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Evaluation of sulphation baking and autogenous leaching behaviour of Turkish metallurgical slag flotation tailings

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Abstract: Turkish metallurgical slag flotation tailing's (MSFT) that has not been evaluated yet sulphation baking phase transformations and autogenous leaching behaviour were investigated. The MSFT in the study consists of the residual fayalite (FeO-SiO₂) phase from the flotation, with a copper recovery of 87%, of the slag released during the smelting of the copper sulphide mine in northern Turkey, and the non-soluble glassy/amorphous structure containing the 0.34%Cu, 4.16%Zn and 0.15%Co base metals locked and doped to this phase. The effects of temperature (350 -650°C) and sulphuric acid dosages (4-10 ml) on sulphation baking were investigated by X-ray diffraction and sulphur analyses of the baked MSFT (B-MSFT) to produce soluble base metal sulphates. Since sulphated metals are a kind of metal salt, autogenous leaching was applied to the B-MSFTs only with purified water to dissolve copper, zinc and cobalt. X-ray diffraction patterns show the transformation of fayalite to oxide and sulphate phases due to sulphation baking. All dissolution values of Co and Zn obtained by autogenous leaching of B-MSFTs produced under all determined conditions are almost the same as one another. This indicates that Co and Zn are doped to fayalite together and that part of cobalt is doped to the zincite structure and liberated and sulphated together. This study showed that MSFTs decompose leading to liberation and sulphation of the doped base metals in its structure at a rate of ≥90%, and that they autogenously dissolve under atmospheric conditions leading to recovery in a simple and economic manner.

Keywords: copper smelter slag, flotation tailings, sulphation baking, autogenous leaching, base metals extraction

1. Introduction

Tailings resulting from failure of metallurgy plants to operate at an efficiency of 100% have become a very valuable raw material because of the decline in the reserve grade, operation of extractive metallurgy plants at very high tonnages by their nature, increased environmental awareness and high metal prices. When considered from this point of view, processing of "slag", the tailings which is released at high amounts by metallurgy plants that use pyrometallurgical techniques, leading to storage problems and adverse environmental effects has gained high importance (Tümen and Bailey, 1990; Yang et al., 2010; Muravyov et al., 2012; Nadirov et al., 2013; Dimitrijevic et al., 2016). In some cases, the amount of slag reaches millions of tons, which may have metal grades even more than run of mine grade. Copper smelting slags are one of the main metallurgical slags. About 2.2 tons of slag is discharged per 1 t of copper produced, and the annual global output of copper smelting slag is ~25 Mt (Gorai et al., 2003). Studies were conducted to evaluate many methods applied to these slags such as atmospheric sulphuric acid leaching, atmospheric leaching following sulphation roasting with the addition of pyrite, ammonium chloride leaching, bioleaching, acidithiobacillus thiooxidans bacterial leaching or direct reduction-magnetic separation with the addition of Na₂CO₃ and CaO, or to recover copper only such as sulphating copper and dissolved of copper or recovery from solution following oxidizing leaching (Tümen and Bailey, 1990; Banza et al., 2002a; Yang et al., 2010; Muravyov et al., 2012; Nadirov et al.,

2013; Miganei et al., 2017; Mikoda et al., 2019; Li et al., 2019; Song et al., 2019; Gabasiane et al., 2019). Recently, because of its valuable metal and copper contents, copper in slags is recovered by a new flotation process in many smelting plants. However, this method recovers only copper as a base metal from slags, while structures containing Co, Zn, Al, Au etc. remain as flotation wastes. This fact prompted us to find new ways to copper smelting slag flotation tailings processing (Nadirov et al., 2013). Chemical composition of copper smelting slags varies, depending on the reserve origin. In the tailings of which 85-88% of the free copper and compounds are removed through flotation, generally the main components are Fe and SiO₂ promoted that is chemically inert phase as named fayalite (Scales, 1986; Demopoulos, 1998; Langmuir et al., 2006; Perederiy and Papangelakis, 2017). Fayalite is an amorphous slag phase with the general formula of FeO SiO₂, which has magnetic property due to wustite (FeO) and magnetite (FeO Fe₂O₃) complexed with SiO₂, is glassy due to silicon, and has doped Co/Cu/Ni/Zn etc. base metals in the silicon lattice due to rapid cooling (Li et al., 2009; Perederiy et al., 2012). For such tailings which have base metal contents at beneficiable grade, much effort has been increasingly placed on hydrometallurgical processes to recover (Herreros et al., 1998). However, due to the amorphous structure, issues such as extraction of the doped base metals due to chemical inertia property and silica gel formation in direct leaching have constituted an obstacle to industrial applications. Additionally, for copper smelting slag flotation tailings, only a single study was developed in which copper was recovered using hydrometallurgical methods with ferric leaching, and all other studies and evaluations were conducted on copper smelter slags (Carranza et al., 2009). Unlike all studies conducted in literature, this study aimed to examine the mineralogical transformation of MSFT with sulphation baking at different temperatures and acid dosages, and to determine the dissolution behaviour of Cu, Co, Zn base metals doped fayalite by atmospheric autogenous leaching of B-MSFTs.

