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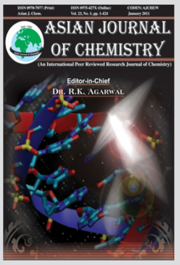

Hydrometallurgical Evaluation of Zinc Leach Plant Residue

E. Güler, A. Seyrankaya[*] and I. Cöcen

Department of Mining Engineering, Faculty of Engineering, Dokuz Eylül University, Division of Mineral Processing, 35160 Buca, Izmir, Turkey

*Corresponding author: Fax: +90 232 4530868; Tel: +90 232 4127519; E-mail: a.seyrankaya@deu.edu.tr

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Continuous decrease of zinc metal production worldwide, which is among primary resources have resulted in zinc metal production from secondary resources. In this study effect of sulfating roasting conditions on metal solubility and extraction conditions of zinc was investigated. It is possible to produce the soluble metal salts and decompose the ferritic structure by roasting of leach residue containing 20.28 % Pb, 12.73 % Zn and 8.43 % Fe. About 90 % Zn was recovered after sulfating roasting followed by water leaching. The secondary leach residue was exposed to NaCl complex solution so that Pb dissolved and was obtained in the form of $PbCl_2$. At the optimal conditions, lead and silver efficiency was determined as 92 and 62.4 %, respectively. This study aims beneficiation of Çinkur plant leach residue, recovery of zinc, lead and silver and thereby extermination of potential environmental risks. Hydrometallurgical methods were adopted due to their less energy requirement and more eco-friendly nature. Besides, a plant flow chart was developed in the light of results of the selected methods.

Key Words: Zinc, Roasting, Leaching, Leach residue, Lead, Hydrometallurgy.

INTRODUCTION

The fact that the zinc metal production from the primary resources are decreasing day by day in the world has made it imperative to produce the necessary zinc metal from the secondary resources such as zinc ash, zinc dross, fly ash of the electric arc furnaces and leaching residues. This way, recovering and recycling of other metals in the leaching residues that can have a toxic characteristic like lead and cadmium will be possible. The technology that is advancing in this context has been leading the researchers to look for economical and environment friendly techniques to exploit the secondary resources.

Almost 80 % of the world's zinc production uses the electrolysis acquisition method after placing the concentrated zinc or oxide compound base metals in diluted sulfuric acid solution[1]. When carbonated base metals are used, calcines are produced by the Waelz process which is immediately followed by the clinker process. The calcine which is acquired by both processes goes through hydrometallurgical zinc acquisition phases. The acquisition of zinc out of calcine through hydrometallurgical techniques is realized by leaching, cleansing the leach by precipitation and cementation and electrolysis and fusion-infusion phases[2-4]. Some of the zinc acquired at the end of the roasting and clinkering processes are in the form of zinc oxide (ZnO) while some of them are in the form of zinc ferrite. While zinc oxide can easily dissolve in sulfuric acid solutions, zinc ferrite requires high degrees of heat (above 90 ºC) and a higher concentration of sulfuric acid solutions (50-150 g/L)[1]. Because of very low dissolution of lead sulfate in water (4.1 mg/100 mL at 20 ºC) it stays as solid waste[5]. Since the sulfuric acid is consumed by ZnO and PbO due to reactions (1) and (2), there is no acid left for a reaction with zinc ferrite. Because of this reason, the zinc ferrite in calcine remains in the leach residues along with $PbSO_4$. The reactions that take place during the leaching process are as follows:

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O \quad (1)$$

$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O \quad (2)$$

Zinc can be produced from the secondary resources in addition to the primary resources through pyrometallurgical and hydrometallurgical techniques or through a combination of both. The production methods differ according to the mineralogical composition of the base metals and according to the quantity of the impurities. There has been much research related to recycling and reusing of leach and other metallurgical residues (scraps, dust from electric arc furnaces, junk batteries *etc.*) and related to the re-acquisition of their metals through pyrometallurgical and hydrometallurgical techniques[4,6-24]. Hydrometallurgical techniques are commonly preferred because of their environment friendly nature and their need for less energy.

Çinkur establishment was started in 1976 in Kayseri, Turkey which had the capacity to produce 35,000 ton/year Zn and

125 ton/year Cd from oxide-carbonated zinc base metals. Due to economic reasons, the establishment had to stop its activities in 1999. Since economic reasons halted the work in the lead and silver department which was planned to be used for producing 6,000 ton Pb per a year along with 4.5 ton Ag per year, about 1.2 million ton neutral leach residues rich in lead (with heavy soluble metals harmful to environment) had to be stored in the residue storing area[3,25]. There are many studies indicating the treatment of Çinkur zinc plant residues[26-32].

This study examines the conditions of sulfating roasting to break the ferrite structure and to turn the metals in the form of salt in order to recycle the leach residue. It was obtained significant amount of zinc and lead from zinc plant residue by a two staged process which included NaCl leach applied to secondary residue after sulfating roasting with H_2SO_4. The effects of these conditions on the solution behaviour of metals are also examined.

EXPERIMENTAL

The materials that were used in this study were collected from Çinkur establishments leach residue field, sieved by wet method, dried in the oven and blended. With these preparation methods, materials with dimensions of -75 μm were acquired. 80 % of the material used in the tests were approximately under 20 μm and mean particle size was 9 μm (Fig. 1). A Rigaku brand X-ray diffractometer (XRD, model D/Max-2200) was used to analyze the mineralogical structure. In the equipment, a copper targeted X-ray tube was used. The obtained results are given in Fig. 2. According to these results, main minerals composing the zinc plant leach residue are determined as bassanite ($CaSO_4 \cdot 0.5H_2O$), lead oxide (Pb_2O_3), gypsum ($CaSO_4 \cdot 2H_2O$), anglesite ($PbSO_4$), calcium oxide (CaO_2), franklinite ($ZnFe_2O_4$) and quartz (SiO_2). In addition to that, the micro analysis of the surface of the materials and the identification of the element distribution was obtained by scanning electron microscopy (SEM) and EDS analyses. Jeol brand JSM-6060 model scanning electron microscope was used in the analyses. As the amount of zinc minerals except for franklinite ($ZnFe_2O_4$) were below XRD limits, they were not detected in the graphics. However, other forms of zinc were determined as oxide (ZnO), silicate (Zn_2SiO_4) and sulfate ($ZnSO_4 \cdot xH_2O$) in SEM analysis. SEM BEC image provided for identification of zinc minerals are given in Fig. 3.

Diognastic leach tests were undertaken on the material in order to determine the mineralogical structure for the zinc and it was seen that the material consisted of 0.46 % zinc sulfate, 5.10 % zinc oxide and metallic zinc, 5.76 % zinc ferrite and 1.41 % zinc silicate. This results show that more than half of the zinc is in ferrite and silicate structure.

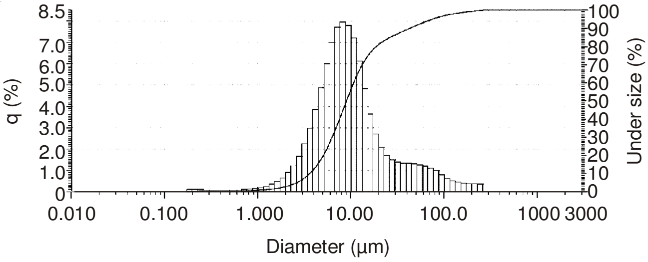


Fig. 1. Size distribution graphic of material used in the tests

For chemical analysis, approximately 0.25 g sample was weighed in a platinum crucible and 3 g lithium tetraborate was added before it was left in an 1000 ºC-furnace for 1 h. The crucibles that were taken out of furnace were cooled in the desiccators and dissolved by the help of a magnetic stirrer after adding a 10 % 100 mL. HNO_3. The solution then was transferred to a flask and added distilled water up to the level of 250 mL and elements identification was completed by the help of Analytik Jena Model NovAA 300 atomic absorption spectrometer. Chemical analysis results of Çinkur leach residue were summarized in Table-1.

