



## Influence of grain size on chalcopyrite ore leaching in acidic medium

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**Abstract:** This work presents an investigation of column leaching of a chalcopyrite ore using sulphuric acid where dissolved oxygen and iron(III) ions play the role of oxidants. The investigations were carried out in PVC columns, diameter 110 mm and height 1000 mm, by percolation of the leaching solution through the ore layer. The influence of ore grain size on the degree of leaching and acid consumption was examined. The formation of gypsum on limestone results in the comminution of the initial raw material during leaching. The grain size of chalcopyrite was found to have no important influence on the leaching rate of copper. A higher consumption of sulphuric acid was found for the fractions (–3+1) mm, (–5+0) mm and (–5+3) mm than for the fractions (–10+5) mm, (–20+10) mm and (–20+0) mm.

**Keywords:** chalcopyrite ore, column leaching, grain size.

### INTRODUCTION

Classic methods of copper recovery from chalcopyrite ores are associated with the formation of large quantities of out-of-balance raw materials. Further treatment of such raw materials and copper recovery from them is possible by leaching these minerals and subsequent copper extraction from the leaching solutions. Leaching of such out-of-balance raw materials is carried out on heaps, dumps and *in situ*. Both oxide and sulphide copper ores are leached, whereby acid leaching<sup>1,2</sup> and bioleaching<sup>3–6</sup> are the most often employed methods. However, if  $\text{CuFeS}_2$  is the most common copper mineral in the dumps and heaps, the leaching rate is lower than for other minerals because this mineral is not very reactive. Due to this, stronger oxidants have to be used for the decomposition of chalcopyrite. On the laboratory scale, for this purpose, strong oxidants have to be employed, such as: chlorine,<sup>7</sup> nitric acid,<sup>8</sup> ozone,<sup>9</sup> and chromium(VI)<sup>10,11</sup> but, decomposition of chalcopyrite may also occur in the presence of some weak oxidants, *i.e.*, iron(III)<sup>12–15</sup> and oxygen,<sup>16</sup> which are more favourable for direct use.

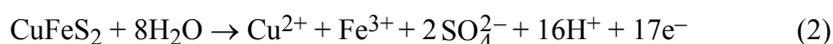
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Previous investigations have shown that the oxidation process of chalcopyrite is very complex, where dissolution is assumed to occur *via* the following Equations:<sup>17</sup>

– oxidation to elementary sulphur



– oxidation to sulphate



For potential values  $> 700$  mV, massive dissolution of the chalcopyrite occurred according to Eq. (1) or (2).<sup>18</sup> Oxygen and  $\text{Fe}^{3+}$  ion can oxidize the mineral because the redox pairs  $\text{O}_2/\text{H}_2\text{O}$  ( $\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ ) and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ( $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$ ) have a standard redox potential of 1.23 V and 0.77 V, respectively.

Both, elementary sulphur and sulphates may be obtained as the final products of chalcopyrite oxidation. Sulphur formation retards the dissolution of this mineral due to passivation.<sup>19–22</sup> Many factors influence the dissolution rate: the nature of the passive layer,<sup>14</sup> galvanic interactions on the surface of the mineral,<sup>23,24</sup> activation of the mineral,<sup>25</sup> particle size,<sup>26,27</sup> *etc.* Using electrochemical methods, important data were obtained and employed to explain the behaviour of chalcopyrite in solution (the nature and existence of a passive layer, the influence of reactants on the dissolution rate, *etc.*), indicating the complexity of the chalcopyrite oxidation process.<sup>28–31</sup>

In this work, the oxidation of chalcopyrite ore from the Bor River ore body was analysed using sulphuric acid solutions as the leaching solution and dissolved oxygen as the oxidant, as well as the iron(III) formed during the leaching. The influence of grain size on the dissolution rate of chalcopyrite was investigated using sulphuric acid solutions (pH 1.0) at a solid/liquid ratio of 1:1. The experiments were performed in columns by percolation of the leaching solution through the ore. In addition to the content of copper, those of iron, silicon, aluminium, magnesium and calcium were determined in the leaching solutions. The untreated sample and the solid residues obtained after the leaching process were analysed by X-ray diffraction analysis.