2. Materials and methods

2.1. Materials, characterisation and analysis of samples

The Cu/Zn/Co doped fayalite, which is the Turkish Metallurgical Slag Flotation Tailings (MSFT), was used in all experimental studies. The X-ray diffraction pattern for mineralogical composition and the chemical composition of the MSFT samples studied are given in Fig. 1 and Table 1, respectively. Quantitative determination of 34 elements and minerals in the MSFT was performed by ICP-AES and X-ray diffractometer, respectively.

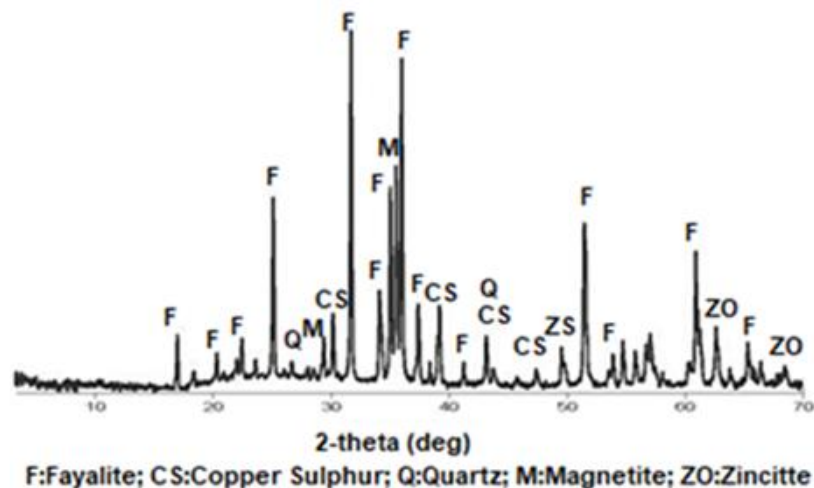


Fig. 1. X-ray diffraction pattern of the MSFT

Table 1. Chemical composition of the MSFT

Element	Fe	Cu	Zn	Co	S
%	38.44	0.34	4.16	0.15	0.26

MSFT consists of 67.6% fayalite (Fe_2SiO_4), 15.9% magnetite ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$), 6.7% zincite (ZnO) and 9.8% quartz (SiO_2). As indicated by the XRD pattern, unlike the elemental content, there is no mineral peak containing any base metal except for zinc, copper and iron. This further emphasized that base metals are doped to the fayalite crystal lattice structure. Free zinc is observed in zincite while iron is observed in the fayalite and magnetite structures. The ICP-AES analysis performed after the chemical fusion of the MSFT showed that there are Fe (38.44%), Cu (0.34%), Zn (4.16%) and Co (0.15%) base metals at limits recoverable in economic quantities. The MSFT has magnetic property due to its magnetite content of about 16%. Since they are flotation tailings, no size reduction was applied to the MSFT and the grain size was found to be under $56\mu\text{m}$ at a rate of 80%.

In the sulphation baking and autogenous leaching experiments Sigma Aldrich (MERCK) grade concentrated sulphuric acid of 96% by weight ($\rho:1.84\text{ g/cm}^3$) and de-ionized water were used, respectively. Elemental analysis was performed by ICP-AES 34 elements for leaching experiments and X-ray diffraction and atomic adsorption spectrometry analysis for baking experiments.