TABLE-1
CHEMICAL ANALYSIS RESULTS
OF ÇINKUR LEACH RESIDUE

Element (%)					
Pb	Zn	Fe	Al	Mn	Sb
20.28	12.73	8.43	1.96	0.37	0.19
Element (mg/kg)					
Cu	Ni	Cd	Cr	Ag	Co
981	391	340	332	265	148

Acid leaching method: Leaching processes were conducted in order to determine solution ratios of metals contained in zinc plant leach residue, with water and H_2SO_4 and without any preliminary preparation process. 10 g material was used in these tests and the process was conducted in a glass beaker with a magnetic stirrer with 1000 rpm speed and with 20 % solid ratio at 25 ºC. 0-100 g/L H_2SO_4 was added in the mixture and it was applied for 1 h duration.

Sulfating roasting method: In sulfating roasting tests, 10 g leach residue was mixed with predetermined amounts of H_2SO_4 and the process was conducted in different temperature intervals (100-700 ºC) and durations (0.5-2.0 h) in a porcelain crucible in a Vecstar muffle furnace closed to atmosphere. In some of the tests, the leach residue was humidified with different amounts of water (5-200 %) before being mixed with acid in order to form a hydrated structure.

In order to determine the effects of parameters such as H_2SO_4 amount, roasting temperature, duration and humidity

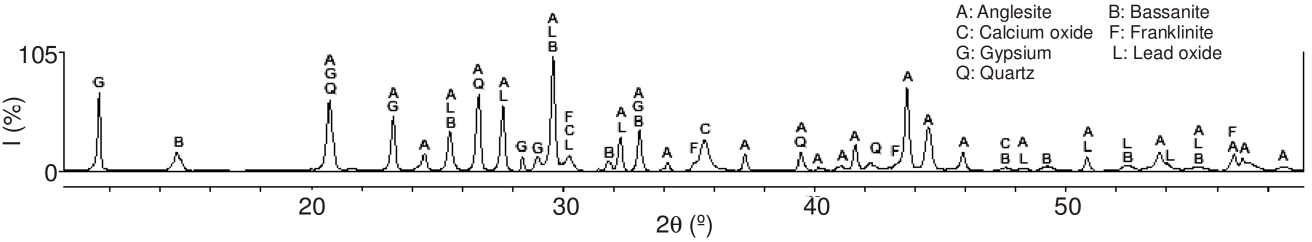


Fig. 2. XRD diagram of the zinc plant residue

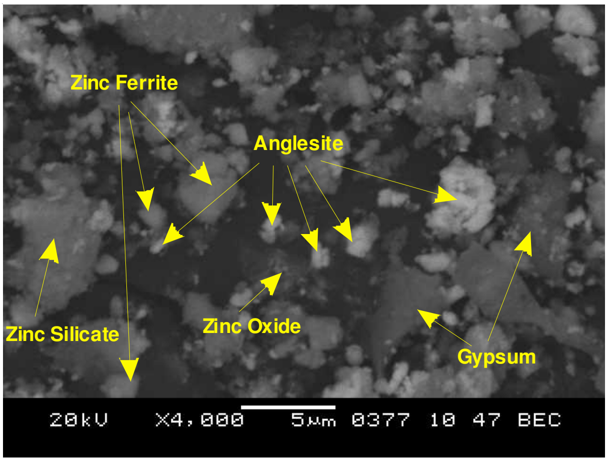


Fig. 3. SEM BEC image of plant leach residue

ratio on metal dissolution efficiencies and the roasted product was leached by using a magnetic stirrer at 1000 rpm speed at 20 % solid ratios, at 25 ºC for 1 h duration by using distilled water. After leaching, the mixture was filtrated under vacuum. The solid part was washed and the obtained solution was added to the main solution, while the final solid was dried and used afterwards in lead-silver recovery processes.

Water leaching method: Water leaching processes were used to dissolve sulfated structures which were formed after roasting processes. The roasted material was exposed to dissolution processes in distilled water and in a glass beaker, using Heidolph MR Hei-Tech model contact thermometer mounted digital magnetic stirrers, at different temperatures (25-90 ºC), with different solid ratios (10-50 %) and different durations (0-8 h). The speed of the stirrer was defined as 1000 rpm.

Brine leaching method: In order to recover lead and silver, brine leaching was applied to water leaching residue material which consisted high ratios of lead. Brine leaching processes were conducted in different concentrations with an analysis quality NaCl solution prepared by Heidolph MR Hei-Tech, in glass beaker; using Heidolph MR Hei-Tech model contact thermometer mounted digital magnetic stirrers, at different temperatures, solid ratios and durations. The mixture was filtrated after leaching and element analysis was performed for the solution. Effects of leaching parameters such as salt concentration, leach temperature, solid ratio and leach duration on Pb and Ag dissolution were studied.

Diagnostic leach tests: Diagnostic leach tests were conducted for leach residue and the solid obtained after each leaching process to find out the amounts of zinc forms such as $ZnSO_4$, metallic Zn, ZnO, zinc silicate (Zn_2SiO_4), zinc ferrite ($ZnFe_2O_4$)[2].

RESULTS AND DISCUSSION

Acid leaching tests: In the tests H_2SO_4 concentrations of different amounts between 0-100 g/L were experimented. The obtained results are shown in Fig. 4. According to these results, in the water leaching tests, Cd extraction was 6.5 % while other metal extractions were below 1 %. Cu extraction was 60 % in 25 g/L acid concentration; higher acid concentration was ineffective. Similarly, Zn and Cd extractions increased up to 40 % in 12.5 g/L acid concentrations and above this concentration, Zn extraction stabilized while Cd extraction slightly increased up to 43 %. However, Mn dissolution gradually increased in parallel with the increasing acid concentration and reached 27 % in 100 g/L H_2SO_4. When extraction of other metals (Fe, Ni, Co, Al, Cr and Ag) were considered, they had similar trends and after 1 h extraction process in 12.5 g/L acid concentration, metals were dissolved at the following ratios; Cr 2.3 %, Ni 6.7 %, Fe and Co 10 %, Al 13.5 %. It is shown in Fig. 4 that increase of acid concentration did not have significant effect on the dissolution of these metals. The extraction rate of 40 % for Zn in acid leach tests shows that the residue consists of the same rate of oxide + metallic zinc. Diagnostic leach tests results were summarized in Table-2. At low acid concentration (50 g/L) ferritic zinc extraction was too low (2 %). Even at high acid concenration (200 g/L), ferritic and total zinc extraction was about 51 and 82 %, respectively.