## EXPERIMENTAL

### Material

Samples for laboratory investigation were taken from the Bor River ore body, East Serbia. The sample was crushed to  $(-20+0)$  mm and samples for study were prepared by additional crushing and sieving. The following fractions were used in this study:  $(-3+1)$  mm,  $(-5+3)$  mm,  $(-5+0)$  mm,  $(-10+5)$  mm,  $(-20+10)$  mm and  $(-20+0)$  mm. The results of the chemical analyses of the ore samples of various size ranges are presented in Table I.

The grain size distributions of an untreated and treated sample within the size range of  $(-20+0)$  mm are presented in Fig. 1.

It was estimated using mineralogical and X-ray analysis of the samples that the most common copper mineral was chalcopyrite and pyrite, whereby the ratio of chalcopyrite/pyrite 1:3. Based on

qualitative mineralogical analyses, the amounts of magnetite, hematite, rutile, leucoxene and limonite, as well as of trace amounts of chalcocite, covellite and bornite were estimated. The background minerals in the analysed sample were based on quartz-carbonate-silicate.

TABLE I. Chemical analysis of the ore samples

Constituents	Content / %					
	Size range / mm					
	-3+1	-5+0	-5+3	-10+5	-20+10	-20+0
Cu <sub>uk</sub>	0.51	0.58	0.53	0.57	0.48	0.64
Cu <sub>ox</sub>	0.007	0.01	0.013	0.009	0.019	0.027
Fe	4.00	3.92	4.60	3.67	3.84	3.93
S	5.18	5.57	5.09	5.76	4.80	3.74
CaO	4.31	6.3	4.59	5.25	5.52	5.94
MgO	1.56	1.69	1.70	1.67	1.48	1.76
SiO <sub>2</sub>	57.64	53.10	55.90	54.4	53.48	54.06
Al <sub>2</sub> O <sub>3</sub>	12.48	12.97	13.19	12.71	12.05	12.89

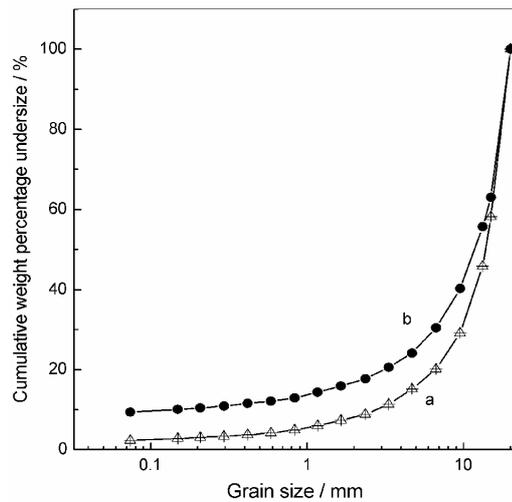


Fig. 1. Grain size distribution for the size range (-20+0) mm, a) untreated sample, b) treated sample.

#### Column leaching experiments

Dissolution of all the samples was carried out in PVC columns of, diameter 110 mm and height 1000 mm, using sulphuric acid solutions as the leaching solution. Eight kilograms of ore of a definite size range, (-3+1) mm, (-5+3) mm, (-5+0) mm, (-10+5) mm, (-20+10) mm or (-20+0) mm, was loaded into a column. A bed of silicon dioxide of about 1 cm thickness was layered over the ore in order to assure uniform distribution of the solution. Sulphuric acid solution of pH 1.0, at ratio of solid/liquid of 1:1, was used as the leaching solution. The pH values were adjusted by addition of sodium hydroxide, and the output solutions were re-circulated upon adjustment of the pH. The sulphuric acid consumption was calculated based on the sodium hydroxide consumption. At definite time intervals, 5 ml of leaching solution was taken and transferred into a 100 ml volumetric flask. The solutions were made up to a volume of 100 ml with distilled water and the amounts of copper and iron were measured using atomic absorption spectrophotometry (AAS). Aluminium and

silicon were measured by inductively coupled plasma–atomic emission spectroscopy (ICP–AES). Upon 90 days of leaching of following fractions: -20+10 mm, -20+0 mm and -5+3 mm, the contents of Ca and Mg were determined in the output leaching solutions by atomic absorption spectrophotometry (AAS).

