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Investigation of iron selectivity behavior of copper smelter slag flotation tailing with hematitization baking and base metals leaching methods

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Abstract: In this study, iron selectivity behaviour of copper smelter slag (CSS) flotation tailings (38.08% Fe, 0.35% Cu, 4.48% Zn, 0.16% Co, 0.37% S) having fayalite and magnetite as major minerals was investigated with hematitization baking and base metals leaching methods using mineralogical and chemical analyses. For selectivity of iron, it was baked at temperatures of 650-690-700-710-730°C. The aim of the baking is to transform the almost all of the iron in the fayalite into the oxidized (non-soluble) form and the base metals into the sulphated (soluble) form. The temperature that had the lowest hematitization rate of iron was found to be 650°C, and the highest temperature was found to be 730°C. To examine the dissolution behaviour of baked CSS flotation tailing was leached at 50°C at a 1/10 (w/v) for 1 hour by using water. After baking at 690°C calcine and leaching residue, S values were determined to be approximately 17% and 9%, respectively. Baking made at 700°C, amount of sulfate also decreased to 10% and S content was measured as 4% of its leaching residue. As a result of this study, 690°C/700°C was determined as optimum conditions of hematitization baking and base metals were extracted selectively when the iron was remained at leaching residue in Fe₂O₃ phase. It was determined that, hematitization is high and the sulphates of the base metals are preserved at 700°C temperature. The fayalite phase completely decomposed into Si-O/Fe-O/Zn-S-O/Co-S-O compounds at 700°C baking which was the highest iron selective and base metals dissolute temperature.

Keywords: iron selectivity, hematitization baking, copper smelter slag flotation tailing, base metal leaching

1. Introduction

Today, 24.6 million tons of slag is discharged in copper production with smelting methods annually (Gorai et al., 2003; Mussapyrova et al., 2021). Considering the environmental and economic adverse effects of storage or disposal of copper smelting slags (CSSs) that have 0.5-2% Cu content, which is released in high amounts, these wastes must be made use of with recycling processes, be alternative to limited resources and eliminate harmful effects on the environment (Sibanda et al., 2020; Zander et al., 2011). CSS contains base metals such as Cu, Co, and Zn in economic amounts, and this is an indication of its extractability as secondary raw material (Zhang et al., 2020). In recent periods, when metal reserves and grade values continue to decrease, resources in the form of waste are accepted as raw materials (Roy et al., 2015). As a result of the literature review, it was seen that many studies were conducted on making use of CSS as a product with high added value, and various pyrometallurgical and hydrometallurgical methods were developed (Gorai et al., 2003). The leaked copper in CSS is recovered by many plants with the flotation process. Since this process is generally suitable for liberated metallic copper and sulfide minerals (Shen and Forssberg, 2003), it cannot be applied for the recovery of oxide or doped to slag forms of other precious base metals (e.g. Co, Zn, Ni) (Aatach et al., 2020). After CSS flotation process, CSS-flotation tailing that has 32-52% Fe content is formed in fayalite (major) and magnetite (minor) phases (Curlook et al., 2004; Li et al., 2009). In these tailings, fayalite (FeO · SiO₂) is

the amorphous phase that forms as a result of the chemical reaction with silica when iron sulfide is oxidized and doped into crystal structure of base metals (e.g. Co, Zn, Ni, Cu) with sudden cooling (Li et al., 2009; Yang et al., 2010). The recycling of fayalite slags that contain extractable base metals was the subject of many previous studies. As a result of the literature review, many studies were found conducted by using water leaching methods after chlorinating or sulfating-roasting processes regarding the recovery of base metals (e.g. Cu, Co, Zn, Ni) from CSSs. Therefore, researchers used ammonium chloride (D'yachenko et al., 2013; Nadirov et al., 2013), ammonium sulfate (Sukla et al., 1986; Hamamcı and Ziyadanoğulları, 1991), iron sulfate (Altundoğan and Tumen, 1997), pyrite (Tumen and Bailey, 1990), and sulfuric acid (Sukla et al., 1986; Hamamcı and Ziyadanoğulları, 1991; Arslan and Arslan, 2002; Uzun et al., 2016; Dimitrijevic et al., 2016; Uzun Kart, 2021). Many results were reported on the extraction of base metals with these processes. Also, direct leaching processes applied without roasting and by using solvents such as acid and aqueous sulfur dioxide did not yield successful results because of the high iron solubility and silica gel formation during solid-liquid separation and recovery of metals from pregnant solution (Li et al., 2009; Li et al., 2015; Huang et al., 2015). Since the removal of iron in these pregnant solutions is a complex and expensive process, the detection of minimum level iron before the leaching process provides a great advantage during base metal recovery (Yang et al., 2010, Arslan and Arslan, 2002).

Considering that most of the previous studies were directly conducted with CSSs, there are limited studies on base metal recovery and iron selectivity from CSS-flotation tailings in the literature. When the previous studies reported in the literature on the recovery of base metals from CSS-flotation tailings by using sulfating-acid baking methods were examined, the tailing contents were found to be different from the Turkish tailing used in this study (Dimitrijevic et al., 2016). Uzun Kart (2021) was evaluated of sulphation baking at 350 -650°C temperature and autogenous leaching behavior of all metals (Fe, Cu, Zn, Co) even if the contents were the same sample of this study named as metallurgical slag flotation tailing (MSFT), she was not examined the selectivity of iron at indicated temperatures (690-700-710-730°C) for hematitization baking, which created the need to investigate the selectivity of iron from Turkish CSS-flotation tailings.