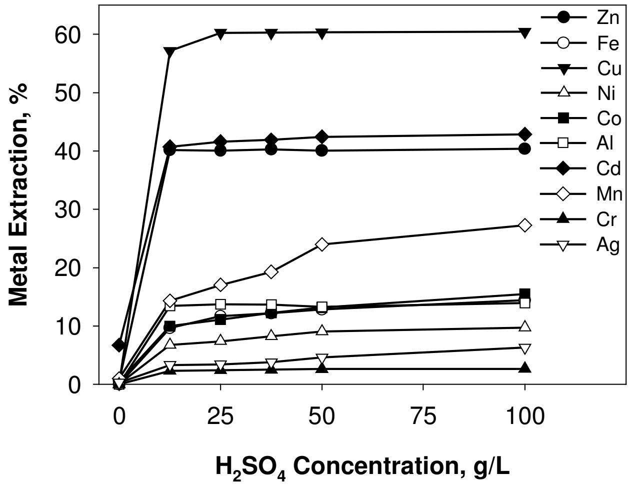


Fig. 4. Effect of H_2SO_4 concentration on metal extractions (solid ratio: 20 %; leaching temperature: ambient; leaching time, 1 h)

TABLE-2
DIAGNOSTIC LEACH RESULTS

H_2SO_4 conc. (g/L)	Reaction duration (min)	Total zinc extraction (%)	Zinc ferrite extraction (%)
50	30	63.35	1.91
	120	64.87	2.00
100	30	66.46	10.33
	120	72.15	25.53
200	30	72.88	27.48
	120	81.98	51.82

Temperature: 95 ºC, solid ratio: 20 % w/w.

Sulfating roasting: In addition to forming soluble metal salts from metal oxides, another aim for sulfating roasting is producing zinc sulfate and iron sulfate by breaking the zinc ferrite structure. In hydrometallurgical processes, zinc ferrites can dissolve at 90-95 ºC in high sulfuric acid concentrations. The reaction can be summarized for the zinc ferrite during the sulfating roasting as follows:

$$ZnO{\cdot}Fe_2O_3 + 4H_2SO_4 \rightarrow ZnSO_4 + Fe_2(SO_4)_3 + 4H_2O \quad (3)$$

According to the results of tests undertaken to determine the acid levels during sulfating roasting, H_2SO_4/solid rates were found to be higher than 1:1 and the metal dissolution levels stayed constant (Fig. 5). In lower acid concentrations (0.5:1.0) the metal dissolution levels were lower comparatively. Due to this reason, optimum acid/solid rates were determined to be 1:1. Under these conditions, Zn extraction was 86 %.

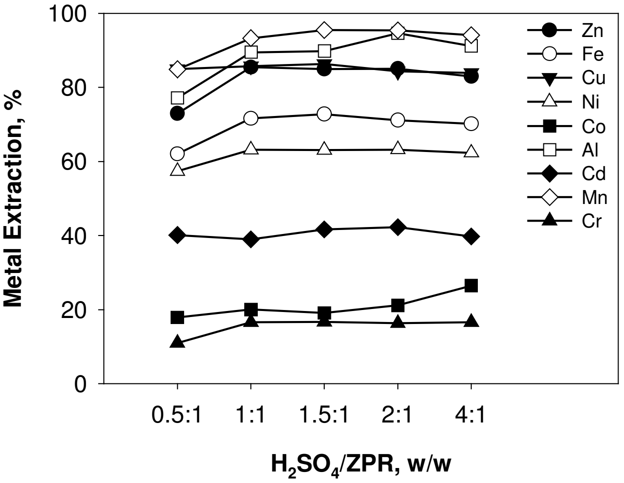


Fig. 5. Effects of H_2SO_4/solid rates on metal extractions in roasting

Sulfating roasting and zinc ferrite decomposition process is possible in the interval of 150-500 ºC but the maximum Zn extraction (86 %) takes place in 200 ºC with 1 h of roasting. This also shows that zinc ferrite changes its structure and decomposes into a sulfate structure after the roasting process.

Thermal decomposition steps for zinc sulfate can be written as follows[33]:

$$ZnSO_4 \cdot 7H_2O \rightarrow ZnSO_4 \cdot 6H_2O + H_2O \quad (4)$$

$$ZnSO_4 \cdot 6H_2O \rightarrow ZnSO_4 \cdot H_2O + 5H_2O \quad (5)$$

$$ZnSO_4 \cdot H_2O \rightarrow ZnSO_4 \cdot xH_2O + (1-x)H_2O \; (x = 0.8\text{-}0.9) \quad (6)$$

$$ZnSO_4 \cdot xH_2O \rightarrow ZnSO_4 + xH_2O \quad (7)$$

$$3ZnSO_4 \rightarrow ZnO \cdot 2ZnSO_4 + SO_3 \quad (8)$$

$$ZnO \cdot 2ZnSO_4 \rightarrow 3ZnO + 2SO_3 \quad (9)$$

The first four steps in this thermal decomposition take place below 277 ºC and form anhydrous $ZnSO_4$. The decomposition of anhydrous zinc sulfate also requires two steps. The first steps creates the basic zinc sulfate salt ($ZnO \cdot 2ZnSO_4$) and the second step causes the salt to decompose to form the zinc oxide. Reactions for the first step start at 590 ºC while the second step requires 837 ºC heat to be completed[34,35]. The Zn extraction is higher than 80 % up to 550 ºC and rapidly decreases after 600 ºC (Fig. 6). This finding can be explained by the formation of basic zinc sulfate salt during the roasting process which requires more temperature.

The $FeSO_4$ and $Fe_2(SO_4)_3$ lose their crystal water and form iron sulfate in the form of anhydrate. In the interval of 200-500 ºC, sulfate structure of the iron is conserved but the sulfate is decomposed after 500 ºC and iron turns into an oxide structure up to 600 ºC[34,35]. Fig. 7-A showed that the Fe dissolution decreases gradually after 150 ºC up to 500 ºC at which heat the decrease rapidly quickens. For this reason, the iron decomposes into Fe_2O_3 in high roasting heat. The slow pace of dissolution for iron(III) sulfate in the form of anhydrate in water with low degrees also explains the decrease in the extraction in heat interval of 150-500 ºC. These findings are consistent with the literature[35].

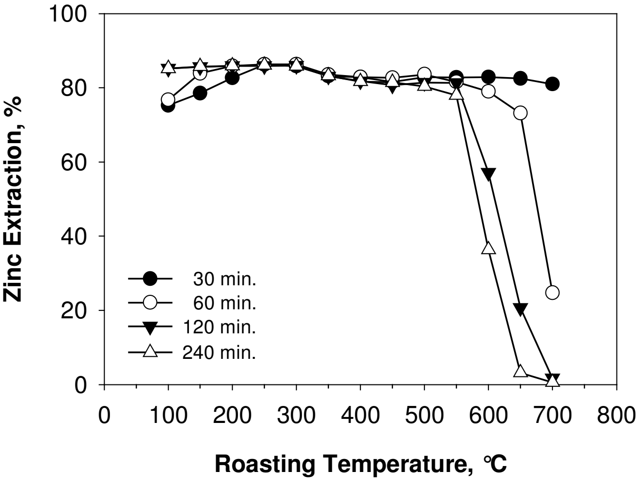
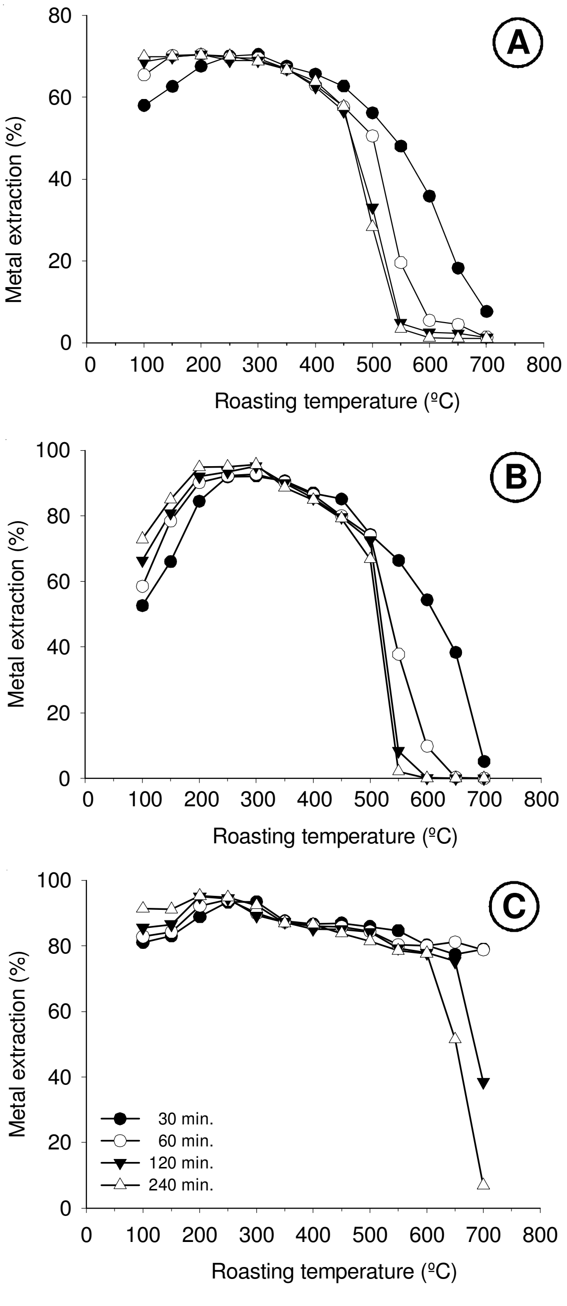


