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Investigation of zinc extraction from different leach residues by acid leaching

A. Rüßen¹  · M. A. Topçu¹

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Abstract With different properties, zinc is one of the most important non-ferrous metals and it is used in various application areas, especially as an anti-corrosion agent. In Turkey, zinc production was based on zinc carbonate ores (ZnCO_3), at Çinkur plant from establishment to 1997 due to high reserves of zinc carbonate. After that, zinc concentrate coming from Iran was used in this plant over the last two decades. Thus, two different leach residues called as Turkish leach residue (TLR) and Iranian leach residue (ILR) were accumulated more than one million ton in Çinkur stock piles. In this study, it is aimed to investigate zinc recovery for each leach residue by use of sulphuric acid (H_2SO_4) and to compare the TLR and the ILR. Initially, detailed chemical, mineralogical and thermal analyses of these different leach residues were carried out. In order to investigate the effect of acid concentration and reaction duration on zinc recovery, leaching experiments were carried out at following conditions: 95 °C, 100 g/L pulp density and 600 rpm stirring rate. According to the characterization results, the chemical compositions for both residues are nearly similar; however, experimental results show that zinc recovery per cent of the ILR was higher than that of TLR for all experimental durations and acid concentrations. This may be due to the presence of Zn-containing compounds in the both residues at different percentages.

Keywords Hydrometallurgy · Zinc recovery · Sulphuric acid · Leach

Introduction

With the growing technology and increase in population, world has need many searches for metal production and extraction from different sources. Also, finding and processing of the new sources have become compulsory because of the depletion of metallic ores. For this reason, metallic wastes, which occur during the industrial activities, are considered as new sources by many scientists for metal recovery over the past few decades (Kiyak et al. 1999). Industrial wastes are classified as a hazardous material due to their chemical nature which is composed of heavy metals such as Zn, Pb, As, Cd. Due to the environmental pollution risks, easily soluble fraction under natural atmospheric conditions and from economic point of view, these industrial wastes must be disposed (Safarzadeh et al. 2008; Ahmed et al. 2012). Significant numbers of various solid wastes have been investigated to recover fundamental metals, and remarkable results were obtained successfully (Sarrafı et al. 2004; Ismael and Carvalho 2003; Barakat 1998). In the world, 90% of zinc is produced from primary sulphide ores, as well as less amount from oxide-carbonate ores. Remaining part of zinc is recovered from different secondary resources such as zinc ash, zinc dross, flue dust of electric arc furnace and brass smelting, automobile shredder scrap, rayon industry sludge due to depletion of high-grade ores (Jha et al. 2001; Turan et al. 2004; Şahin and Erdem 2015). Zinc leach residues (ZLR) come up after traditional zinc production by metallurgical processes which include leaching, electrowinning, galvanizing, casting, smelting, scrap recycling. These residues

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are stockpiled by zinc plants for next treatment or used as secondary sources for recovery of valuable metal content (Zhang et al. 2012; Li et al. 2013).

Up to the present, many studies have been carried out to recover valuable metals from secondary residues by using hydrometallurgical/pyrometallurgical method or combination of them. Due to the less environmental pollution and less energy consumption, the hydrometallurgical method is more accepted method with an eco-friendly process instead of pyrometallurgical process (Li et al. 2013).

Many researchers have investigated the optimum conditions for recovery of Zn and Pb from secondary resources, especially zinc leach residues (ZLR) by using different leaching agents such as sulphuric acid (Oustadakis et al. 2010; Ruşen et al. 2008; Sethurajan et al. 2016), ammoniacal solutions (Blanco et al. 1999), caustic soda (Youchi and Stanforth 2000; Xia and Pickles 1999; Lin 2000), brine (Raghavan et al. 1998; Farahmand et al. 2009) or based on chloride (Nunez and Vinals 1984; Olper 1993).

Çinkur (Zinc-Lead Metal Ind. Co.) is the only plant in Turkey which produces Zn from zinc carbonate ($ZnCO_3$) as a major Zn-based mineral during its operation time. In Çinkur, Waelz processing—dilute acid leaching and electrowinning—was followed to produce Zn from primary ore until company faced financial difficulties and depletion of local high-grade ores in 1997. After this year, oxidized ore concentrates were imported from Iran until this plant was bankrupt. For this reason, there are two different kinds of leach residues (LR), namely Turkish leach residue (TLR) and Iranian leach residue (ILR) in Çinkur stockpiles. Recently, the plant continues to operate with the name of ÇINKOM. However, due to the lack of optimum operating conditions, these two leach residues in different characteristics produced over the years are at disposal area in total amount about 1.2 million tons. About 90% of these wastes are Turkish leach residues, and the remains are Iranian leach residues (Altundoğan et al. 1998).

Although there are two different leach residues (Turkish and Iranian) in the Çinkur's stockpile area, all of studies have focused on the Turkish ones. Therefore, recovery process is prepared by considering the Turkish leach residue. While the chemical compositions for both residues are similar, their compositions especially percentages of the each Zn form are different, which results in different dissolution ratios in the H_2SO_4 media. Some of the studies mentioned above have been carried out by researchers about Çinkur leach residue obtained from its discarded stock area at different dates. However, none of them have developed a feasible or applicable process for this residue. Therefore, in this study, it is aimed to propose two different leaching conditions for two types of residues after investigating physical, chemical and mineralogical characterizations of the leach residues in detail. By this way, more

appropriate and economic method could be proposed to assess two different residues separately in terms of both zinc recovery and environmental impacts by using less concentrated H_2SO_4 and shorter leaching time.

Material and method

The zinc leach residues (TLR and ILR) used in this study were obtained from Çinkur leach stockpiles. In characterization of the materials, firstly the physical characterizations of TLR and ILR were done to determine their moisture content, bulk density and specific gravity. Residues were also analysed chemically to find out their chemical compositions by using atomic absorption spectrophotometer (AAS) and X-ray fluorescence (XRF). Then, the mineralogical characterizations of each sample and the blend were done by X-ray diffractometer (XRD). At last, thermal gravimetric analysis (TGA) of different LRs were done to investigate the thermal behaviour of the sample.

Physical analysis

Physical characterization of TLR and ILR started with moisture determination. First results showed that TLR contained 19.5 wt% physically bonded water, while ILR had 30.9 wt%. These initial findings gave a rough idea that the samples had different characteristics. After moisture analysis of the residues, each one was dried at 105 °C, then pulverized in order to disperse the sticking fine particles and used for this study. Characterization of TLR and ILR continued with bulk density and specific gravity analysis. To determine its bulk density, each residue was filled in a 1-L measuring cylinder and weighed with tare. In addition, specific gravity of each leach residue was determined by using a water pycnometer and a helium pycnometer. Bulk density and specific gravity of TLR and ILR at 25 °C are given in Table 1.