The liquid flow rate through column was  $3.3 \text{ cm}^3 \text{ min}^{-1}$ . The all leaching experiments lasted three months under atmospheric conditions.

#### RESULTS AND DISCUSSION

Influence of grain size on the dissolution rate of chalcopyrite was analysed for six size fractions, *i.e.*, (-3+1) mm, (-5+3) mm, (-5+0) mm, (-10+5) mm, (-20+10) mm and (-20+0) mm). The results of the leaching experiments are presented in Figs. 2 – 7.

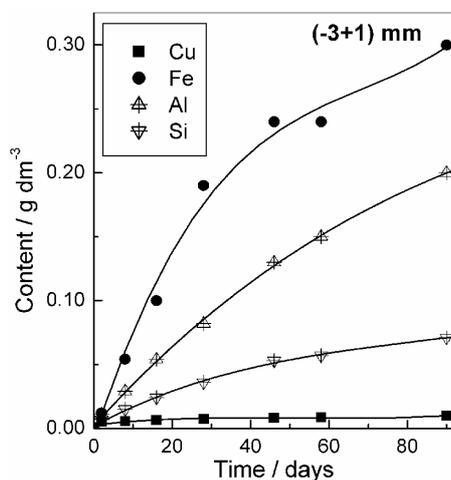


Fig. 2. Dependence of the concentrations of copper, iron, aluminium and silicon in the leaching solution on time after copper ore treatment with sulphuric acid (pH 1.0, S:L = 1:1) for the size range: (-3+1) mm.

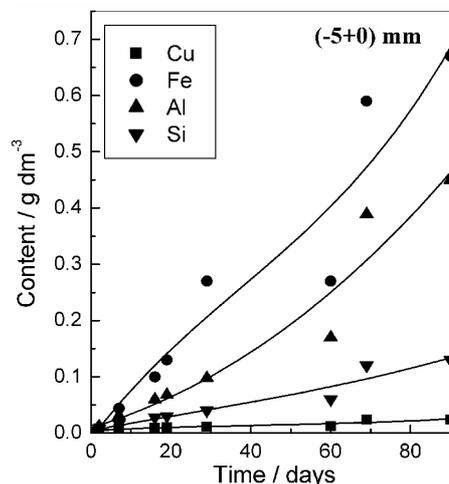


Fig. 3. Dependence of the concentrations of copper, iron, aluminium and silicon in the leaching solution on time after copper ore treatment with sulphuric acid (pH 1.0, S:L = 1:1) for the size range: (-5+0) mm.

From the dissolution curves (Figs. 2 – 7), it can be seen that concentration of the selected elements increased with time. The copper(II) concentration in these solutions after leaching for three months was in the range of  $0.011 - 0.024 \text{ g dm}^{-3}$ ; iron, aluminium and silicon in the range  $0.22 - 0.68 \text{ g dm}^{-3}$ ,  $0.14 - 0.45 \text{ g dm}^{-3}$  and  $0.039 - 0.13 \text{ g dm}^{-3}$ , respectively. The calcium(II) concentration was in the range of  $0.030 - 0.062 \text{ g dm}^{-3}$ , and of magnesium  $0.134 - 0.460 \text{ g dm}^{-3}$ .

Low calcium concentration can be explained by the formation of sparingly soluble calcium sulphate.<sup>15</sup> The experimental results show that the grain size of the ore, for these size ranges, had a minor influence on the dissolution rate. Also, the oxidation rate of chalcopyrite under these conditions was low, as shown by the low copper(II) ions concentration in the output solutions (Fig. 8).