2.2. Sulphation baking of MSFT

Sulphation baking experiments were performed in 50ml pyrex reactor. In each experiment, 10g of MSFT of which physical water (moisture) had been removed and which had been stored in vacuum containers. Physical water of the MSFT had been removed by keeping in a furnace at 105°C for 24 hours. The variable parameters in the baking experiments were the baking temperature and the amount of sulphate added. The literature reviews demonstrated thermal treatment temperatures ranging from 400 to 1200°C for copper smelting slags (Gorai et al., 2003; Shen and Forssberg, 2003). Based on stoichiometric calculations, the lower and higher amounts to sulphate the base metals (Cu, Co, Zn) doped to the MSFT were calculated, and it was decided to add 4, 6, 8 and 10ml H_2SO_4 .

In sulphation baking experiments, 10g of MSFT was placed in a pyrex reactor and then 4, 6, 8 and 10 ml of sulphuric acid was poured on to MSFT. The prepared pulp was placed in a furnace, and after reaching the desired temperature, baked for 1 hour. The B-MSFT was transferred to a vacuum desiccator and allowed to cool to room temperature, and the weight difference was calculated after weighing on an analytical scales to find the amount of sulphur after the elemental analysis. All baking experiments, the experimental parameters and the measurements/calculations of weight changes are given in Table 2.

Table 2. Sulphation baking of MSFT experimental parameters and calculations

Baking Temperature $^\circ\text{C}$	Baking Time h	Amount of H_2SO_4 ml	Amount of H_2SO_4 g	Amount of B-MSFT g	Total H_2SO_4 + MSFT g	Amount of B-MSFT g
350	1	4	7.36	10.00	17.36	14.90
		6	11.04		21.04	16.53
		8	14.72		24.72	18.99
		10	18.40		28.40	17.87
450	1	4	7.36	10.00	17.36	14.94
		6	11.04		21.04	16.91
		8	14.72		24.72	17.67
		10	18.40		28.40	18.11
550	1	4	7.36	10.00	17.36	14.91
		6	11.04		21.04	16.77
		8	14.72		24.72	17.51
		10	18.40		28.40	17.47
650	1	4	7.36	10.00	17.36	13.39
		6	11.04		21.04	15.12
		8	14.72		24.72	16.32
		10	18.40		28.40	16.47

The optimization of baking experiments were done at 350°C, 450°C, 550°C, 650°C temperatures, 4, 6, 8, 10 ml acid addition with a constant baking time (1h). After completion of the baking experiments, B-MSFTs were weighed and analyzed by XRD analyses to identify the mineralogical transformation of fayalite/ copper sulphur/ magnetite/ zincite/ quartz.

2.3. Autogenous leaching of B-MSFT

In the autogenous leaching experiments, 10g B-MSFT was used to determine the dissolution behaviour of Cu, Zn and Co metals in 50°C de-ionized water with 1 h leaching time at atmospheric pressure for all experiments.

Autogenous leaching experiments were performed in a 600ml pyrex reactor that was placed in a bath whose temperature was controlled by a thermocouple within a constant agitation speed of 400rpm to keep all the particles in suspension form and 1/10 solid/liquid (w/v) as shown in Fig 2.

After completion of the autogenous leaching experiments, the leachates were separated by vacuum filtration followed by de-ionized water washing to pour both dissolved ions into the pregnant solution. Then, the washed leachates were dried in a furnace for 8h at 75±5°C and analyzed for Co, Cu, Zn and Fe by ICP-AES analyses to calculate the base metal extraction recoveries.

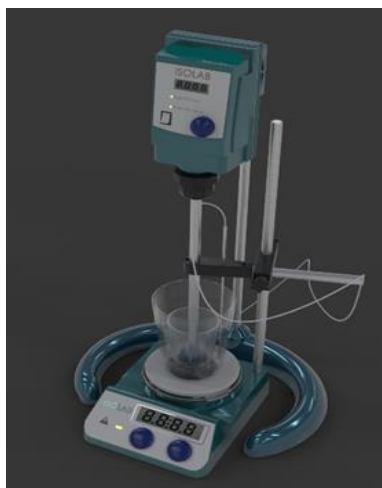
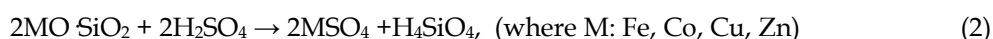