When the specific gravities of TLR and ILR are compared to the specific gravities of both LR in Table 1, the values measured by water pycnometer are lower than those determined by He pycnometer. This was due to the presence of soluble compounds such as $ZnSO_4 \cdot 7H_2O$ in the LRs.

Table 1 Bulk density and specific gravity of TLR and ILR at 25 °C

Physical property	Sample	
	TLR	ILR
Bulk density (g/cm^3)	0.97	0.77
Specific gravity by water pycnometer	3.28	3.69
Specific gravity by He pycnometer	3.44	3.84

Chemical analysis

Characterization of TLR and ILR goes forward with chemical analysis which was performed by using PerkinElmer PinAcclle 900T AAS in Karamanoglu Mehmetbey University. Only Zn, Pb and Fe contents of the initial samples (TLR and ILR) were determined by AAS. The other components of the original TLR and ILR were analysed by Rigaku NEXCG model XRF in the Department of Metallurgical and Materials Engineering of Necmettin Erbakan University (NEU). Secondary leach residues after hot acid leaching trials were also analysed by XRF at NEU. In order to check initial percentages of the important metals in original TLR and ILR, they were also analysed by AAS (Zn, Pb and Fe) and XRF (full elements) in the Department of Metallurgical and Materials Engineering of METU. The results of chemical analyses obtained by AAS and XRF were compared with those of previous researchers, and the results were found to be meaningful with reasonable deviations. The chemical analyses of TLR and ILR are given in Table 2. It can be seen from Table 2 that the leach residues are primarily composed of zinc, lead, iron and silica with the high contents.

XRD analysis

The XRD patterns were carried out to detect mineralogical phases of these different leach residues by using Bruker Advance D8 model X-Ray Diffractometer (in Karamanoglu Mehmetbey University) with Cu radiation at 30 kV at a scanning rate of 0.4°/min. Mineralogical analysis also was done after leaching experiments for evaluating the change of mineralogical phases of two different leach residues. The XRD patterns were detected for initial leach residues and after leaching experiments for two different leach residues. XRD patterns of the TLR and ILR are illustrated in Fig. 1a, b, respectively. According to the XRD results, the leach residues were composed of mainly PbSO₄, SiO₂ and zinc with different structures such as

Table 2 Chemical composition of different Çinkur leach residues

Elements	Content (wt%)	
	TLR	ILR
Zn	11.9	16.3
Pb	16.5	8.2
Cd	0.04	0.2
Fe	6.8	5.5
CaO	8.3	4.1
SO ₃	19.7	22.5
SiO ₂	15.9	20.1
Al ₂ O ₃	3.9	6.6
MnO	0.6	1.7
MgO	0.9	1.3

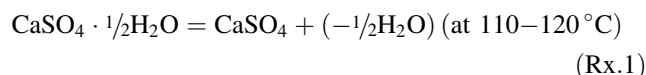
ZnFe₂O₄, ZnSO₄·7H₂O, ZnSO₄·H₂O and ZnSiO₄. The other minor components were determined as Fe₂O₃, Fe₂SiO₄, CaSO₄·½H₂O and CaSiO₄.

Thermal analysis

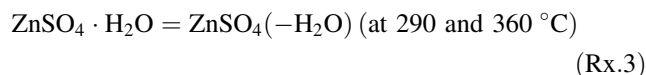
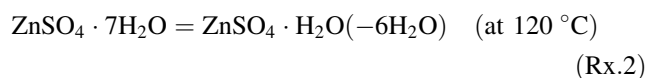
Thermogravimetric analyses (TGA) of TLR and ILR were carried out to find out the thermal behaviour of both leach residues from 30 to 1100 °C. TLR and ILR were analysed by Tetra TG/DTA 6300 with a linear heating rate of 20 °C/min. under nitrogen atmosphere. Results of the TGA of TLR and ILR are given in Figs. 2 and 3, respectively.

It is generally accepted that each peak belonging to endothermic property can be associated with dehydration, dehydroxylation, decomposition of structures, transformation of one structure into another, magnetic changes, sintering of substances and melting of or sublimation of minerals (Kloss 1982). According to the thermogravimetric analysis of leach residues (Figs. 2, 3), gradual weight losses were observed with increasing temperature for both of leach residues in different amounts. Evaporation of the chemically bonded water and several decompositions are the main reason for the weight loss which occurs during the thermal analysis. When investigating in terms of weight losses on the thermal curves of the leach residues, the first decrease corresponding to the moisture removal is nearly same for the both leach residues (~1.5%).

The TLR and ILR contain two main compounds including chemically bonded water based on zinc sulphate hydrate and calcium sulphate hydrate. When looking at the both thermal curves in Figs. 2 and 3, the second decrease in the weight losses corresponding to endothermic peaks around 100–150 °C indicates the dehydration process of calcium sulphate hemihydrate (CaSO₄·0.5H₂O) to transform the anhydrite calcium sulphate (CaSO₄) according to the following reaction (Rx. 1) (Todor 1976):



As seen from the thermal curves of TLR and ILR, there is a dissimilarity at peak positions around 270–310 °C indicating endothermic reactions. Initial dehydration of ZnSO₄·7H₂O starts at 120 °C and goes up to 380 °C with following reactions (Liptay 1971);



According to the XRD analysis of the residues, TLR contains ZnSO₄·7H₂O structure, while ZnSO₄·H₂O compound is present in the ILR. As mentioned later,