In the present study, in which selective hematitization baking of iron that was never before studied at indicated (650-690-700-710 and 730°C) and leaching of base metals (Co, Cu, Zn) conditions were investigated for the Turkish CSS-flotation tailings. The optimum conditions for iron selectivity behaviour were determined by examining the mineralogical transformations, microstructures, and elemental compositions of the calcines (that were obtained with hematitization acid baking applied at high temperatures) and solid residue of leached calcines that were not studied previously in literature.

2. Materials and methods

2.1. Materials and analyses

CSS flotation tailing that contained Cu, Zn, and Co was used in experimental studies. The quantitative mineralogical and elemental analysis of CSS flotation tailing was performed by using X-ray diffraction (XRD) and inductively coupled plasma atomic emission spectroscopy (ICP-AES), respectively. The mineralogical composition of the raw sample is given in Fig. 1, and its chemical composition is given in Table 1. In this respect, 38.08% Fe, 0.35% Cu, 4.48% Zn, 0.16% Co, and 0.37% S were detected as a result of ICP-AES analyses. Although mineral peaks that contained Fe, Si, Cu, and Zn were detected in the XRD patterns, no liberated mineral peaks that contained Co were detected. The detection of cobalt, which did not yield liberated mineral peaks in Fig. 1, and the detection of it as a result of ICP-AES analysis in Table 1, emphasizes the idea that it is doped within the siliceous fayalite crystal structure (Uzun Kart, 2021).

Merck-quality H₂SO₄ (96%, d: 1.84 g/cm³) and de-ionized water were used in acid baking and water leaching experiments. The mineralogical structures of the CSS flotation tailing, calcines, and leaching residues used in experimental studies were determined with the XRD analysis. The sulfur and microstructure determination of the calcines, and their leaching residues that were obtained at optimum acid baking temperatures were made with the Scanning Electron Microscopy-Energy Distribution Spectrometry (SEM-EDX) analysis.

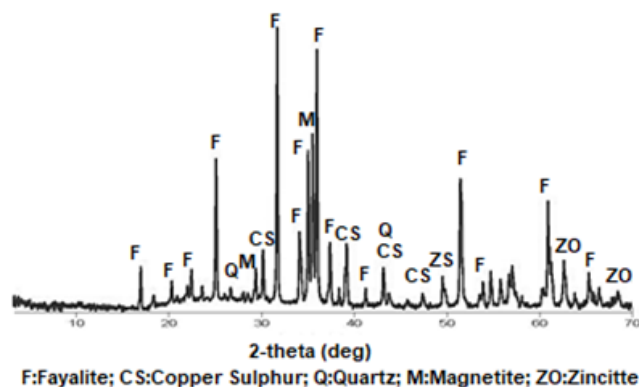


Fig. 1. XRD pattern of the CSS flotation tailing (Raw sample) (Uzun Kart, 2021)

Table 1. Mineralogical and chemical compositions of the CSS flotation tailing (Uzun Kart, 2021)

Fe	Cu	Zn	Co	S	FeO _(TOTAL)	SiO ₂	TiO ₂	Al ₂ O ₃
%	%	%	%	%	%	%	%	%
38.08	0.35	4.48	0.16	0,37	49.9	32.5	0.10	2.63

2.2. Baking and leaching methods

In this respect, a 10 g CSS flotation tailing sample was used after removing the physical water at 105°C for 24 hours in acid baking experiments, and after keeping stored in vacuum containers. The baking temperature was determined as the variable parameter by keeping the amount of H₂SO₄ and the constant time in the experimental study. Uzun Kart (2021) obtained maximum all metal recovery by adding 10 ml H₂SO₄ at 650°C and by applying the sulphation (non-selective) acid baking process to Turkish CSS flotation tailing within the temperature range of 350-650°C. Altundogan and Bailey (1990) added pyrite (FeS₂) to CSS and subjected it to a roasting process within the temperature range of 450-700°C, and emphasized the importance of roasting temperature in the recovery of base metals from copper smelting slag. Dimitrijevic et al. (2016) applied acid baking to CCS flotation tailing, which did not contain Co and Zn, and made a selective copper recovery after reducing the Fe solubility within the temperature range of 600-800°C. Arslan and Arslan (2002) applied leaching to copper smelting slag, which they obtained as a result of acid baking with H₂SO₄ at 650°C, and could leave the iron in the leaching residue without dissolving. In this study, in which non-ferrous selective base metal recovery was examined from CSS flotation tailing, it was decided to perform at temperatures of 650°C, 690°C, 700°C, 710°C, and 730°C. Hematitization baking was performed for 1 hour at varying temperature parameters by adding H₂SO₄ to CSS flotation tailing at a solid-liquid ratio of 1/1 (w/v). The 1-hour period that was determined for acid baking was initiated when the furnace reached the desired temperature after placing the mixture in the cold furnace. The calcines, cooled to room temperature in vacuum desiccator, were weighed after the acid baking experiments were done. The resulting weight changes are given in Table 2.