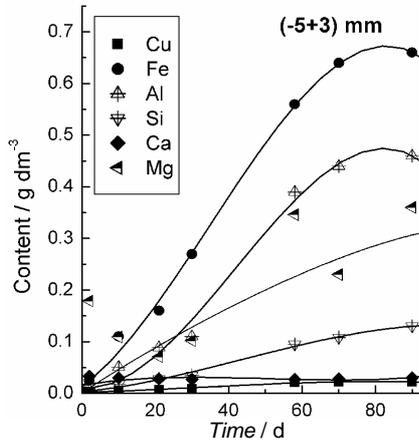


Fig. 4. Dependence of the concentrations of copper, iron, aluminium, silicon, calcium and magnesium on time after copper ore treatment with sulphuric acid (pH 1.0, S:L = 1:1) for the size range: (-5+3) mm.

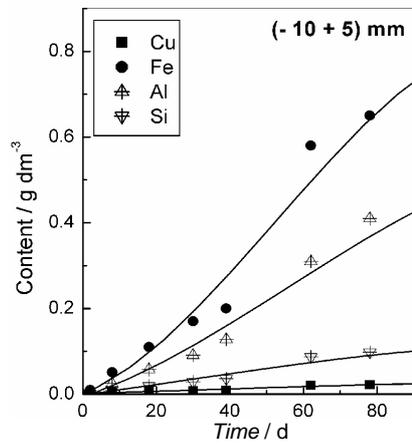


Fig. 5. Dependence of the concentrations of copper, iron, aluminium and silicon in the leaching solution on time after copper ore treatment with sulphuric acid (pH 1.0, S:L = 1:1) for the size range: (-10+5) mm.

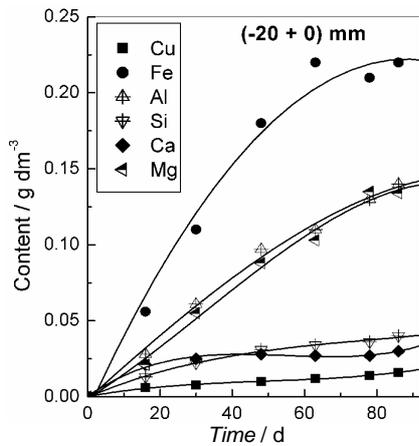


Fig. 6. Dependence of the concentrations of copper, iron, aluminium, silicon, calcium and magnesium on time after copper ore treatment with sulphuric acid (pH 1.0, S:L = 1:1) for the size range: (-20+0) mm.

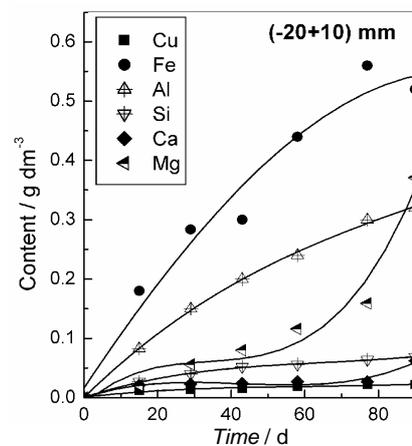


Fig. 7. Dependence of the concentrations of copper, iron, aluminium, silicon, calcium and magnesium on time after copper ore treatment with sulphuric acid (pH 1.0, S:L = 1:1) for the size range: (-20+10) mm.

Insignificant influence of grain size on the dissolution rate of chalcopyrite may be explained as follows: in the initial period of leaching, oxidation of chalcopyrite occurs on the surface of the ore grains. Due to the reaction between sulphuric acid and the matrix minerals, calcium ions are released, which react with the sulphate anions forming calcium sulphate (gypsum) as a precipitate. The

formation of this compound during leaching was confirmed by X-ray diffraction analysis of the solid residue (Fig. 9). Precipitate formation may occur when the formation front moves to the interior of the ore grains. Due to the large volume of the precipitate, small cracks form in the grain exposing new chalcopyrite surfaces. This phenomenon results in a comminution of the initial raw material during leaching, which may be seen from the curve of the grain size distribution of the solid residue (Fig. 1, curve b). Ritsema and Groenenberg<sup>32</sup> in 1993 proposed that the following reaction occurs on limestone in acidic medium in the presence of iron(III) (during pyrite oxidation):