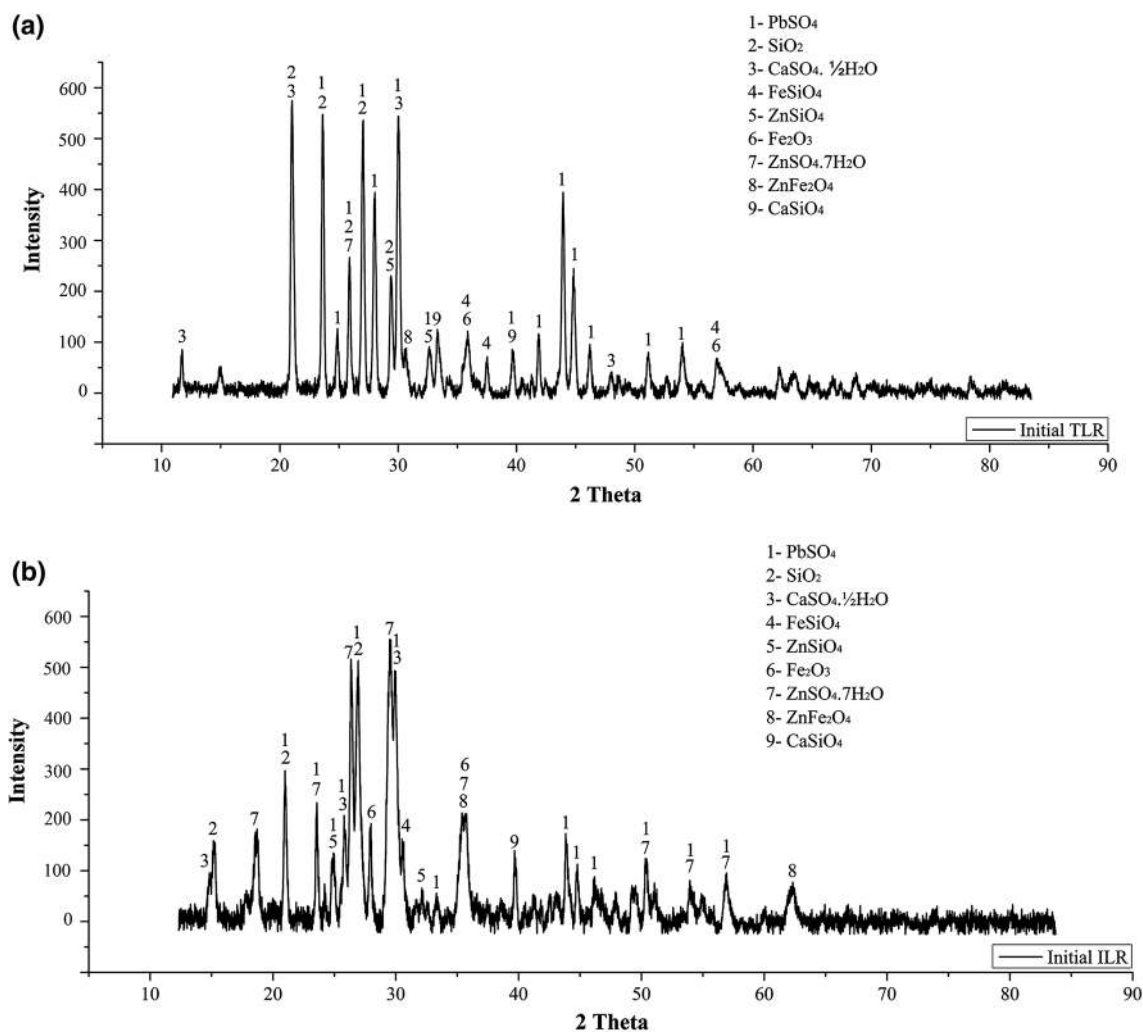


Fig. 1 XRD patterns of original leach residues. **a** TLR and **b** ILR

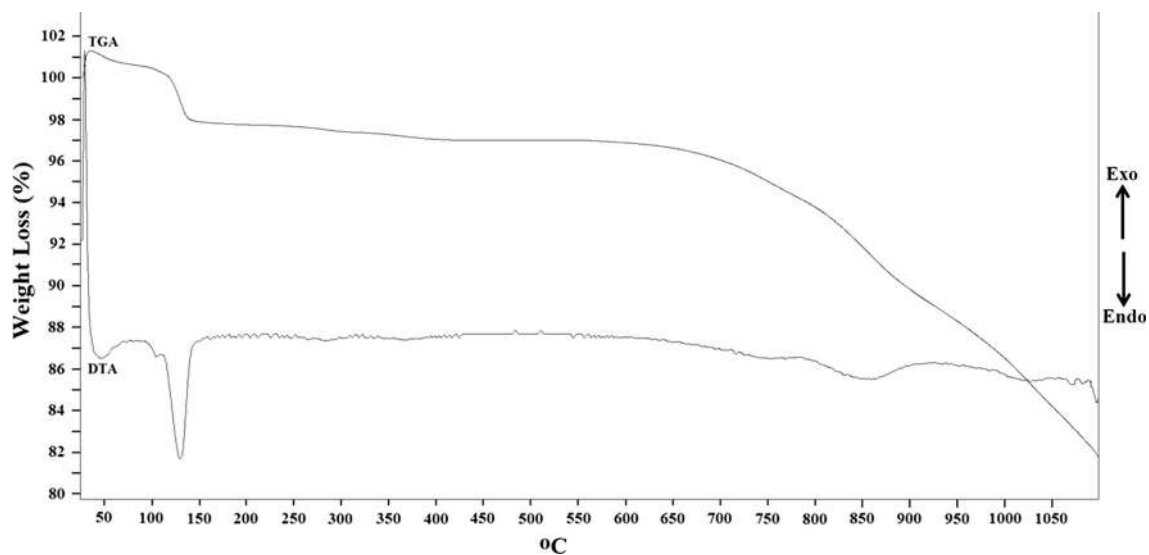


Fig. 2 Thermogravimetric analysis of TLR

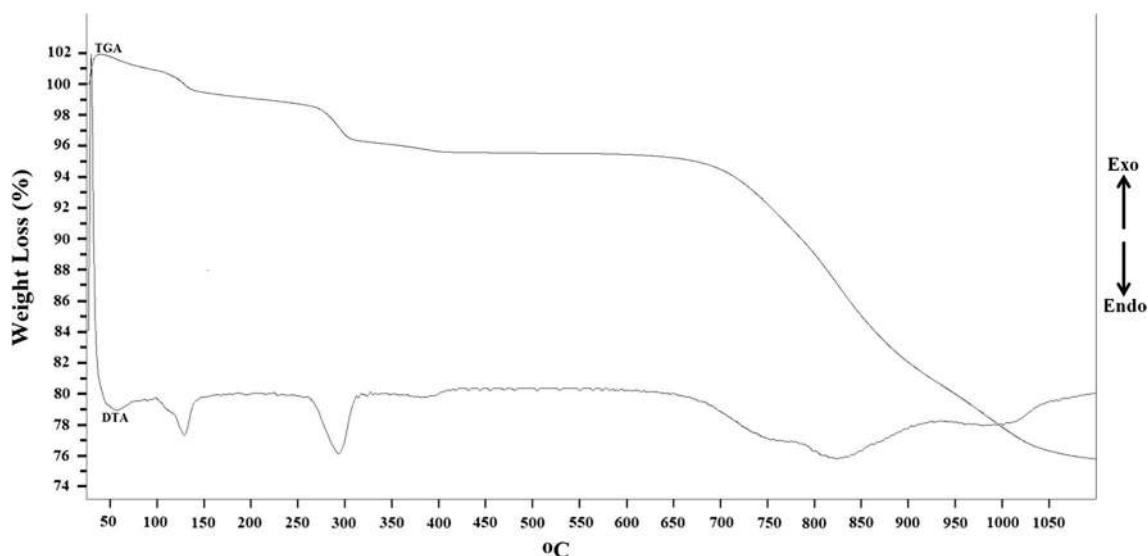
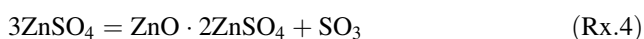