Fig. 2. Autogenous leaching experimental procedure

3. Results and discussion

3.1. Mineralogical transformation of MSFT

Sulphation baking results in liberation of base metals from fayalite complex which is known as non-soluble slag. Metal sulphates are generated according to baking with sulphuric acid. The reactions in baking process summarized by Altundoğan and Tümen (1997) and Uzun et al. (2016) are shown below:



The sulphation baking process, which was the first chemical stage of the experimental studies, aimed to determine the effects of thermal pre-treatment for separation of the base metals doped to the fayalite crystal structure from the amorphous phase and for selectivity. During the baking process, the amount of sulphuric acid and the temperature were investigated, and it was tried to determine the optimum conditions for sulphation of base metals at high level. Sukla et al. (1986) reported the boiling point of sulphuric acid as 337°C. Altundoğan and Tümen (1990, 1997) reported that iron in the form of fayalite transforms to hematite at 700°C. Therefore the baking processes were performed at the temperatures of 350°C, 450°C, 550°C and 650°C with the addition of 4, 6, 8 and 10ml of H₂SO₄. The X-ray diffraction patterns obtained from B-MSFTs to which sulphation baking was applied at all temperature conditions with the addition of 6 and 8 ml of H₂SO₄ are given in Fig. 3A1-A5 and Fig. 3B1-B5. X-ray diffraction patterns show the transformation of fayalite to hematite, base metal sulphates, iron sulphate and

amorphous silica or quartz, magnetite to hematite, zinc oxide to zinc sulphate due to sulphation baking. The base metals (Cu, Co, Zn) and iron are most stable in silicate forms as shown in Fig. 1, Fig. 3A1 and Fig. 3B1. Based on stoichiometric calculations, it was determined that the addition of 6ml and 8ml of acid is the optimum condition for sulphation baking, and experiments were also performed with addition of amounts lower and higher than these values (i.e. 4ml and 10ml). Therefore, it was deemed

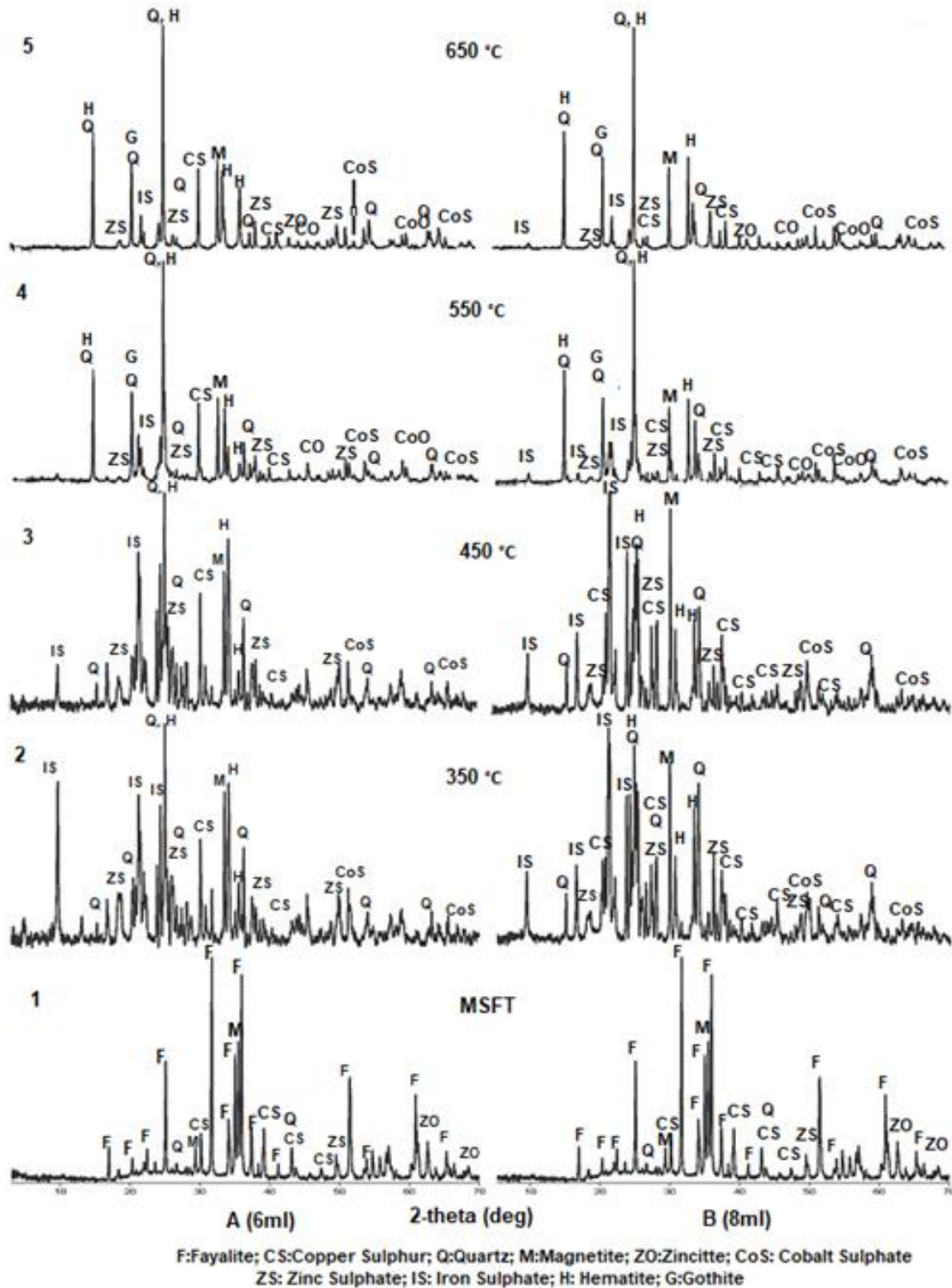
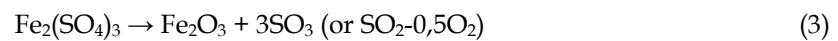