Fig. 6. Effects of roasting temperature on the Zn extraction (roasting time: 1 h; H_2SO_4/solid ratio: 1:1; solid ratio: 20 %; leaching temperature: ambient; leaching time: 1 h)



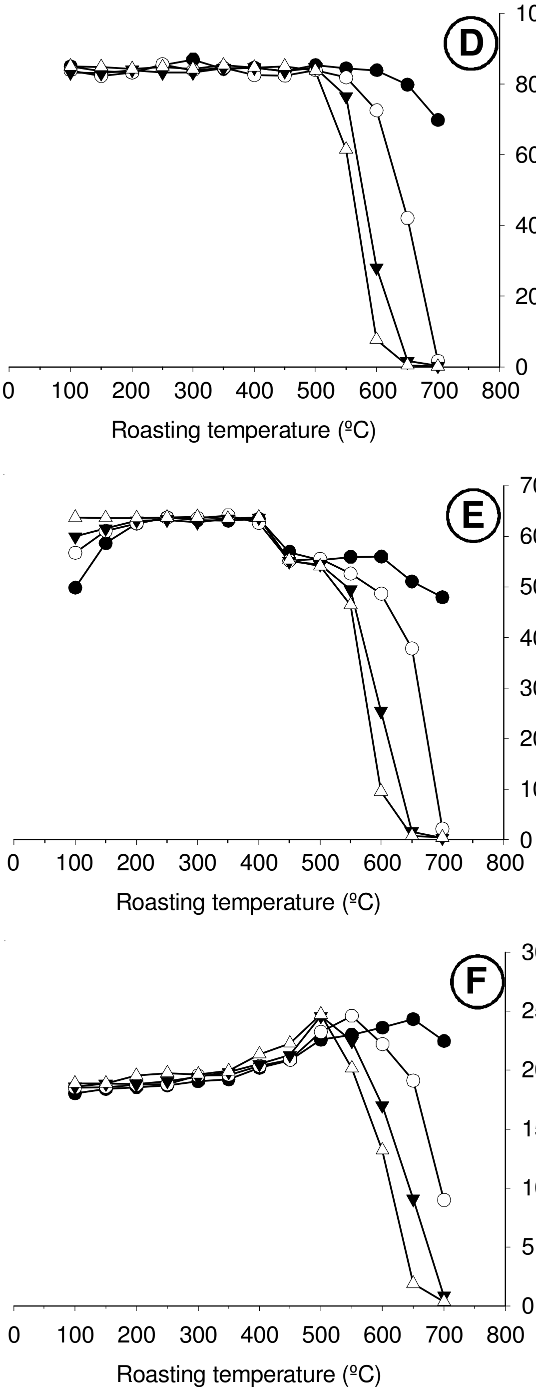


Fig. 7. Effects of sulfating roasting temperature on metal extractions (A: iron, B: aluminum, C: manganese, D: copper, E: nickel, F: cobalt) (roasting time: 1 h; H_2SO_4/solid ratio: 1:1; pulp density: 20 %; leaching temperature: ambient; leaching time: 1 h)

The dehydration of the copper sulfate is also observed in 100-200 ºC temperature range just as it is for iron. The copper which stays in the form of sulfate up to 600 ºC decomposes after this point and forms basic copper sulfate salt ($CuO \cdot CuSO_4$). After 700 ºC, copper form copper oxide[35].

In the condition of existence of iron oxide (Fe_2O_3) in the atmosphere, the sulfates break and form ferrites: for example copper ferrite ($CuO \cdot Fe_2O_3$) starts forming at 600 ºC. The structure of $CuO \cdot Fe_2O_3$ stay stabilized up to 1100 ºC. Because of this reason, ferrite formations are not desired during sulfating roasting process.

$$CuSO_4 + Fe_2O_3 \rightarrow CuO \cdot Fe_2O_3 + SO_3 \qquad (10)$$

As can be seen in Fig. 7-D, during 0.5 h roasting process copper can dissolve into a solution of 85 % up to 600 ºC heats. After 600 ºC the extraction levels show a sharp decrease. This finding confirms the information in the literature about the sulfate decomposition[35]. In the same lines, the recovery for nickel gradually increases up to 400 ºC and rapidly declines after 450 ºC (Fig. 7-E).

Aluminum sulfate loses its crystal water between 25-350 ºC and turns into anhydrous $Al_2(SO_4)_3$. Between 580 and 805 ºC this sulfate structure disintegrates and forms Al_2O_3. Fig. 7-B shows that aluminum dissolution can increase up to 96 % in 300 ºC for all roasting periods and after this heat, declines gradually for 0.5 and 1 h roasting periods while declining sharply after 500 ºC in 120 and 140 min roasting durations.

Dehydration of manganese sulfate takes place between 115-238 ºC and results in turning the material into anhydrous $MnSO_4$. Up to 828 ºC, it changes form and turns into Mn_3O_4. According to the results of sulfating roasting test, the Mn dissolution increased to 95 % up to 300 ºC and then decreased to 80 % gradually up to 700 ºC. When the duration for roasting increased, manganese dissolution showed decrease for degrees higher than 650 ºC in 2 h roasting and 600 ºC in 4 h roasting (Fig. 7-C).

Cobalt sulfate loses its crystal water up to 265 ºC and turns into oxide[36] by losing all its sulfate structure up to 800 ºC. Fig. 7-F shows that 0.5 h roasting process up to 650 ºC increases the dissolution productivity to 25 %. But there is a decline to 22.5 % at 700 ºC.

Humidification tests: Sulfating roasting tests under the conditions specified below were applied to the sample since sulfate compounds have hydrate structures that can dissolve in the water. The results are given in Fig. 8. Roasting heat : 200 ºC, H_2SO_4/solid rate: 1:1, duration for roasting: 1 h, humidification rate (water:solid): 10-200 %.