Fig. 3 Thermogravimetric analysis of ILR

according to the water leaching results, Zn amount of the sulphate form is more than 20% in the ILR and lower than 10% in the TLR. As $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ dehydration with limited quantities in the TLR does not cause a significant reduction in weight loss on its thermal curve, it can be stated that most of the dehydration of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in the TLR takes place with $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ at 110–120 °C. On the other hand, considering the weight of $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ in the ILR, the presence of an endothermic peak and weight losses with more than 3.5% at around 300 °C on the ILR curve can be explained by Rx. 3. After the hydrated zinc compound was transformed to anhydrite zinc sulphate (ZnSO_4), there was no any thermal effect and significant weight decrease in further heating of both residues until starting to desulphurization of any sulphate compounds.

Next step in the thermal curves of the leach residues is weight losses corresponding to endothermic peaks result from decomposition of any sulphates (ZnSO_4 , PbSO_4 , CaSO_4) in the residues. According to the thermal curves (Figs. 2, 3), decomposition of sulphates begins at about 650 °C and continues up to end of curve (1080 °C) for both of leach residues.

Several researchers have identified the first decomposition temperature of zinc sulphate as 610, 646 and 675 °C different from each other (Kolta and Askar 1975). On the basis of the literature (Güler et al. 2011), sulphate decomposition process of zinc sulphate takes place mainly by two steps (Rxs. 4, 5):



In this study, the first weight losses that resulted from decomposition of zinc sulphate were observed for TLR and

ILR at 630 and 670 °C, respectively. It is determined from the thermal curves that ZnSO_4 desulphurization of TLR and ILR occurs between 700 and 780 °C with an endothermic peak. After this temperature, zinc is only available ZnO form in the residues (Liptay 1971).

The other endothermic peak on the curves observed between 780 and 1140 °C for both leach residues is assigned to the desulphurization of anglesite (PbSO_4). According to the researchers (Frost et al. 2005, Sajadi 2011), the decomposition of PbSO_4 occurs between 789 and 1142 °C by the following reaction (Rx. 6);



When looking at thermal curves of the residues, it can be concluded that weight losses that stem from decomposition of PbSO_4 are in harmony with their amount in the residues. Weight loss originated from sulphurization on curves of ILR and TLR equals totally about 19 and 15%, respectively. However, it should be noted that decrease in mass on TLR curve continues even after 1100 °C, while it ends up at about 1080 °C. Since CaSO_4 does not exhibit any thermal effect up to 1200 °C, there is no any curve belonging to CaSO_4 desulphurization on TGA results.

Method

After characterization of two different leach residues, experimental conditions were chosen as 95 °C, 1/10 solid–liquid ratio (100 g/L pulp density) and 600 rpm stirring speed. All leaching experiments were conducted with 25 g leach residue by using constant volume of leaching solution (250 mL) round bottom three-necked flask of 500 mL. In the leaching experiments, temperature was controlled by

a contact thermometer having ± 1 °C sensitivity. Merck quality sulphuric acid (~ 98 wt%) and de-ionized water were used to form leach solution. Acid concentration and leaching time were chosen as in the range of 50–250 g/L and 0.5–4 h, respectively, to investigate the effect of zinc recovery efficiency.

In this study, recovery term (%R) was used to state the amount of metal which could be taken into leach solution. For this reason, the chemical compositions of these different leach residues were analysed after leaching experiments by XRF to calculate the efficiency of zinc recovery by using the following equation:

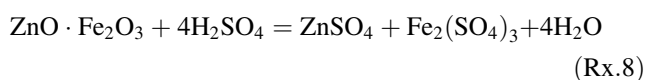
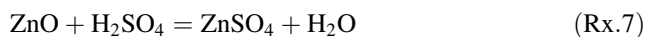
$$\%R = \left[\frac{(W_{lr} \times C_{lr}) - (W_{sl} \times C_{sl})}{W_{lr} \times C_{lr}} \right] \quad (1)$$

where W_{lr} is weight of initial leach residues in grams, W_{sl} is weight of secondary leach residues in grams, and C_{lr} is weight per cent of metal (Zn and Fe) in initial leach residues. C_{sl} is weight per cent of metal (Zn and Fe) in secondary leach residues.

Results and discussion

Effect of acid concentration on zinc recovery

As stated and approved by many researchers, sulphuric acid has been employed mostly for the hydrometallurgical extraction of zinc from ores or secondary resources since zinc oxide (ZnO) and zinc ferrite ($\text{ZnO} \cdot \text{Fe}_2\text{O}_3$) are the most important compounds soluble in concentrated sulphuric acid. Actually, zinc oxide can be dissolved even with dilute sulphuric acid but not zinc ferrite. Zinc oxide and zinc ferrite react with sulphuric acid according to the following reactions (Rxs. 7, 8) (Jha et al. 2001):



Therefore, in this study, the effect of acid concentration was investigated in order to determine the sufficient amount of acid under following conditions: leaching duration: 1 h, leaching temperature: 95 °C, solid–liquid ratio: 1/10 (g/mL) and the stirring speed: 600 rpm. The sulphuric acid concentration was in the range of 50, 100, 150, 250 g/L. The zinc and Fe content in the secondary leach residues was determined by XRF, and zinc recovery was calculated by using Eq. (1).