Fig. 3. Mineralogical transformation of MSFT to B-MSFT at different baking temperature with (A) 6ml and (B) 8ml acid addition

sufficient to obtain X-ray diffractions for 6 and 8ml. When the patterns were compared, it was found that the transformations show almost same behaviour. With both the added amounts of acid, it was observed that the fayalite structure decomposes starting from 350°C, and that the base metals doped to its structure were sulphated. During the baking process performed at 350°C, the peaks at 25 θ , 31 θ , 35 θ , 52 θ and 61 θ , which are among the most important fayalite peaks, were transformed to quartz, hematite, copper sulphate and magnetite peaks (Wang et al., 2019). This is a transformation expected based on Eq1 and Eq2. The noise seen in the patterns obtained at 350°C and 450°C was replaced by clear sharp peaks as the temperature was increased up to 550°C and 650°C. This is an evidence of replacement of the silica in the amorphous phase by the crystal quartz, meaning that the bonds of the slag structure break to transform to new crystals and the liberation of base metals. The baking processes performed at 350°C with the addition of 6 and 8ml of acid (Fig. 3A2,3B2) resulted in 52.7% and 55.1% iron sulphate; 8.2% and 7.4% zinc sulphate, 10.7% and 6.5% hematite and 9.5% and 11.9% quartz, respectively. Iron sulphate transformed to hematite with increasing temperature (Fig. 3A4, 3B4, 3A5 and 3B5) (Wang et al., 2019). Altundoğan and Tumen (1997) observed steady decline in the iron sulphate concentration for roasting temperature of 450°C to 650°C. These negative trends are explained by the following reaction (Tümen and Bailey, 1990);



Transformation of zincite to zinc sulphate, copper sulphur to copper sulphate/magnetite and fayalite to iron sulphate/quartz were observed with both acid dosages at 350°C, and when the temperature was increased, cobalt was separated from fayalite and transformed to the cobalt sulphate form. When 8ml of acid was added during the baking process, the iron sulphate phase continued to exist unlike the addition of 6ml at 550°C and 650°C (Fig. 3B4, 3B5). This was emphasized as being as a result of the presence of excess SO₃ as shown in Equation 1 (Yang et al., 2010). Fig. 3B2, B3, B4 and B5 show that the amounts of the sulphate phases resulting from the baking process an acid dosage of 8ml at 350°C and 450° were more than those resulting from the addition of 6ml. In these patterns, the peak number of copper sulphate, zinc sulphate and iron sulphate were higher and the intensity values were stronger than 6ml acid addition.