Then, 10 g calcine was subjected to atmospheric agitation leaching at 50°C by using de-ionized water at a solid-liquid ratio of 1/10 (w/v) for 1 hour to determine the dissolution behaviour of CSS flotation tailings calcines. Leaching experiments were done in an 800 ml pyrex reactor in a water bath as shown in Fig. 2. The reaction was performed by using a propeller for agitation and a thermocouple, which was required to keep the water bath temperature constant. The mixing speed was kept constant at 160 rpm with an accuracy of ±5 rpm to ensure that all calcine particles would be suspended and not stick onto the wall of the pyrex reactor with the effect of centrifugal force. When the leaching experiments were completed, the leaching residue and pregnant solution were obtained by filtrating with a vacuum filter. The pregnant solution was stored in a volumetric flask, the washed leaching residue was dried at 65°C for 24 hours, and the moisture was completely removed. Solid residues that were obtained after drying were weighed for metal recovery calculations.

Table 2. Acid baking of CSS flotation tailing experimental parameters and calcine weights

Baking Temperature, °C	Baking Time, h	Amount of H ₂ SO ₄ , ml	Amount of CSS Flotation tailing, g	Calsine, g
650	1	10.00	10.00	16.47
690	1	10.00	10.00	13.40
700	1	10.00	10.00	11.80
710	1	10.00	10.00	11.26
730	1	10.00	10.00	11.20

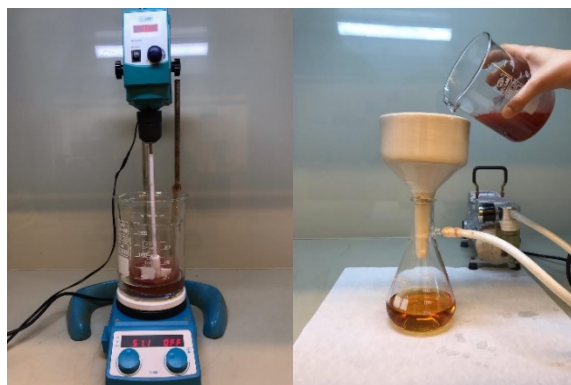


Fig. 2. Experimental procedure of water leaching and filtration

3. Results and discussion

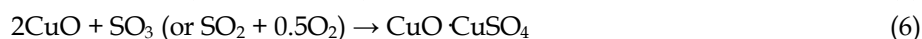
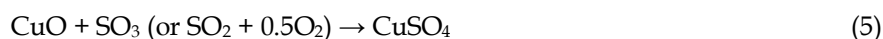
3.1. Baking behaviour of CCS flotation tailing

Acid baking is based on the decomposition (calcination) of the crystal structure of fayalite and the transformation of base metals (Cu, Zn, Co) into metal sulfate salts, which dissolve easily in water after sulfation. Oxide and silicate refractory structures must be decomposed by acid baking to extract base metals from fayalite (Altundoğan and Tümen, 1997). For this reason, the purpose of this study, in which selective base metal recovery was investigated, was to transform the metallic compounds in CSS flotation tailing into metal sulfate compounds, which are easily dissolved in water by using H₂SO₄ as a sulfate source in baking experiments. The baking experiments were done to determine the optimum acid baking temperature at which iron is highly hematitized (in its water-insoluble form). The effect of acid baking temperature was examined by keeping the amount of H₂SO₄ that was added and the time constant. The reactions in the baking process summarized by Uzun Kart, (2021) and Altundoğan and Tümen (1997) are shown below (Eq. 1-2):



The Fe^{+2,3}, which dissolved in the pregnant solutions obtained after leaching, has a negative effect on the solvent extraction of base metals. Also, as removing a high amount of soluble iron from the pregnant solution will cause operational complexity and economic disadvantages, the minimum presence of iron in the pregnant solution provides a great advantage in base metal recovery; and therefore, it is of great importance that iron is found in low amounts for solvent extraction of base metals with maximum efficiency (Yang et al., 2010, Arslan and Arslan). Considering this, iron must be in the form of hematite (Fe₂O₃), which is water-insoluble, after acid baking experiments. Sarfo et al., (2017) reported that fayalite was converted into hematite and quartz at ~750°C, and magnetite into hematite at ~400°C as a result of Thermogravimetric (TG) and Differential Thermal Analysis (DTA) on CSS. As a result of the literature review, it was found that the hematitization behaviour of the Turkish CSS flotation tailing at temperatures that were higher than 650°C was not examined. For this reason, acid baking experiments were performed at 650°C, 690°C, 700°C, 710°C, and 730°C by using 10 ml H₂SO₄. Also, previous studies