Effect of H_2SO_4 on Zn recovery and Fe dissolution from different leach residues (TLR and ILR) is illustrated in Figs. 4 and 5, respectively. As seen from Fig. 4, the leaching efficiency increased significantly with the

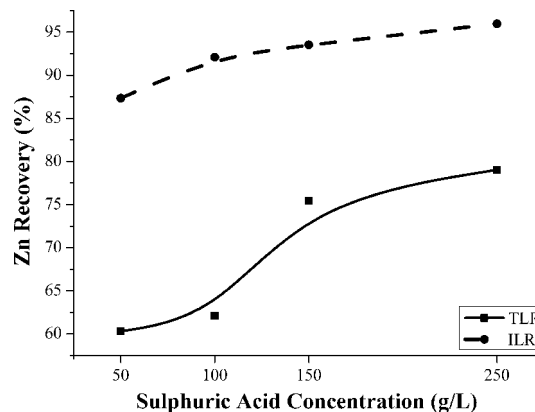


Fig. 4 Effect of acid concentration on Zn recovery from TLR and ILR

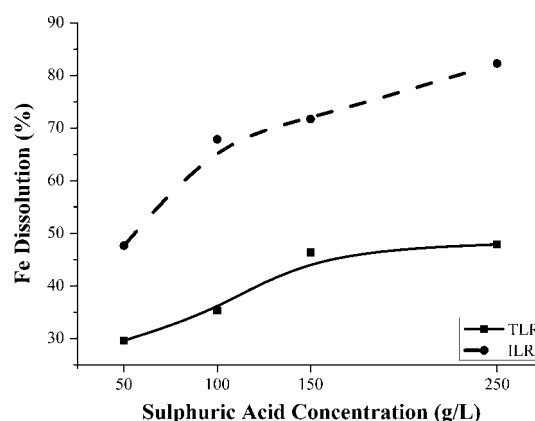


Fig. 5 Effect of acid concentration on Fe dissolution from TLR and ILR

increasing concentration of H_2SO_4 for both TLR and ILR. With increase in H_2SO_4 concentration from 50 to 250 g/L, zinc recovery was increased from 60.29 to 79.03% and from 87.34 to 95.96% for TLR and ILR, respectively. When comparing the lines in Fig. 4, it can be seen that zinc recoveries from TLR are lower than those from ILR for all acid concentration levels. The reason for this difference was thought to be due to the fact that the per cent of each composition of the zinc forms in the TLR and ILR was different from each other, especially in terms of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and Zn_2SiO_4 . Taking into account that zinc silicate is limited soluble in concentrated sulphuric acid, zinc silicate content in TLR may be greater than the amount of zinc silicate in the ILR.

Zinc recovery from the TLR increased significantly when the H_2SO_4 concentration is more than 100 g/L. On the contrary, zinc recovery ensures very high value for the ILR even though at very low acid consumption (50 g/L). According to experimental results, a remarkable increase in zinc recovery was gained from ILR when the acid concentration increased from 50 to 100 g/L. The maximum

value for zinc extraction of about 96% could be obtained at a temperature of 95 °C, in a period of 1 h and with a solid to liquid ratio 1/10 g/mL at a concentration of sulphuric acid of 250 g/L. It can be concluded that increase in acid concentration directly affects the extraction of zinc from both of the leach residues.

According to Rxs. 7 and 8, zinc ferrite dissolves at hot acid leaching conditions, and so zinc and iron are present in the leach solution. Iron is an undesirable element in the leach solution, and its elimination is a major operational problem in zinc hydrometallurgy. The removal of iron from such solutions is usually carried out by precipitation as jarosite, goethite or haematite. Among them, jarosite is the first iron removal process and is still the most widely used process in the zinc industry today due to the production of a filterable iron residue on a commercial scale (Ismael and Carvalho 2003). It can be seen from Fig. 5 that line of Fe dissolution for both residues resembles those of Zn recovery. That is, Fe dissolution in the pregnant solution increases with increasing acid consumption. Considering the recovery of zinc together with Fe dissolutions in the pregnant solutions, lower acid consumption (<100 g/L H₂SO₄) can be offered for ILR, while higher acid consumption (>150 g/L H₂SO₄) can be used for the TLR.

Effect of leaching duration on zinc recovery

The effect of the leaching time on zinc recovery was studied under the conditions that leaching temperature was 95 °C, solid–liquid ratio was 1:10 (g/mL), and the stirring speed was 600 rpm. 150 g/L sulphuric acid was prepared for leaching experiments. The Zn recovery and Fe dissolution were calculated by means of Eq. (1) and XRF results of the secondary leach residues. The results for the TLR and the ILR are shown in Figs. 6 and 7 with regard to Zn recovery and Fe dissolution per cents, respectively.

According to the experimental results given in Fig. 6, it can be observed that Zn recovery nearly 81 and over 96% after 4 h for the TLR and the ILR, respectively. It is clear that the leaching time has a remarkable effect on the zinc recovery from both leach residues. In general, the zinc recovery increases with increasing leaching time and the maximum zinc recovery was obtained after 4 h for both leach residues. Although Zn recovery increased as the reaction duration increased for both of them, a minor increase in Zn recovery was observed for the ILR by increasing the reaction duration from 0.5 to 4 h. Zn recovery for ILR after 0.5 and 4 h was obtained as 94 and 97%, respectively. That is, Zn recovery from ILR was developed only 3% in the whole range of the reaction time. On the other hand, zinc dissolution in the TLR was nearly the same between 0.5 and 2 h. However, zinc in the TLR was dissolved a bit more after longer than 2 h. When

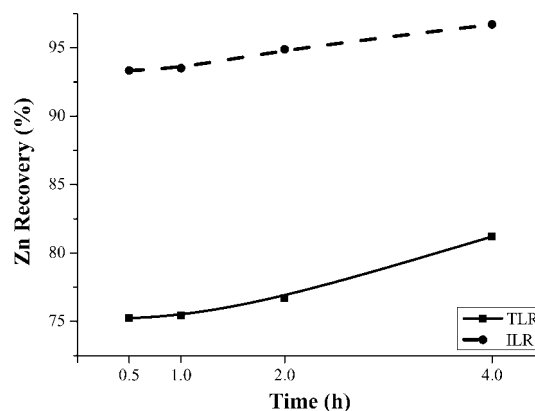


Fig. 6 Effect of leaching duration on Zn recovery from TLR and ILR

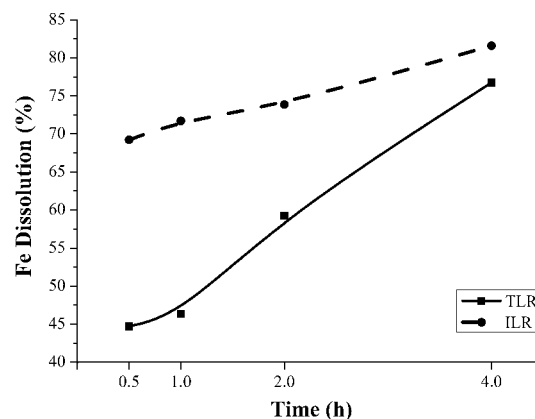


Fig. 7 Effect of leaching duration on Fe dissolution from TLR and ILR

comparing two different residues, this situation can be explained by the presence of zinc in various forms in the different leach residues. Probably, the amounts of acid-soluble zinc form (ZnFe₂O₄ and ZnSO₄·7H₂O) in ILR are higher than those in TLR. Therefore, all zinc forms in each leach residue should be revealed explicitly before performing a leaching test.