3.2. Extraction of base metals

During the baking process, the mineralogical transformations of the MSFT were completed at different temperatures and with different acid additions. Apart from the B-MSFTs, of which the XRD patterns are shown in Fig. 3, the B-MSFTs produced at the same temperatures by adding 4ml and 10ml of acid undergone autogenous leaching under atmospheric conditions and the base metal extraction lines shown in Fig. 4 were obtained. The curves showing the effect of baking with different amounts of acid at the same temperatures demonstrate increased dissolution values of the base metals when the acid dosage was increased to 8ml. The highest recovery at 350°C, 450°C and 550°C was obtained from the B-MSFTs produced with an acid dosage of 8ml.

It can be said that the obtained recovery values are among the highest ones when compared to those obtained in similar studies in the literature (Tümen and Bailey, 1990; Yang et al., 2010; Muravyov et al., 2012; Nadirov et al., 2013; Miganei et al., 2017). Under all conditions at the dosage of 8ml, the recovery of all base metals were $\geq 93\%$. Almost the entire amount of the copper was recovered at 550°C and 650°C. Altundoğan and Tumen (1997) reported the maximum copper extraction of about 90% following roasting at 500°C, which then decreased, first slightly 85% at 650°C, then sharply to practically zero at 700°C. Despite the increase seen in the recovery rates of the base metals with increasing temperatures of baking, the recovery rates of iron decreased sharply particularly at 650°C. Based on this situation, the B-MSFTs produced at all temperature conditions with acid dosages of 6ml, 8ml and 10ml were analysed for sulphur, and provided in Fig. 5 in comparison with the dissolution rates as the secondary axis. As seen in the Fig., unlike the base metals of which the dissolution values tend to increase, the amount of sulphur and the dissolution behaviour of iron showed the same trend and decrease behaviour. As seen in the XRD patterns, this confirmed that decreased amounts of sulphur and insolubility of iron cause oxidization of iron sulphate leading to hematitization. The graphs show that the recovery of Fe and the amount of sulphur are at the lowest levels at 650°C with the low acid dosage (i.e. 4ml). At the