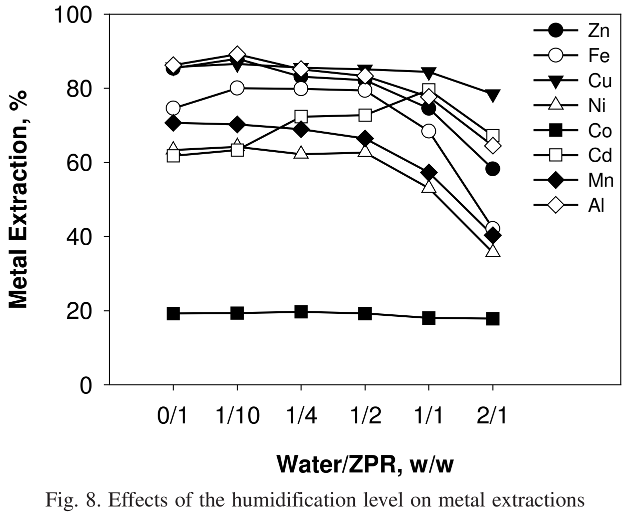


Fig. 8. Effects of the humidification level on metal extractions

Kar and Swamy[37] have shown in their study with ferrochrome in which they studied the nickel acquisition by sulfating roasting that 20 % humidification level caused 6-16 % nickel recovery compared to the case where there was no humidification. As seen in Fig. 8, humidifying the sample

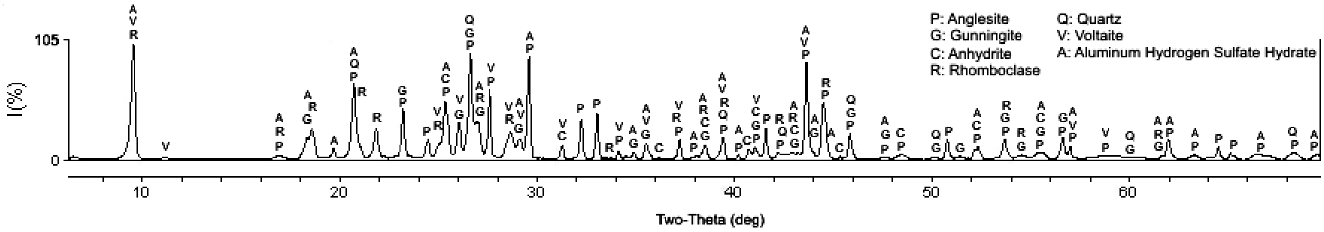


Fig. 9. XRD analysis graphics for the product for which sulfating roasting was applied

with water for 10 % helped increase the recovery of metals compared to acid use only. This finding is consistent with literature[37]. But increasing the amount of water caused a substantial decrease in the recovery the metals other than cadmium. Because of this reason, 10 % humidification rate was seen as the optimum level for which the zinc recovery was about 90 %.

Fig. 9 depicts the material which was taken into sulfating roasting along with Çinkur establishment leach residue under optimum conditions.

According to the results, the product for which sulfating roasting was applied consisted of anglesite [$PbSO_4$], gunningite [$ZnSO_4{\cdot}H_2O$], anhydrite [$CaSO_4$], rhomboclase [$FeH(SO_4)_2{\cdot}4H_2O$], voltaite [$K_2Fe_5Fe_3Al(SO_4)_{12}(H_2O)_{18}$], aluminum hydrogen sulfate hydrate [$Al_2H_2(SO_4)_4{\cdot}8H_2O$] minerals. The results did not specify any oxide structures in this product. But gypsum was found to have changed into anhydrite [$CaSO_4$] by losing all water in its structure. Fig. 10 depicts the SEM image of the product for which sulfating roasting were applied.

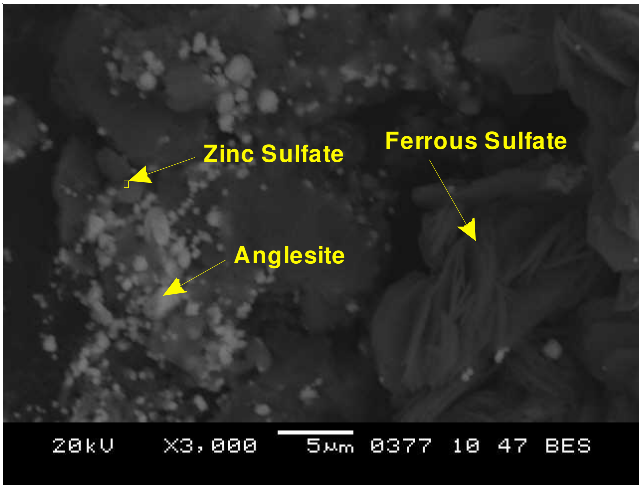


Fig. 10. Roasting product × 3,000 SEM image (200 °C)

Water leaching experiments: In this part, water leaching conditions for Zn extraction from the sample, whose roasting conditions were previously defined, were attempted to be determined. Effects of temperatures, solid-liquid ratios and duration on metal extractions were studied. The results obtained are presented in Figs. 11-13. As it can be seen in Fig. 11, when temperature increased from 25-90 °C, Zn extraction increased from 86 % up to 90 %. Leach temperature did not have a significant effect on the extraction of metals.

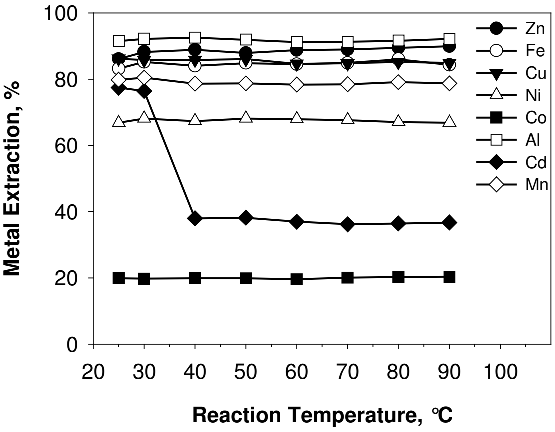


Fig. 11. Effects of leach temperature on metal extractions (duration: 1 h, solid ratio: 20 % w/w)

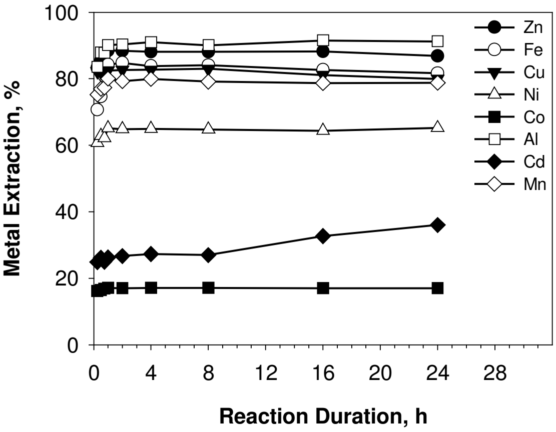


Fig. 12. Effects of leach temperature on metal extractions (temperature: 30 °C, solid ratio: 20 % w/w)

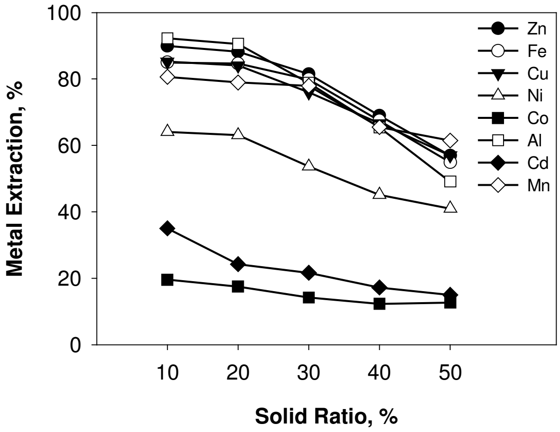


Fig. 13. Effects of solid ratio on metal extractions (temperature: 30 °C, duration: 1 h)