emphasized that metal sulfate compounds would decompose and transform to oxide compounds with the effects of the increasing temperature (Hammerschmidt and Wrobel, 2009). Depending on the increased temperature, decreased recovery of base metals other than Fe were also explained in the literature. Since it will reduce the solvent extraction costs by minimizing the dissolved iron from pregnant solution, a reasonable decrease in the extraction recovery of base metals can be accepted (Yang et al., 2010, Arslan and Arslan). The XRD patterns of the calcines that were obtained after acid baking processes applied to CSS flotation tailing at different temperatures are given in Fig. 3. When the XRD patterns were examined, it was seen that the bonding structure of fayalite was decomposed after acid baking at 650°C, and the fayalite peaks given in Fig. 1 were replaced by hematite (Fe₂O₃), magnetite (Fe₃O₄), quartz (SiO₂), iron sulfate, and base metal sulfates (CuSO₄, CoSO₄, and ZnSO₄, etc.) (Uzun Kart, 2021). Cobalt, which was detected in the chemical composition of fayalite, but there was not seen any peak in the XRD pattern (Fig. 1), separated from the glassy structure after the decomposition of the fayalite structure, and was detected as cobalt sulfate in 16, 19, and 26 2θ (ref. code: 01-072-1656), and as cobalt sulfate hydrate in 27.41 2θ (ref. code: 01-070-2104). Also, the zinc oxide at 63 2θ in CSS flotation tailing was sulfated, and was replaced by zinc sulfate at 24 and 34 2θ (ref. code: 00-001-1075) (Uzun Kart, 2021). It was also seen that the copper sulfide was converted into copper oxide at 35 2θ, and into copper sulfate at 26 and 32 2θ at 650°C (Sun et al., 2020). In the literature, the decomposition temperature of copper was determined to be 650°C (Weast, 1980; Tumen and Bailey, 1990). The copper oxide/sulfate formations in XRD patterns are compatible with the decomposition temperatures defined in the literature data. The reactions of metallic copper and copper compounds in acid baking are given below (Eq 3-6) (Altundogan and Tumen, 1997).



Iron selectivity was investigated in the present study, and after acid baking at 650°C, iron sulfate conversion occurred at 14, 20, 24, 30, 32, 37, 51, 59, 65 2θ (ref. code: 01-073-0148), and iron sulfate hydroxy hydrate conversion occurred at 16 2θ (ref. code: 00-028-0497). Iron sulfate peaks almost continued to exist at 690°C. Iron sulfate decomposes at high temperatures and is converted into hematite when SO₂ leaves the medium. The fact that the intensity values of hematite peaks at 690°C were stronger than those of hematite peaks at 650°C is an indication that hematitization increases with increased temperature (Tumen and Bailey, 1990). Acid baking was performed at 700, 710, and 730°C to examine the hematitization behaviour of iron at higher temperatures.

As a result of the baking performed at 710°C and 730°C almost the same calcine weights were measured as 11.26 g and 11.20 g, respectively (Table 2). When this situation was seen, a water leaching was done quickly to calcines (710°C and 730°C) and the leaching residue weights obtained in both were same weight and the pregnant solutions were also colorless (Fig. 5.). After the measurements, calcines, leaching residues and pregnant solutions at 730°C and 710°C, were determined at the same results, therefore, it was considered adequate to examine only the baking process at 710°C in the scope of the present study.

No iron sulfate peak was detected in the calcine as a result of the acid baking at 700°C and 710°C, and the new hematite peak that was formed at 43 2θ at 700°C confirms the conversion of iron sulfates into hematite (ref. code.00-006-0502). Also, the increased number of hematite peaks because of increased temperature and stronger intensity values of peaks indicated increased hematitization. Altundogan and Tümen (1990, 1997) explained that iron in the form of fayalite transformed into hematite at 700°C. In this study, the absence of iron sulfate peaks after acid baking at 700°C is indicative of the fact that it is compatible with the literature data. In Table 2, decreased weight of calcines because of the increased temperature was associated with the SO₂ leaving the medium during the conversion of metal sulfate compounds (especially iron sulfate) to oxide compounds (Tagawa, 1984). Guo et al., (2009) emphasized that there is a sharp weight loss in the calcines because of the decomposition of iron sulfate between 600°C and 650°C. For this reason, when iron sulfate conversions in XRD patterns are examined, calcine weights decrease with increasing hematitization. Also, the strongest intensity value of the hematite

peaks was detected after acid baking at 710°C during which 710°C was identified as the temperature value at which hematitization was most intense. As a result of the acid baking at 710°C, no sulfate compounds of other base metals were detected except for the zinc sulfate peak observed in 24 and 34 2 θ (ref. code: 00-001-1075) (Liu et al., 2015). Especially the cobalt sulfate peak that was observed at 36 2 θ at 650, 690, and 700°C was replaced by cobalt oxide (Tang et al., 2020).