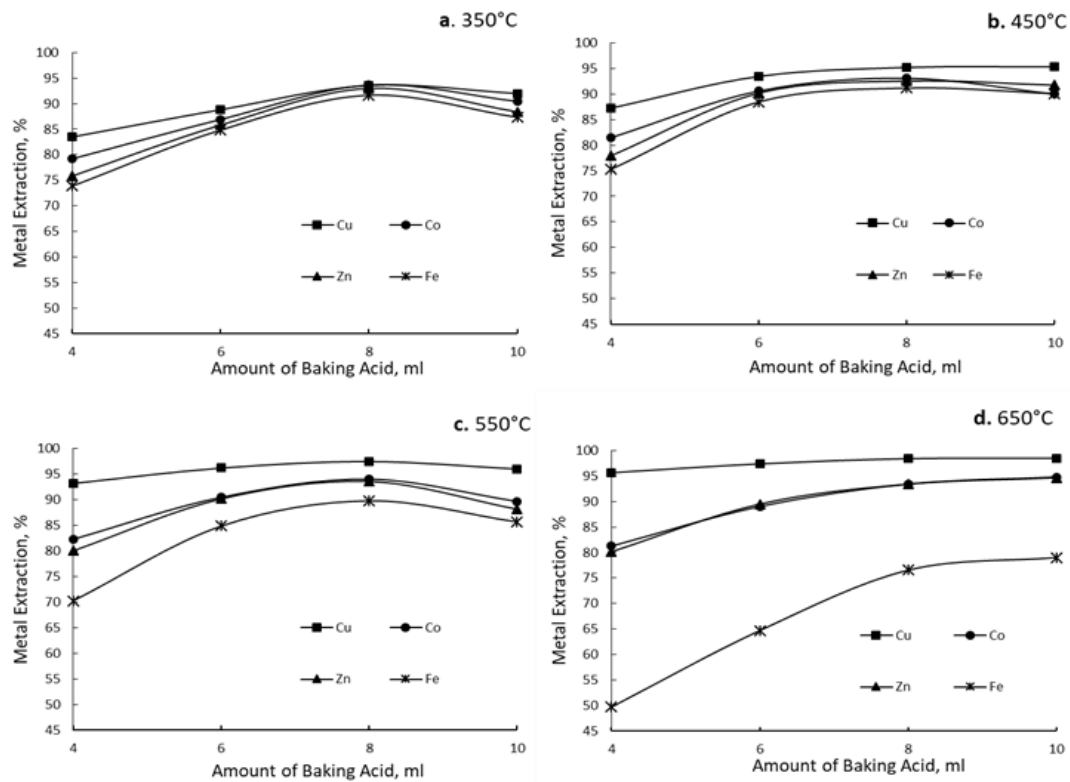


Fig. 4. Effects of H_2SO_4 dosages in baking at different temperatures on extraction of base metals in autogenous leaching (a. 350°C, b. 450°C, c.550°C, d.650°C)

same temperature, the recovery of iron and the amount of sulphur increased with increasing acid dosages.

When all conditions are examined at the dosage of 6ml, the extractions of Cu, Co, Zn are 89%, 87%, and 86%, respectively, at 350°C; 94%, 91% and 90%; respectively, at 450°C; 96%, 91% and 90%, respectively, at 550°C, and 97%, 89% and 90%, respectively, at 650°C (Fig.4). When the acid dosage was increased to 10ml, lower recovery rates compared to 6 and 8ml were obtained as a result of autogenous leaching of B-MSFTs produced at temperatures up to 650°C. These decreasing of metal extractions with 10ml acid dosage at 350°C, 450°C and 550°C baking temperatures may be due to the partial pressure of SO_2 gas during the baking process, because of the very excessive amount up to 8ml.

Copper has the highest recovery rate (at which the $CuSO_4$ formation is greatest) under all conditions, 650°C being the condition with the highest value. This is caused by two factors as seen in the XRD patterns of the MSFT and B-MSFTs;

- i. MSFT contains copper not only in the form of doped to fayalite but also as free minerals and metallic forms,
- ii. Hematitization was at the highest level at 650°C, and the catalytic effect of hematite to produce $CuSO_4$ in sulphation baking is an important point mentioned in the literature (Prasad and Pandey, 1999; Uzun et al., 2016).

The consistence of the dissolution behaviour of Zn and Co, of which the recovery rates are almost the same under all conditions, are examined in Fig. 6. If Co and Zn dissolve in identical proportions, it can be assumed that Co is uniformly doped in the zincite phase (Adeel et al., 2021). The peak of zincite ($2\theta:68$) disappears, in the XRD pattern of MSFT by the baking process and this peak substitutes with cobalt sulphate in the XRD patterns of B-MSFT.

4. Conclusions

Sulphation baking and autogenous leaching experiments were conducted for recovery of the base metals (Cu: 0.34%, Zn:4.16%, Co:0.15%), of which a large part is doped to the fayalite phase, in the copper smelter slag's tailings which was re-used by flotation method as copper source. Firstly, the