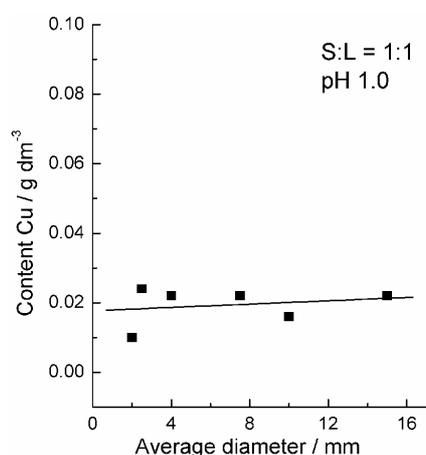
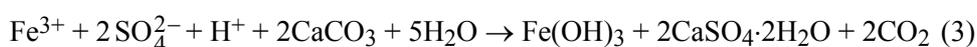


Fig. 8. Dependence of copper concentration on the average diameter of ore grains after leaching (pH 1.0, S:L = 1:1, leaching time: 90 days).

They found that carbonate particles become coated with gypsum and amorphous ferric oxyhydroxides are formed in reaction (3). Simon *et al.*<sup>33</sup> showed tabular crystals composed of S and Ca (gypsum), based on SEM-EDS analysis of the coatings. These facts are in accordance with the present results.

Mineralogical analysis showed that carbonate minerals existed in the initial raw material. These minerals react with sulphuric acid forming a porous layer, which enables contact of leaching solution with minerals in the grain interior. Auck and Wadsworth<sup>1</sup> found that, during acid leaching of copper ore, the copper leaching rate increases with decreasing ore grain size, but the leaching rate was not proportional to the reciprocal value of diameter. Lu *et al.*<sup>22</sup> found that for chalcopyrite leaching particles of a various diameters in solutions of 0.8 M H<sub>2</sub>SO<sub>4</sub> containing 1 M NaCl, identical copper concentrations were obtained in the solution after 9 h of leaching. A lack of dependence of the concentrations of leached ions on the size of the ore was also registered for other raw materials. For example, during the oxidation of As-bearing gold ore, it was found out that the grain size had no influence on the arsenic and iron concentrations in the leaching solutions.<sup>33</sup> The differences in behaviour are probably due to the variable composition of the ores.

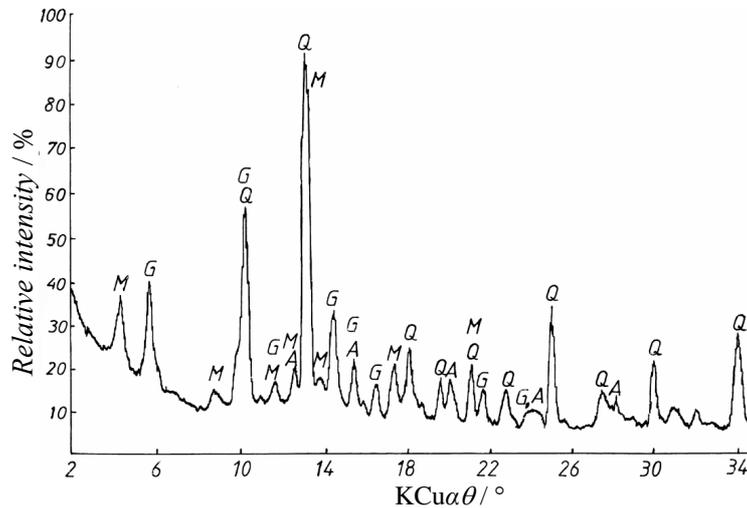


Fig. 9. X-Ray diffraction pattern of the residue after 90 days of leaching: gypsum (G), quartz (Q), anhydrite (A) and muscovite (M). Conditions:  $\text{H}_2\text{SO}_4$  (pH 1.0), S:L = 1:1; for size range (-3+1) mm.

The ore grain size had a small influence on the consumption of acid. As seen in Table II, the acid consumption was in the range of  $56 - 73 \text{ g kg}^{-1}$  ore, for various grain sizes. Ahonen and Tuovinen<sup>4</sup> performed experiments of bacterial leaching of a complex sulphide ore containing chalcopyrite and obtained an average acid consumption of  $43 \text{ g kg}^{-1}$  ore.

