highest recovery rates were achieved by autochthonic microbial cultures originating from Smolnik mine area. In particular medium DK2 which achieved highest recovery rate in all fraction sizes.

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