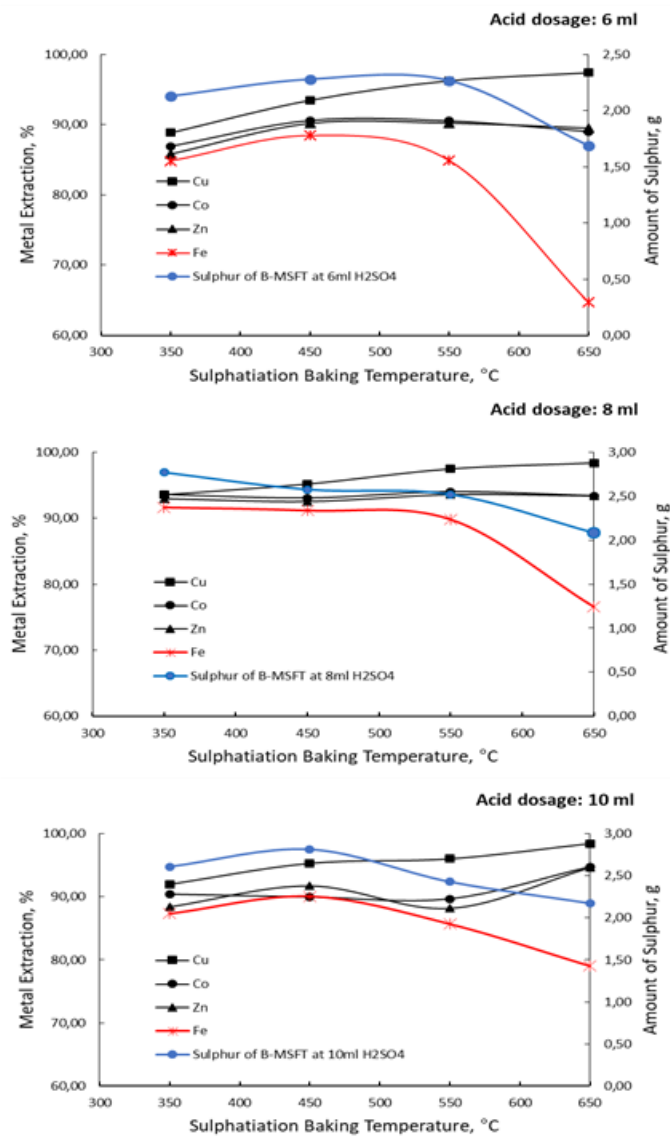


Fig. 5. Trend line between amount of sulphur in B-MSFTs and metal dissolution of base metals/iron

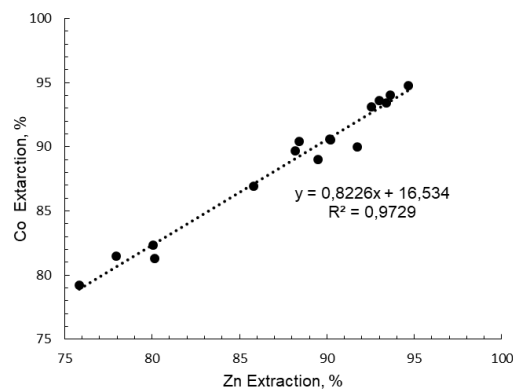


Fig. 6. Relationship between dissolution behaviour of Co and Zn

doped base metals in the insoluble glassy amorphous MSFT were made free and soluble phases through sulphating at high-temperature treatment, and the fayalite phase decomposed completely to transform to copper sulphate, zinc sulphate, iron sulphate, hematite, zinc oxide and quartz at 350°C. Since sulphated metals are a kind of metal salts which are autogenously soluble in water, to dissolve the

copper, zinc and cobalt only water was used in leaching experiments. During this stage, iron also dissolved because transforming to its sulphated forms, but with increasing baking temperatures, its dissolution values decreased from 90% to 49% at 650°C due to hematitization. Under the same conditions, the base metals Cu, Co and Zn dissolved at rates of 96%, 80% and 81%, respectively. With respect to mineralogical transformation, the fayalite phase, which completely decomposed at 350°C, was replaced by doped Co, Cu and Zn sulphates in a crystal lattice structure and iron was replaced by its oxides with increasing temperature and also due to the presence of SO₂. At the acid dosage of 10ml, at which the recovery rates of base metals are the highest, the recovery rates of Cu, Co and Zn are 99%, 95% and 95%, respectively, as a result of baking at 650°C. The fact that copper has the highest recovery rate under all conditions can be explained by the fact that it is also present in MSFT as free minerals and metallic forms, and that hematite shows a catalytic effect on sulphation of copper with increasing formation of hematite. The dissolution values of Co and Zn showed the same behaviour under all conditions, fitting with the model of $y = 0.8226x + 16.534$ with a R² value of $\geq 97\%$. This indicated that, as seen in the B-MSFT XRD patterns, Co and Zn are doped to fayalite and liberated together (transformation of the fayalite peak at 2 θ :52 to cobalt sulphate and zinc oxide) or cobalt is doped to the zincite structure (disappearance of the peak at 2 θ :68, transforming to Cobalt sulphate) and sulphated together.

Acknowledgments

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