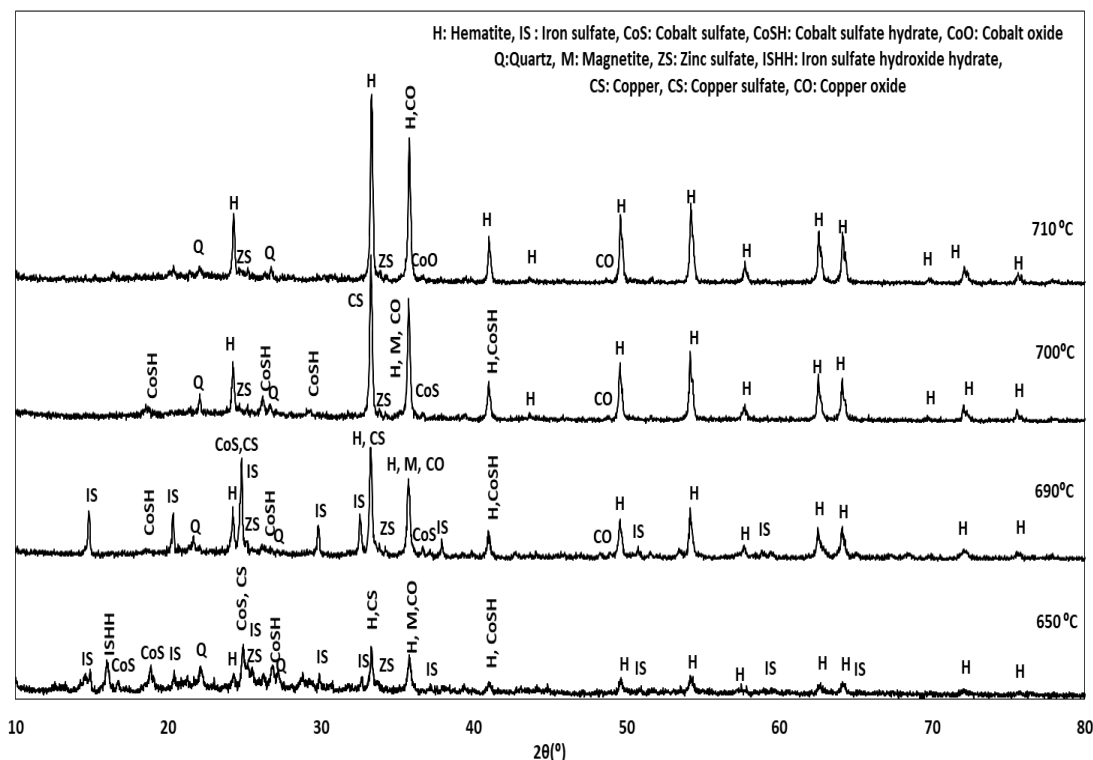


Fig. 3. XRD patterns of baked CSS flotation tailings at different baking temperatures

3.2. Determination of iron selectivity behaviour

To examine the dissolution behaviour of CSS flotation tailings, which baked with acid at different temperatures, after their mineralogical transformations, 10 g calcine was leached at 50°C at a 1/10 solid/liquid ratio for 1 hour by using de-ionized water to examine the dissolution behaviour. When the leaching process was completed, the pH values of the unfiltered pulp were measured (Table 3). Dimitrijevic

Table 3. The pulp pH values of leached calcines

Baking temperature, °C	Pulp, pH
650	1.12
690	1.39
700	1.65
710	2.83

et al. (2016) reported that decreased pH values because of increased temperature were due to the evaporation of H₂SO₄ at high temperatures, and the evaporation of sulfuric acid reduced the metal recovery. Also, decreased amount of SO₄ in calcine causes decreased sulfate ions in the solution. According to Santasalo-Aarnio et al. (2017), decreased pH values were directly proportional to the sulfate ions in the pulp. In this study, it was determined that the pH values decreased because of the decomposition of metal sulfate compounds (especially iron sulfate) and their conversion into metal oxide compounds when SO₂ left the calcine due to increasing temperature, which resulted in decreased

sulfate ions in the pulp. In his study, Uzun Kart (2021) mentioned the relation between the amount of sulfur and the dissolution behaviour and reported that decreased amount of sulfur showed the same trend line as the hematitization behaviour, and the dissolution decreased accordingly. The XRD patterns of leaching residues are given in Fig. 4 to examine the dissolution behaviour of the metal sulfates after leaching that was applied to the calcines.

The hematitization of iron in the acid baking process and the fact that the hematite mineral does not dissolve in the water leaching process are quite important in terms of iron selectivity (Li et al., 2015). In Fig. 4.a., the hematite peaks that were detected at 24, 33, 35, 41, 49, 54, 57, 62, 64 2θ preserved their presence as a result of the acid baking process in the leaching residue (Li et al., 2015). In this study, in which the selectivity of iron was examined, the dissolution behaviour of iron sulfates after leaching was determined. In Fig. 4.a,b, after leaching was performed to the calcines obtained at 650°C and 690°C, the iron sulfate peaks at 14, 20, 24, 29, 32, 37, 51, 53, 59, 65 2θ (ref. code: 01-073-0148) are not found in leaching residue, which indicates that the iron sulfate compounds dissolve into the solution. When the iron selectivity was compared regarding these two temperatures, iron sulfates were dissolved in water, as seen in the calcine and leaching residue obtained as a result of 650°C baking (Fig. 4.a); however, the high intensity of the hematite peaks at 690°C (Fig. 4.b) shows that the hematitization increased after acid baking. The experimental images of the acid-baked calcines, leaching residues, and pregnant solutions are given in Fig. 5. The red color in CSS flotation tailing following the baking process occurred because of the decomposition of the fayalite and the conversion of iron to hematite. Also, the difference in the colors of calcines and pregnant solutions at different temperatures are indicative of the difference in the hematitization rates of iron and the dissolution behaviour of metals due to the effect of baking temperature. When the calcines were examined, it can be argued that hematitization is more intense as can be understood from the color of the calcine at 690°C. The increased amount of hematite in calcine decreases the dissolution behaviour of iron; and in this respect, it can be argued that the amount of iron in the solution is inversely proportional to the amount of iron hematitized in the calcine; and also, the amount of iron in the solution at 690°C is lower than that at 650°C (Li et al., 2015).