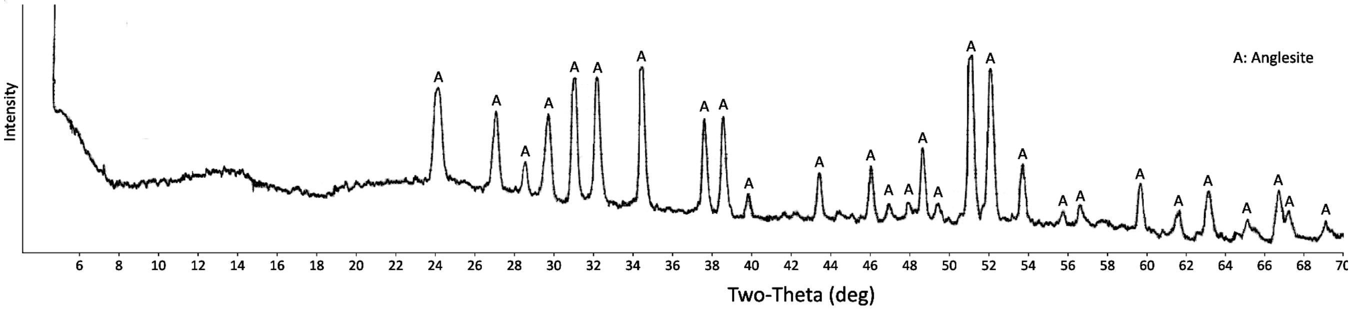


Fig. 14. XRD analysis graphic of lead paste

As it can be seen in Fig. 12, metal salts emerging after roasting could permeate in the solution by water leaching in a short time. Zn extraction reached 83 % in the first 15 min and stabilized around 88 % after 1 h. It can be seen in Fig. 13 that the increase in solid ratio had a negative effect on metal extractions. Zn extraction was approximately 90 % in 10 % solid ratios, while in the experiment conducted with 50 % solid ratios, the extraction dropped to around 55 %.

Minerals identified from the previous XRD analysis results were confirmed from the SEM images obtained, with EDS and map analysis. Moreover, as a result of EDS and map analysis it was determined that an amount of zinc ferrite remained in the body of lead paste obtained as a result of water leaching (Figs. 14-16).

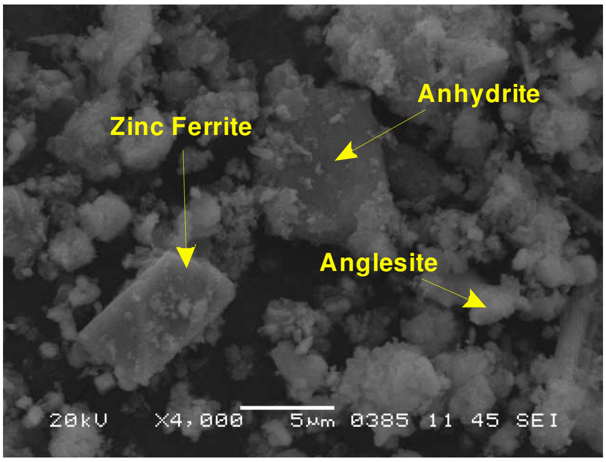


Fig. 15. x3,000 magnified SEM image of lead paste

Lead and silver recovery studies: In general, zinc ore contains some amount of lead and silver as bymetals. These metals oxidize as a result of roasting process dependent on the structure of zinc ore. During neutral leaching phase conducted with sulfuric acid, lead and silver do not dissolve and they remain in neutral leach residue in the form of sulfur or sulfate[38]:

$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O \tag{11}$$

$$Ag_2O + H_2SO_4 \rightarrow Ag_2SO_4 + H_2O \tag{12}$$

$$Ag_2SO_4 \rightarrow 2Ag^+ + SO_4^{2-} \tag{13}$$

$$2Ag^+ + ZnS \rightarrow 2Ag_2S + Zn^{2+} \tag{14}$$

Particularly for recovery of lead in the battery sludge through leaching-electrolysis method; different processes have been developed such as ammonium carbonate leaching, sodium carbonate-sodium hydroxide leaching, ammoniacal ammonium sulfate leaching and HCl-NaCl leaching. Although these processes seem attractive, they require high amounts of energy and multiple process stages. Except for these processes, lead sulfate can transform to lead hydroxide by sodium hydroxide leaching or can transform to lead carbonate by sodium carbonate. Products of both of the methods are not available for supply by sintering machine due to exothermic reactions that occurs during sintering process. Furthermore, high expenditures of sodium hydroxide and sodium carbonate make these methods far from being applicable[38].

Ammonium acetate leaching enables permeation of lead into solution in the ratio of 70-75 %, while silver remains in the leach residue. The leach solution is cemented with aluminum

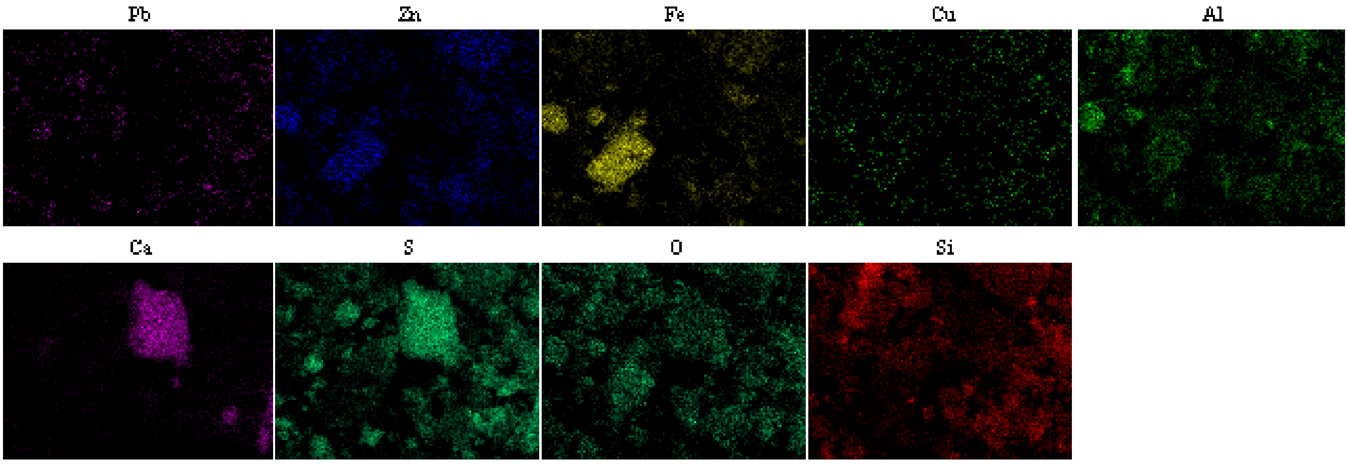


Fig. 16. x3,000 magnified SEM map analysis image of lead paste

crusts or zinc cathode, which produces high quality lead sponge and lead metal is obtained through the following fusion process. However, due to high costs of ammonium acetate and that silver in the leach residue remains in a complex structure, applicability of this method is constricted as well.