When the Fe dissolution curves (Figs. 5, 7) are carefully examined, it can be revealed that the dissolution of iron from leach residues, especially Turkish ones, is more affected from leaching time as compared to the sulphuric acid concentration effect. As seen from Fig. 5, the change in acid concentration more than 150 g/L does not show much effect on Fe dissolution percentage (experiments conditions: acid concentration: 50–250 g/L, reaction duration: 1 h, reaction temperature: 95 °C, solid/liquid ratio: 1/10 g/mL). However, looking at the time-varying experiments (Fig. 7), the Fe dissolution ratio for long-term experiments is almost the same for both residues (experiments conditions: reaction duration: 1–4 h, acid concentration: 150 g/L, reaction temperature: 95 °C, solid/liquid ratio: 1/10 g/mL). This can be revealed by a kinetic study.

Researchers (Filippou and Demepoulos 1993) studying on the dissolution kinetics of some ferrous compounds in acid media have stated that the compound with higher magnetic properties dissolves faster than the less magnetic ones. This indicates that the structures of the ferrous compounds in the residues are different from each. It can be concluded that various magnetic compounds or phases are present in the Turkish LR more than those of Iranian LR. To sum up, it can be stated from Fig. 7 that Fe dissolutions strongly depends on leaching time for the TLR. Fe content in the leach solution is increased sharply from 44.70 to 76.74% when duration goes from half an hour to 4 h. On the other hand, Fe dissolution ratio for the ILR increases slowly as leaching duration progresses.

After obtaining results of the all experiments, it can be concluded that the each residue can be treated under different leaching conditions. Taking into account Fe dissolution and zinc recovery, lower duration should be selected for both residues to avoid excess energy consumption.

XRD examination of secondary leach residues

After the leaching experiments, XRD examination was carried out for secondary leach residues to determine the mineralogical changes of two different leach residues at the selected condition of hot acid leaching, i.e., 250 g/L H_2SO_4 , 95 °C, 1 h, 100 g/L pulp density and 600 rpm. XRD patterns of initial and secondary leach residues (belonging to before and after recovery process) for TLR and ILR are given in Figs. 8 and 9.

Once the XRD patterns of the secondary TLR and ILR attained at the optimum leaching parameters were compared with those of the initial residues for their constituents, it can be concluded that all of the zinc sulphate compound ($ZnSO_4 \cdot H_2O$) and most of the zinc ferrite ($ZnO \cdot Fe_2O_3$) as well as some of Zn_2SiO_4 were let into pregnant solution during acid leaching as seen in Figs. 8 and 9.

Although there are various compounds or phases present in the Turkish LR and Iranian LR as seen in their XRF and