In Fig. 4.c,d, when the calcines and leaching residues are examined, the lack of iron sulfate peaks confirms that almost all iron sulfate structures were hematitized at 700°C and 710°C depending on the temperature increase (Altundoğan and Tümen, 1990, 1997). The conversion of iron to water-insoluble hematite with the acid baking might be associated with decreased amount of iron in the pregnant solution after the leaching procedure. In this case, the iron sulfate peaks, which are not detected in calcines at 700°C and 710°C, show that the iron recovery is minimal at these temperatures (Sun et al., 2020). Sun et al. (2020) ensured that the base metal sulfates were taken to the solution after water leaching; and selective recovery of base metals by leaving the hematite structures in the leaching residue. The pH value of the pregnant solutions of acid-baked calcines made at 650°C, 690°C, and 700°C to determine the amount of iron in the leaching solutions was increased to 3.5 after leaching, and iron was precipitated chemically (Kongolo et al., 2003). The experimental images of the precipitates and the solutions obtained after the precipitation were weighed and after the physical water was removed at 105°C for 24 hours from the solid-liquid separation after precipitation are given in Fig. 6. The amount of the precipitate (i.e. the iron hydroxide) that was obtained with the precipitation experiments decreased as the baking temperature increased, and the increased hematitization in XRD patterns showed agreement. As a result, it can be said that the dissolution behaviour of iron decreased depending on the increased baking temperature.

The dissolution behaviour of base metals has great importance in determining the optimum temperature for the selective removal of iron. When Fig. 4a is examined, it is seen that cobalt sulfate peaks at 16, 19, 26 2θ , copper sulfate peaks at 26 and 32 2θ (ref. code: 00-014-0373), and zinc sulfate peaks at 26, 34 2θ (ref. code: 00-001) are not found in the leaching residue. Uzun Kart (2021) extracted Cu, Co, and Zn with 99%, 95%, and 95% recovery, respectively, with the acid baking that included CSS-flotation tailing with 10 ml H₂SO₄ at 650°C for 1 hour. When the selectivity of iron despite the high recovery values of base metals is considered, it is very important for selective base metal recovery that iron is highly hematitized and less in the solution after acid baking at 690°C and 700°C (Yang et al., 2010, Arslan et al., Arslan). In Fig. 4d, the absence of zinc sulfate that was found in calcine 24 and 34 2θ (ref. code: 00-001-1075) in leaching waste in Fig. 4d, and the absence of the peaks of other base metals confirmed that