This part of the study aimed at recovery of lead and silver by salt leaching method from the lead paste which consisted high ratios of lead and silver and which was obtained after sulfating roasting and water leaching. In this method, the solution which contained a high ratio of sodium chloride as well as lead and silver sulfate compounds was transformed into dissoluble chloride compounds. Sodium chloride was a good solvent for lead sulfate and silver sulfate. After filtration of the obtained leach solution, sodium sulfur was added in the solution and the solution was precipitated in the form of lead and silver sulfur. With this precipitation process, NaCl was recovered as well. The reactions during leaching and precipitation processes can, respectively be defined as follows[15].

Leaching step:

$$PbSO_{4(s)} + 2NaCl_{(aq)} \rightarrow PbCl_{2(aq)} + Na_2SO_{4(aq)} \quad (15)$$

$$Ag_2SO_{4(s)} + 4NaCl_{(aq)} \rightarrow 2NaAgCl_{2(aq)} + Na_2SO_{4(aq)} \quad (16)$$

Precipitation step:

$$PbCl_{2(aq)} + Na_2S_{(aq)} \rightarrow PbS_{(s)} + 2NaCl_{(aq)} \quad (17)$$

$$2NaAgCl_{2(aq)} + Na_2S_{(aq)} \rightarrow Ag_2S_{(s)} + 4NaCl_{(aq)} \quad (18)$$

In the studies which aim recovery of lead and silver from the lead paste, the effects of parameters such as NaCl amount, solid ratio, leach temperature and leach duration on Pb and Ag extractions were analyzed. Chemical analyses of the lead paste used in these tests are given in Table-3.

TABLE-3
CHEMICAL ANALYSIS OF LEAD PASTE

Element (%)					
Pb	Zn	Fe	Sb	Mn	
32.22	1.29	1.58	0.40	0.04	
Element (mg/kg)					
Ag	Cd	Cu	Ni	Co	Cr
322	268	198	170	143	78

Effects of NaCl amount: In order to identify the effect of NaCl amount used in the preparation of the Pb and Ag dissolutions, experiments were conducted under the below stated conditions. The obtained results are given in Fig. 17.

When the results are studied, it is understood that, when the used NaCl amount was between 60-120 g/L, Pb dissolution remained around 17 %, gradually increased until 300 g/L up to 92 % and after this amount, no significant change occurred in the dissolution. Considering the results for silver; when the used NaCl amount increased from 60-120 g/L, Ag dissolution also increased from 55-63 %. From this amount up to saturated NaCl solution (315 g/L), Ag dissolution gradually increased and it became 66 % in the saturated solution (Fig. 17).

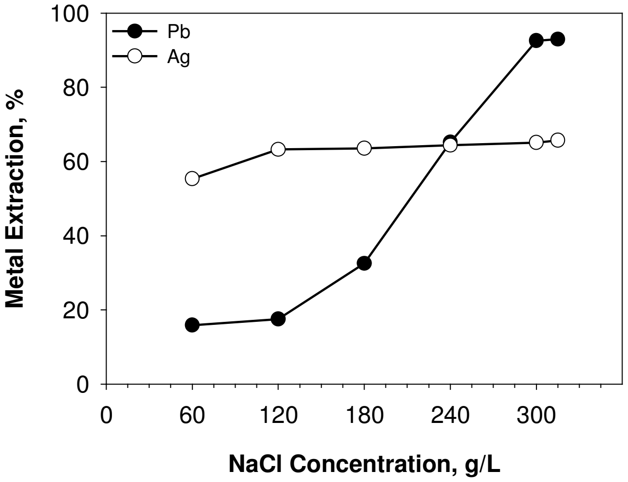


Fig. 17. Effects of NaCl amount on Pb and Ag dissolutions (temp.: 30 ºC, solid ratio: 3 %, duration: 45 min)

Effects of solid ratio: In order to identify the effect of solid ratio on Pb and Ag dissolutions, experiments in the below stated conditions were conducted and the results are given in Fig. 18. It is observed (Fig. 18) that solid rate in leaching process did not have significant effect on Pb and Ag dissolutions until 3 %, however with the increase of solid ratio up from 3 % Pb and Ag dissolutions significantly decreased. In experiments with 0.5-3.0 % solid ratio, Pb and Ag dissolutions were, respectively around 92 and 65 %, while with 15 % solid rate, the dissolution remained at 15 % for Pb and at 10 % for Ag.

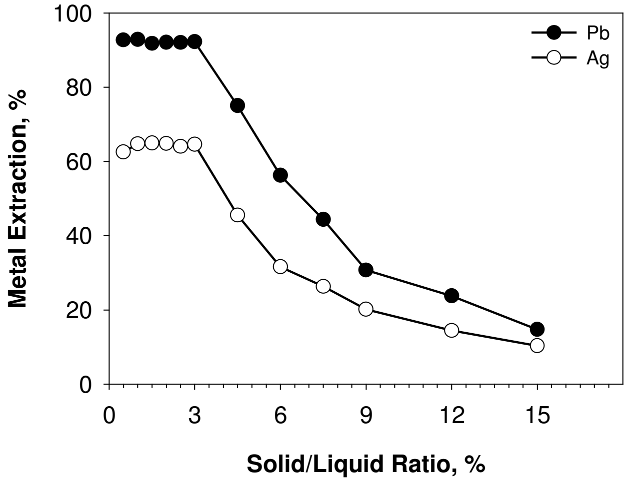


Fig. 18. Effects of solid ratio on Pb and Ag dissolutions (temp.: 30 ºC, duration: 45 min, NaCl cons: 315 g/L)

Effects of leach temperature: In order to identify the effect of leach temperature on Pb and Ag dissolutions, experiments were conducted under the below stated conditions and the obtained results are given in Fig. 19. When Fig. 19 is studied, it is seen that the change in leach temperature did not have any effect on Pb dissolution. Accordingly, Pb dissolution was between 91-92 % at all temperatures. On the other hand, Ag dissolution slightly decreased with the increase of temperature. At 25 ºC, Ag dissolution was 64.3 % and dropped to 61.5 % at 80 ºC.

Effect of leach duration: In order to identify the effect of leach duration on Pb and Ag dissolutions, experiments were conducted under the below stated conditions and the obtained results are presented in Fig. 20. When the results of the experiments conducted to determine optimum leach duration were

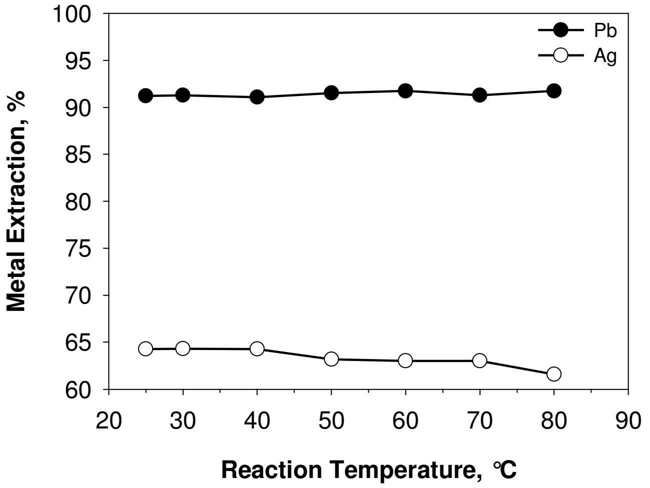


Fig. 19. Effects of leach temperature on Pb and Ag dissolutions (duration: 45 min, NaCl cons: 315 g/L, solid ratio: 3 %)