TABLE II. Influence of grain size on the consumption of sulphuric acid (pH 1.0) after 90 days of leaching

Fraction / mm	-3+1	-5+0	-5+3	-10+5	-20+10	-20+0
Consumption / $\text{g kg}^{-1}$ ore	73	65	67	56	57	61

Siliceous and aluminosiliceous minerals may be altered into other mineral forms during leaching.<sup>35</sup> Some siliceous minerals may be partly dissolved during long-term acid leaching experiments. Siliceous ( $\text{Me}_2\text{SiO}_4$ ) leaching rates are much slower than those for carbonates, but their contribution to acid consumption may be important such as shown by the following reaction:



The experimentally determined acid consumption (Fig. 10 and Table II) show an increased acid consumption with time. This suggests that reactions between basic components and sulphuric acid are continuously contributing to the formation of leaching channels. This result leads to approximately equal leaching rates regardless of the ore grain size. Consumption of sulphuric acid is higher for the fractions (-3+1) mm, (-5+0) mm and (-5+3) mm than for the coarser fractions (-10+5) mm, (-20+10) mm and (-20+0) mm, Fig. 10.

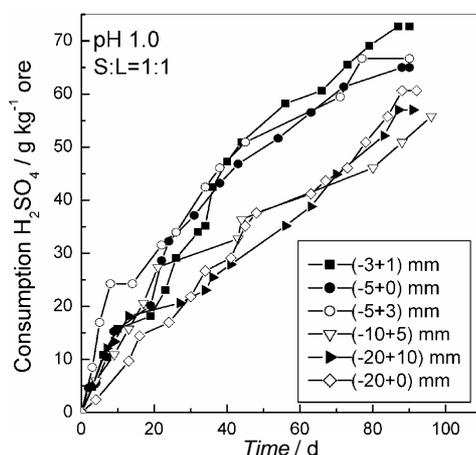


Fig. 10. Dependence of acid consumption on leaching time for various size ranges (pH 1.0, S:L = 1:1).

#### CONCLUSIONS

Based on experimental data, the following could be concluded:

1. Grain size of chalcopyrite ore has a minor influence on the leaching rate of this mineral in sulphuric acid solution.

2. The copper(II) concentration in the leaching solutions after leaching for three months is in the range of 0.011 – 0.024 g dm<sup>-3</sup>. The concentrations of iron, aluminium and silicon are in the range of 0.22 – 0.68 g dm<sup>-3</sup>, 0.14 – 0.45 g dm<sup>-3</sup> and 0.039 – 0.13 g dm<sup>-3</sup>, respectively.

3. The formation of gypsum on limestone results in the comminution of the initial raw material during leaching.

4. A higher consumption of sulphuric acid was found for the fractions of (-3+1), (-5+0) and (-5+3) mm than for the fractions (-10+5), (-20+10) and (-20+0) mm, due to the presence of finer ore particles.

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#### ИЗВОД

#### УТИЦАЈ ВЕЛИЧИНЕ ЗРНА НА РАСТВОРАЊЕ ХАЛКОПИРИТНЕ РУДЕ У КИСЕЛОЈ СРЕДИНИ

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У раду су приказани резултати лужења халкопиритне руде сумпорном киселином где су улогу оксиданаса имали растворени кисеоник и јони гвожђа(III). Испитивања су вршена у колонама од ПВЦ материјала пречника 110 mm и висине 1000 mm, перколацијом раствора кроз слој руде. Испитиван је утицај величине зрна руде на степен излужења и потрошњу киселине. У току лужења халкопиритне руде дешава се уситњавање полазне сировине услед грађења минерала гипса. Величина зрна руде халкопирита, у испитиваном опсегу крупноће, нема велики утицај на брзину лужења тог минерала у раствору сумпорне киселине. Нађено

je da je veća potrošnja sumporne kiseline za klase крупноће (−3+1), (−5+0) и (−5+3) mm него што je код klasa крупноће (−10+5), (−20+10) и (−20+0) mm.

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