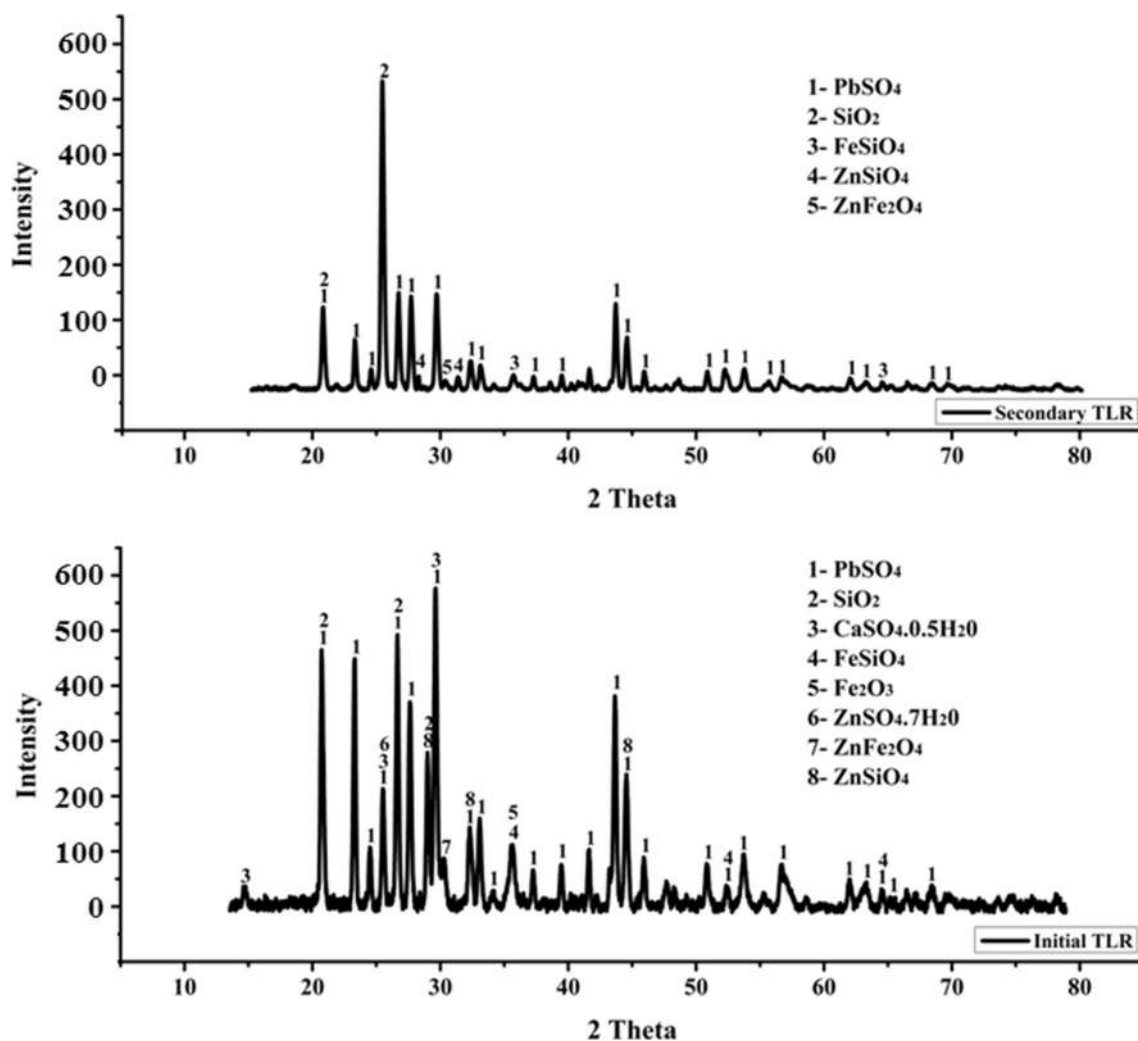


Fig. 8 XRD patterns of TLR before and after hot acid leaching



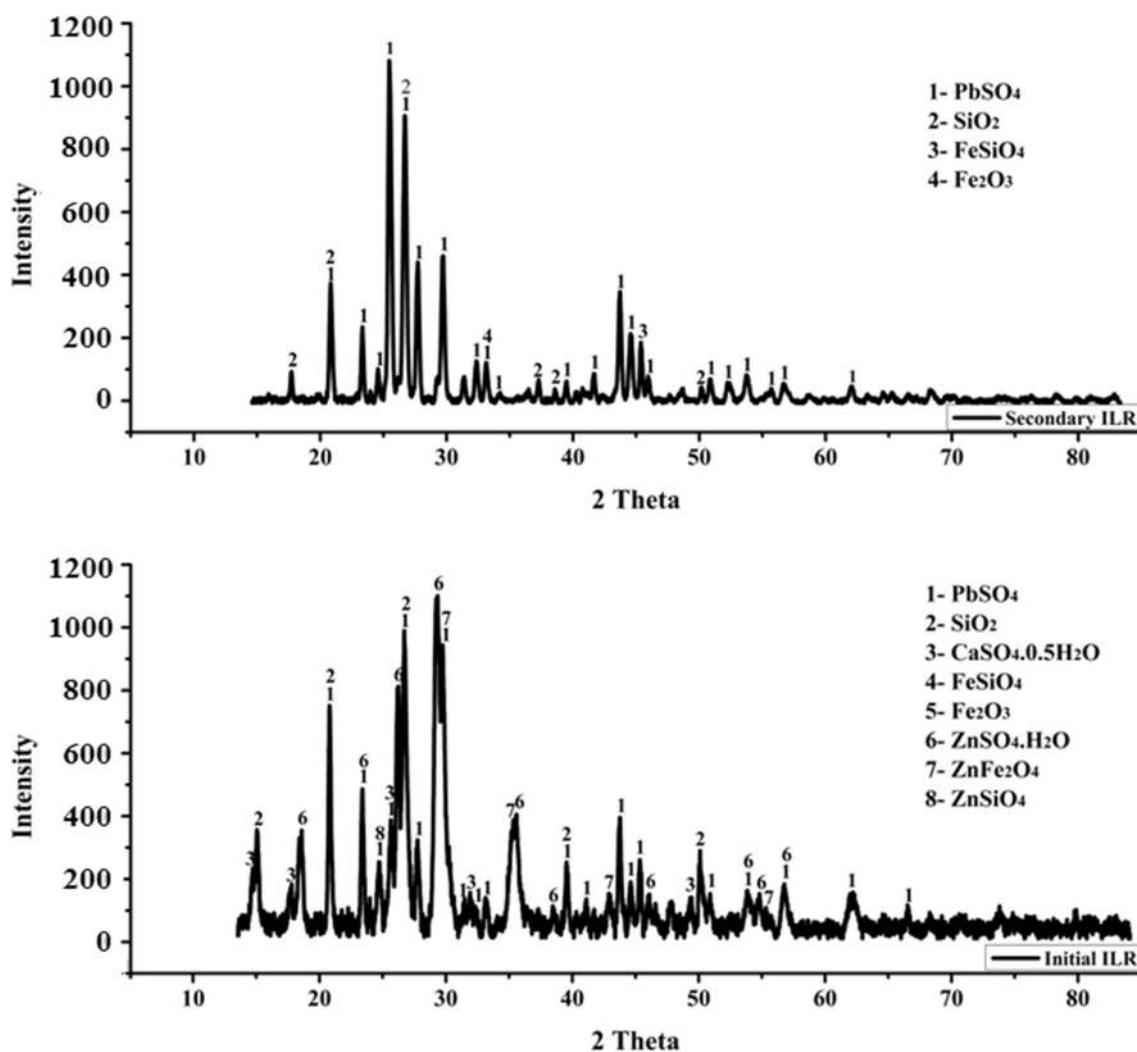


Fig. 9 XRD patterns of ILR before and after hot acid leaching

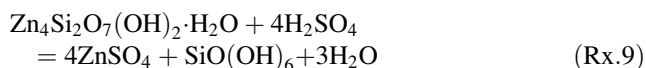
XRD analyses results, some of them could not be determined such as those including Al, Mg, K as well as Zn. From the XRD analysis, it could be determined that both LRs contain three types of zinc compounds, namely zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) which is soluble in the water, zinc ferrite (franklite, ZnFe_2O_4) which is fully soluble in the hot concentrate sulphuric acid and zinc silicate (willemite, Zn_2SiO_4) is soluble in hot sulphuric acid depending on the acid concentration. However, studies (Turan et al. 2004; Addemir et al. 1995) on Çinkur leach residue have showed that Zn could be present not only sulphate, ferrite and silicate, but also oxide and metallic form with different percentages.

In the study, to specify the amount of water-soluble zinc sulphate compound in the ILR and TLR, hot water leaching experiments were carried out at 95 °C, for 2 h and 1/10 S/L ratio. Under these conditions, the maximum Zn recoveries were determined as 27.3 and 15.7% for ILR and TLR, respectively. Taking into account Zn amount in both

residues, these percentages correspond to 21.1 and 8.4% $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in the ILR and TLR, respectively. Considering that $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ is reasonably soluble even in the water at room temperature, this large difference may result from that TLR was relatively older as compared to ILR which was more recently produced and exposed to less rainy weather.

As mentioned before, zinc ferrite (ZnFe_2O_4) and zinc oxide (ZnO) are slightly soluble in lower temperature but fully soluble in hot concentrated sulphuric acid according to Rxs. 7 and 8. On the other hand, according to (Souza et al. 2007), zinc silicate compounds (willemite— Zn_2SiO_4 and hemi-morphite— $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$) are generally found in non-sulphidic Zn ores (especially in Zn-carbonate ores) and also formed after the treatment of conventional RLE (roasting–leaching–electrolysis) process. During hot acid leaching, following reactions take place between the zinc silicate compounds and sulphuric acid;





Studies on the leaching of a zinc silicate ore containing willemite and hemi-morphite showed that zinc extraction could be obtained up to 95% after the trial at elevated temperature (70 °C) with 10% sulphuric acid solution (~1.9 M) for 3 h. They also stated that as acid concentration decreased from 10 to 5%, zinc extraction fell down from 95 to lower than 45% (Abdel-Ael 2000, Souza et al. 2007).