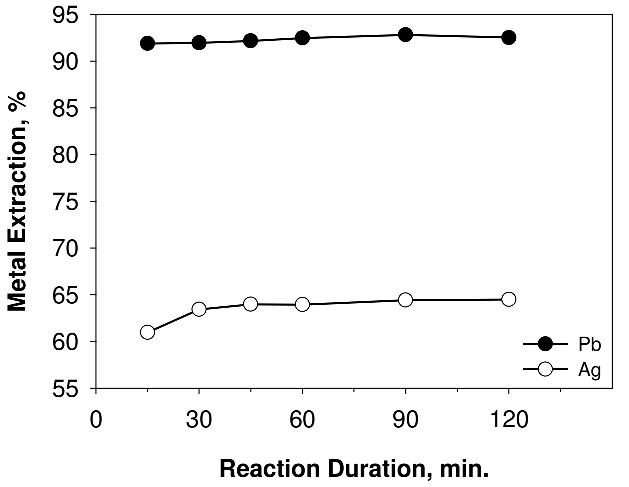


Fig. 20. Effect of leach duration on Pb and Ag dissolution efficiencies (NaCl cons: 315 g/L, solid ratio: 3 %, temp.: 30 °C)

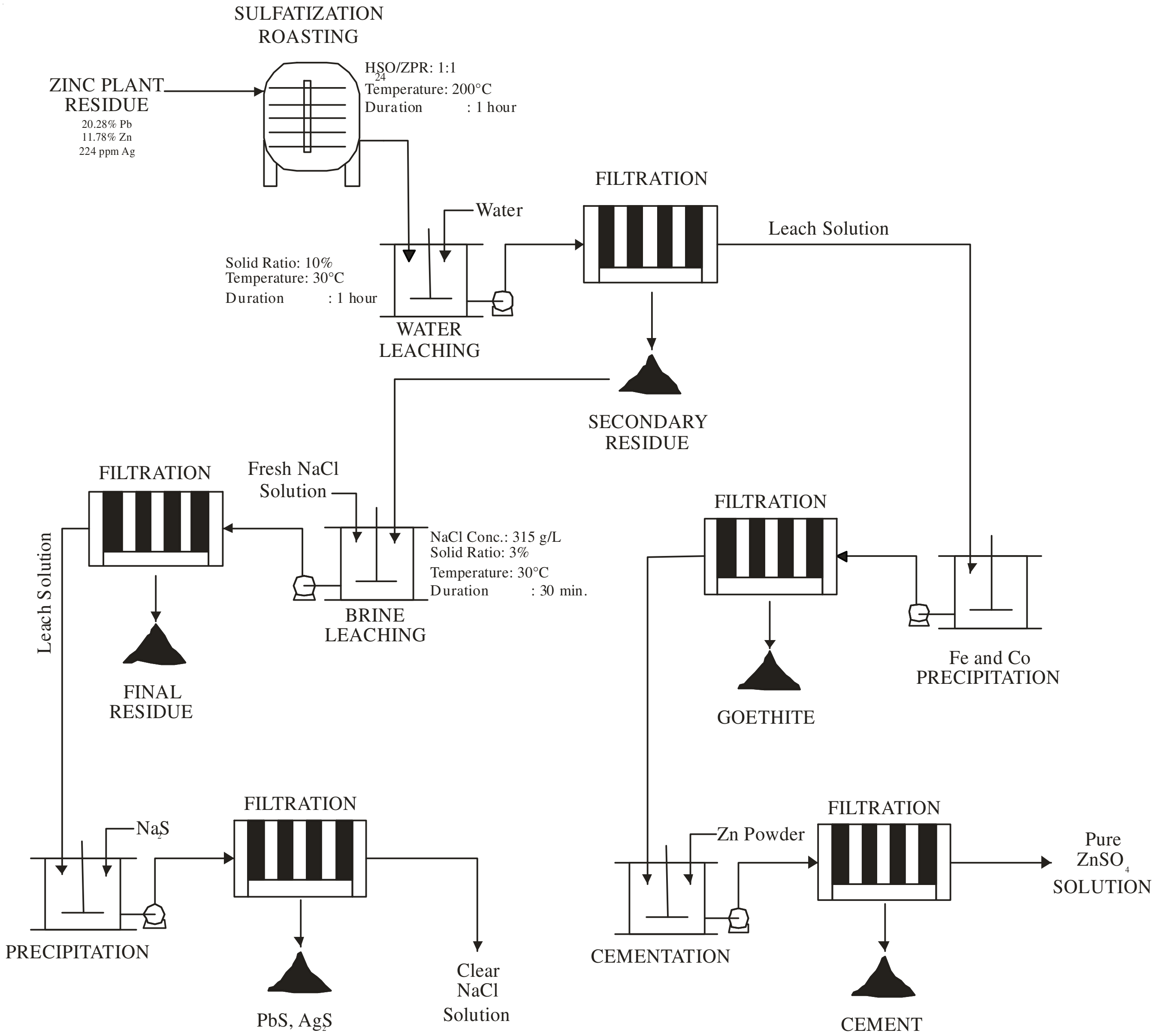


Fig. 21. Suggested flow chart for recovery of Zn, Pb and Ag from Çinkur plant residues

considered, it can be seen that in 15 min leach duration, lead permeated in the solution in the ratio of 92 % and no significant effect of duration increase was detected in Pb dissolution. On the other hand, Ag dissolved in the ratio of 61 % in 15 min and this ratio slightly increased up to 63.4 % in 0.5 h. Increase of the leach duration also did not have significant effect on Ag dissolution. The highest Ag dissolution was obtained in 2 h leach duration, with a 1.1 % increase up to 64.5 % (Fig. 20).

In Fig. 21, the flow chart has been determined in the light of the experiment for recovery of zinc, lead and silver from Çinkur plant leach residues, is suggested.

Conclusion

In this study, the leaching characteristics of the zinc leach residue originating from Waelz oxide leach residue of Çinkur plant in Kayseri, Turkey were investigated. Mineralogical and chemical analyses showed that more than half of the zinc was in ferrite and silicate structure. The chemical extraction of zinc from ferrite is quite difficult due to the stability of the ferrite structure. However, the ferrite structure can be broken by thermal treatment of the ferrite with sulphuric acid. The optimum conditions for zinc recovery from leach residue by a process comprising roasting of the sample/H_2SO_4 mixing followed water leaching were determined. Different sulfuric acid concentrations were used and sulfating roasting was conducted at different temperatures and durations in order to transform metals in the material into metal salt forms and to decompose the ferrite structure. It was determined that metal dissolution efficiency stabilized on conditions above 1:1 H_2SO_4/solid ratio. The best result was obtained at as H_2SO_4/sample weight ratio = 1/1; humidification, 10 %; roasting temperature, 200 ºC; roasting time, 1 h; leaching temperature, 30 ºC; solid/liquid ratio, 1/5 and leaching time, 1 h. At these conditions 90 % of zinc was extracted. Also, hot acid leaching tests were performed on the sample. At low acid concentration (50 g/L) ferritic zinc extraction was too low (2 %). Ferritic and total zinc extraction was about 51 and 82 %, respectively at the optimum conditions of 200 g/L H_2SO_4, 2 h, 95 ºC, 20 % w/w solid ratio. At the last stage brine leaching experiments using sodium chloride (NaCl) were conducted on the residual lead paste to extract lead and silver. At the optimal conditions (315 g/L NaCl, 0.5 h, 30 ºC, 3 % solid ratio) lead and silver extraction was 92 and 63.4 %, respectively.

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