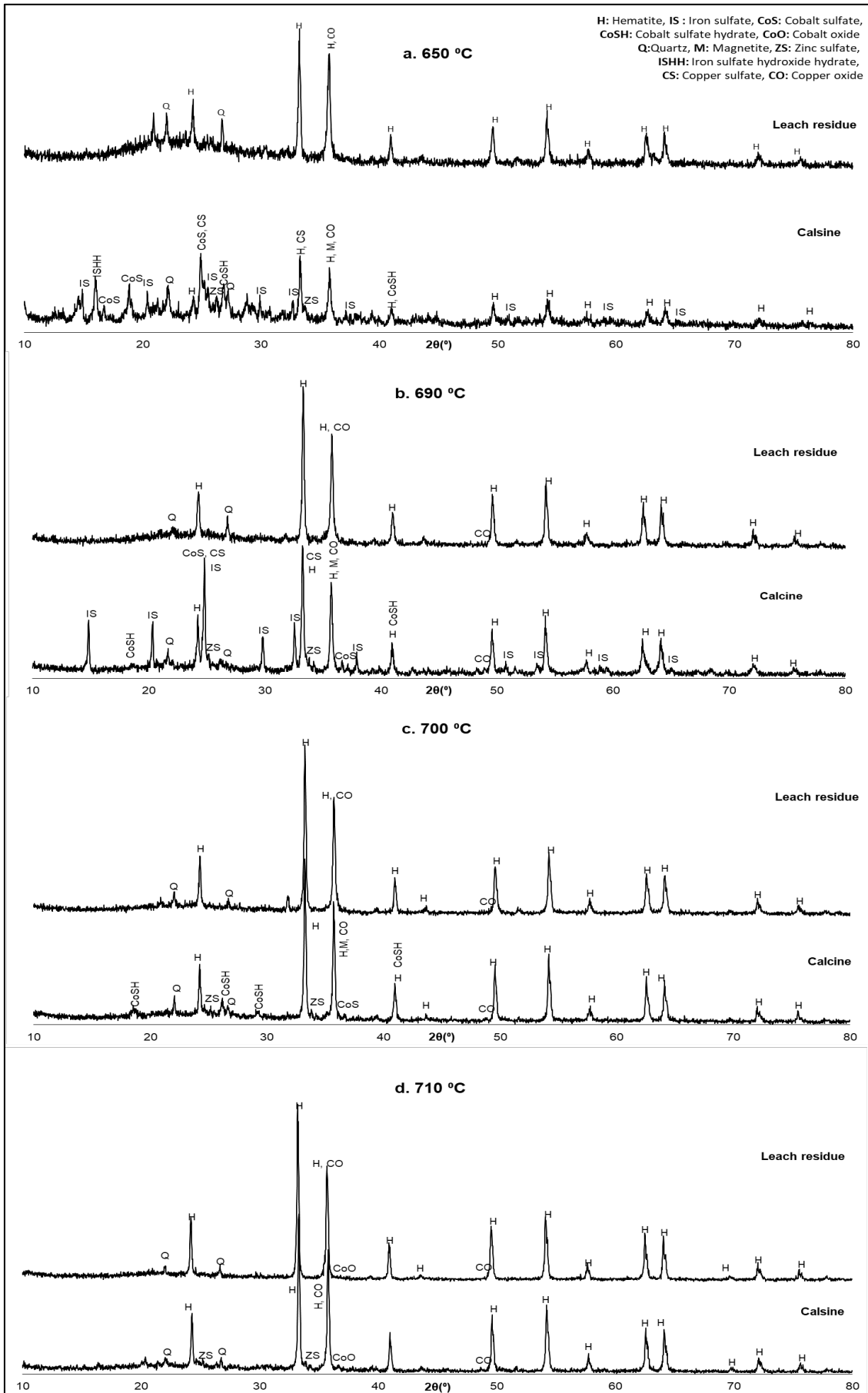


Fig. 4. Calcine and leaching residue XRD patterns at a.650 °C, b.690 °C, c.700 °C, d.710 °C

only zinc sulfate dissolves in water at 710°C (Li et. al., 2015). It was determined that these temperatures are not optimum because of the high iron solubility following the acid baking at 650°C and due to the low base metal solubility following the acid baking at 710°C. Also, the SEM-EDX analysis were made for the calcines and leach residues that were obtained at 690°C and 700°C to optimize the temperature (Fig. 7).

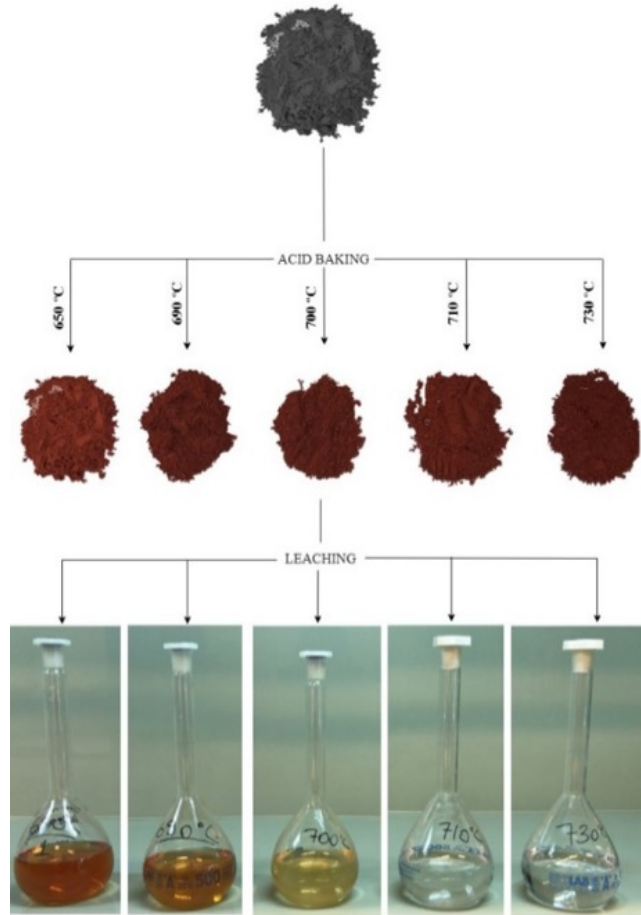


Fig. 5. CSS-flotation tailing calcines and pregnant solutions

Baking temperature °C	Amount of Iron Precipitate g
650	1.65
690	0.82
700	0.20

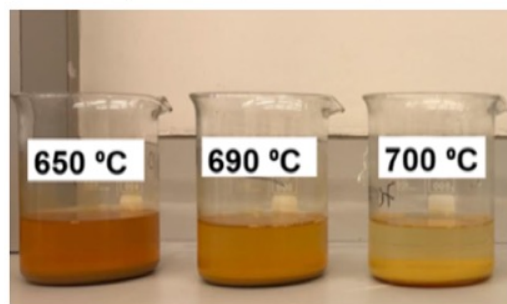


Fig. 6. Precipitation tests and precipitate amounts at 650, 690, 700°C temperature parameter

As seen in SEM images (Fig. 7) and EDX analyses (Table 4) of calcines and leaching residues obtained under optimum (690°C -700 °C, 10 ml H₂SO₄ baking and water leaching) conditions; after the baking process at 690°C, the fayalite structure decomposed, Co, Fe, Zn sulfates and siliceous glassy structures were formed. It has also been frequently seen in oxide forms of iron. This is a demonstration that iron is hematitized. The average S value was calculated to be approximately 17% (Table 4). As expected, the average S value decreased to 9% in the leaching residue obtained from 690 °C calcine leaching. This confirms that sulfate metals are dissolved by leaching. The absence of Zn and Co indicated that the base metals were dissolved. The fact that all of the iron in the residue is in oxidised form emphasizes that the iron is not soluble selectively by hematitization. Baking made at 700 °C showed more iron oxide than 690°C. The amount of sulfate also decreased to 10%. The formation of metal sulfates was also reduced. Looking at the leaching residue, it was observed that the iron was completely oxidized and remained in the solid without dissolving. The S content was measured as 4%. During the baking process, the sulfur was removed as SO₂ and the iron was oxidized but the base metals remained sulfated, which was confirmed by the presence of the Zn-S-O composition in the calcine.