Although willemite (Zn_2SiO_4) as one of the main zinc-containing phase apart from franklinite ($\text{ZnO} \cdot \text{Fe}_2\text{O}_3$) and zinc sulphate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) is present in both of TLR and ILR, hemi-morphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$) is not detected as a constituent from XRD patterns of the residues.

In the acid leaching results, the maximum zinc recoveries for ILR and TLR were achieved as 96.7 and 81.2%, respectively. Considering that Zn-containing compounds other than zinc sulphate are insoluble in water, it can be inferred that $96.7 - 29.3 = 67.4\%$ Zn recovery for ILR and $81.2 - 8.6 = 72.6\%$ Zn recovery for TLR resulted from ZnFe_2O_4 , Zn_2SiO_4 and other possible forms of zinc (oxide or metallic). According to these results, consumed sulphuric acid can be calculated by means of zinc compounds (ZnO , Zn_2SiO_4 and ZnFe_2O_4 form) in the each leach residue because they consume sulphuric acid during the hot acid leaching process according to possible main acidic reactions (Rxs. 7, 8, 10). However, free acid level of the solution could not be calculated due to the fact that amount of the Zn-containing compounds is unknown exactly.

According to some researchers (Addemir et al. 1995), several acid-insoluble zinc compounds such as complex zinc oxides could be present in initial zinc plant leach residues although it was not obviously determined from XRD patterns of them. In addition, some parts of the soluble zinc compounds engaged or trapped within some insoluble phases or PbSO_4 . These problems can lead to the limitation of zinc recovery, especially in TLR, which can be overcome by working with finer milled samples.

As seen from the XRD patterns (Figs. 8, 9), almost all zinc structures disappeared after hot leaching experiments apart from a minor phase of zinc silicate which was observed in the XRD patterns of secondary leach residues due to its limited solubility in the sulphuric acid. Moreover, PbSO_4 peaks in the XRD patterns have become more apparent due to the decrease in residue weight and its insolubility in acidic media. Hence, secondary leach residues are appropriate to recover other base metals,

especially for Pb, after acid leaching experiments for both leach residues. The undissolved residues of the selected hot acid leaching trials for ILR and TLR were analysed for its lead, zinc and iron contents. Considering that around 1/3 of the residues in mass were extracted into pregnant solution, the chemical analysis results for TLR and ILR were found to be 32.1% Pb, 5.1% Zn, 8.0% Fe and 12.9% Pb, 1.3% Zn, 2.4% Fe, respectively.

After recovering zinc in considerable amount by hot sulphuric acid leaching, various agents (NaCl , Na_2CO_3 , NaOH , CaCl_2 , etc.) for the extraction of lead can be applied on the secondary leach residue by taking temperature, time and pulp density into account. Thus, to treat the PbSO_4 -bearing secondary residue efforts were spent on chemical conversion of PbSO_4 into metallurgical treatable compounds like PbCl_2 , PbCO_3 , $\text{Pb}(\text{OH})_2$ (Rusen et al. 2008; Raghavan et al. 1998; Lin 2000; Farahmand et al. 2009). For example, after lead is collected to the pregnant solution by NaCl leaching, cementation of lead from the solution can be performed with aluminium, zinc or iron. Furthermore, after hot acid leaching for zinc recovery, secondary leach residue can be treated with sodium sulphide (Na_2S) solution to convert PbSO_4 into PbS . After floatation of PbS , lead can be obtained by pyrometallurgical treatment of PbS concentrate like Ausmelt and Kivcet.

At the end of this study, it can be concluded that TLR and ILR can be evaluated by applying hot acid leaching with different acid concentrations and leaching times. The simplified schematic representation of proposed process is given in Fig. 10. By this way, more than 95% Zn can be recovered from ILR and over 80% Zn can be obtained from TLR. After the leaching step, Fe removal unit can be installed to clean the pregnant solution by using

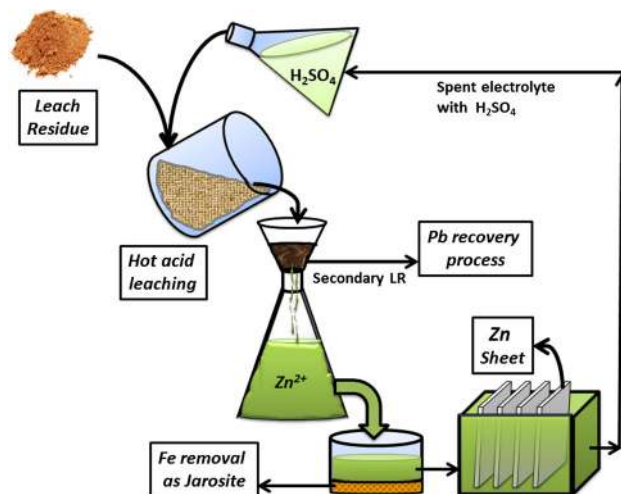


Fig. 10 The simplified schematic representation of proposed process

precipitation method. Hence, to obtain electrolytic zinc most of the zinc content of the residues could be sent to electrowinning step which already exists at Çinkur plant. On the other hand, secondary leach residue including more than 30% Pb for TLR could be treated for lead recovery by converting to suitable forms and then used at rotary kiln furnace after being more concentrated by floatation.

Conclusion

In this study, the leaching behaviour and comparison of leaching efficiency of two different Çinkur leach residues in hot sulphuric acid were studied. After chemical, mineralogical and thermal characterization of the residue, it was specified that considerable amount of zinc remained in the leach residues after Waelz processing—dilute acid leaching and electrowinning route in Çinkur. Besides zinc forms ($ZnFe_2O_4$, $ZnSO_4 \cdot 7H_2O$ and $ZnSiO_4$), $PbSO_4$ phase was detected as the major component by XRD examination.

In acid leaching, it was observed that zinc recovery increased with increasing acid concentration and leaching time. Moreover, the leaching efficiency of ILR was higher in the whole range of the selected leaching parameters. On the other hand, although the higher acid concentration has remarkable effect on zinc recovery from TLR, there is not efficient increase in zinc recovery from ILR after 100 g/L acid concentration. Furthermore, while the short leaching time (0.5 h) was enough for the zinc recovery from ILR, the zinc recovery from TLR was increased after 4 h. To sum up, ILR can be treatable with lower acid consumption and duration in comparison with TLR. After the leaching experiments, the secondary leach residues became suitable in terms of chemical composition for recovering other base metals such as Pb and Cd. Consequently, recycling of these leach residues was very important, especially on environmental awareness and for economic point of view.

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