Table 4. EDX analyses of calcines and leaching residues obtained under optimum conditions

Baking Temperature °C	Fe %	S %	Zn %
690 Calcine	16.39	16.82	5.75
Leach Residue (690°C)	24.43	9.29	6.83
700 Calcine	18.37	10.02	12.40
Leach Residue (700°C)	27.66	4.86	6.71

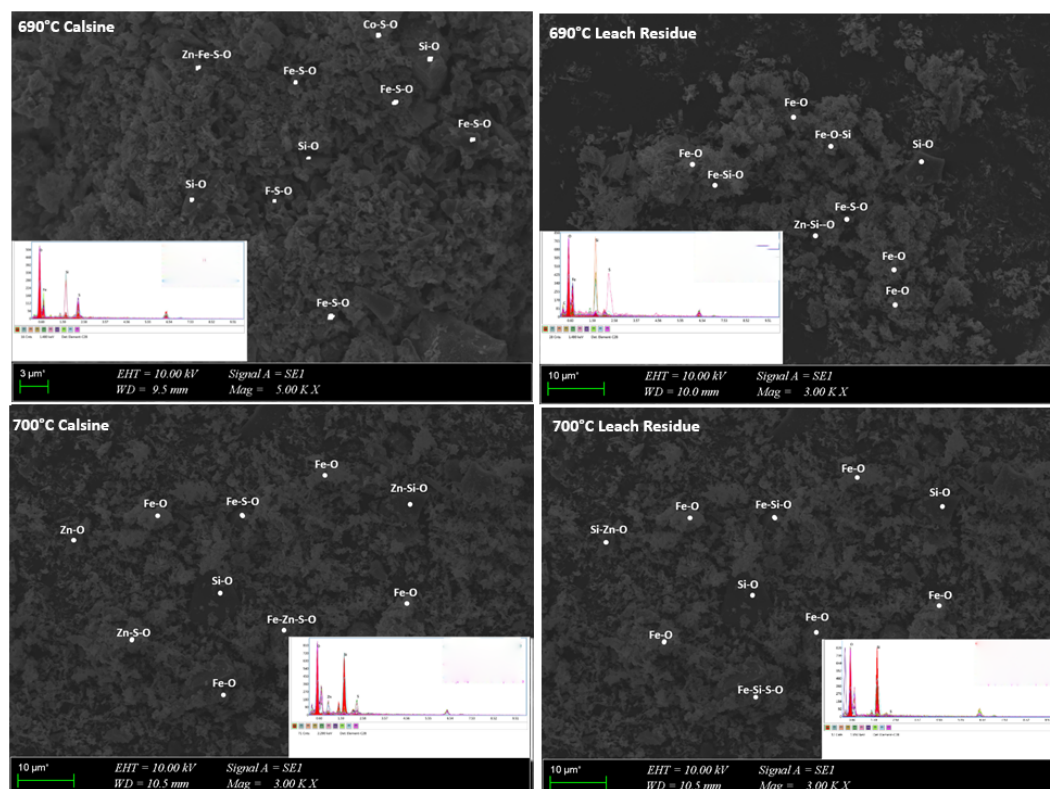


Fig. 7. SEM and EDX analyses of optimum calcines and leach residues at 690°C and 700°C

4. Conclusions

In this study; hematitization H₂SO₄ baking processes were applied to CSS-flotation tailing at different temperatures of 650-690-700-710-730°C; and the fayalite phase was decomposed into

copper sulfate, zinc sulfate, iron sulfate, hematite, zinc oxide, and quartz phases. The transformation of iron and base metals into sulfate, and then, into oxide forms was observed at increasing baking temperatures. Iron sulfate was hematitized and kept in solid-phase without dissolving with water leaching in the present study, in which iron selectivity was investigated. The temperature that had the lowest hematitization rate was found to be 650°C, and the highest temperature was found to be 710°C. The transformation of the base metals (except for Zn) into oxide form at 710°C, when hematitization was at the highest level, caused decreased dissolution efficiency for base metals. Also, the acid baking processes at 650°C and 710°C were not considered to be suitable because of the high solubility of iron at 650°C and low solubility of base metals at 710°C. After the baking process at 690°C, the fayalite structure decomposed, Co, Fe, Zn sulfates and siliceous glassy structures were formed that has also been frequently seen in oxide forms of iron. The average S value was calculated to be approximately 17% in calcine and S value decreased to 9% in its leaching residue because of the dissolution of base metal sulfates. Baking made at 700 °C calcine showed more iron oxide than 690°C. The amount of sulfur of calcine and leaching residue also decreased to 10% and 4%, respectively. The fact that all of the iron in the residue is in oxidised form emphasizes that the iron is not soluble selectively by hematitization.

As a result of this study, hematitization baking process which is one of the pre-heat treatment techniques and water leaching for iron selectivity were applied, and 690°C /700°C was determined as optimum conditions. These conditions were determined as the highest hematitization and base metal sulfation. The glassy slag phase (fayalite), containing 38% Fe, decomposed completely into Si-O, Fe-O, Fe-S-O, Zn-S-O, Co-S-O compounds at 690°C. It was determined that at 700°C, hematitization is high and the sulphates of the base metals are preserved at this temperature.

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