

*Received October 2, 2012; reviewed; accepted March 10, 2013*

## LEACHING OF ZINC FROM LOW GRADE OXIDE ORE USING ORGANIC ACID

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**Abstract:** The leaching of low grade zinc oxide mining tailings by organic acid as a leaching agent was investigated. Zinc was extracted successfully from sample by citric acid leaching. The effects of solid-to-liquid ratio, acid concentration, reaction time, temperature and ore particle size on the leaching efficiency were studied. The results obtained showed that particle sizes and reaction time had not any significant effect on the leaching recovery of zinc from smithsonite in the sizes range of 40-350  $\mu\text{m}$ . Under conditions: temperature of 80°C, reaction time of 60 min, citric acid concentration of 0.5 mol/L, and solid to liquid ratio of 1:10, 82% of zinc could be recovered.

**Keywords:** *leaching, zinc oxide ore, citric acid, smithsonite*

### Introduction

Zinc is one of the most important base metals in the galvanizing, cosmetic, die casting and manufacturing industries. Zinc is extracted mostly from zinc sulfide ores. Zinc sulfide ores especially sphalerite are suitable and useful sources for the production of zinc because they could easily be separated and concentrated by flotation from the gangue (Espiriari et al., 2006; Qing et al., 2010). In this respect, the increasing demand of zinc and zinc compounds, and therefore new sources of zinc such as low grade oxide ores have been considered. The leaching of low grade ore is attracted considerably in recent years. One of the most important sources of low grade ores in zinc mineral processing is zinc mining tailings. Smithsonite ( $\text{ZnCO}_3$ ), hydrozincite ( $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$ ), zincite ( $\text{ZnO}$ ), willemite ( $\text{ZnSiO}_4$ ), gahnite ( $\text{ZnAl}_2\text{O}_4$ ), descloizite ( $\text{PbZnVO}_4\text{OH}$ ), hardystonite ( $\text{Ca}_2\text{ZnSi}_2\text{O}_7$ ) and hemimorphite ( $\text{Zn}_2\text{SiO}_3 \cdot \text{H}_2\text{O}$ ), are mostly zinc oxide ores, an abundance of which include smithsonite and hemimorphite (Jones, 1987). Zinc oxide ores in Iran are abundant and are mainly found in the center and in northwest part of Iran (Espiriari et al., 2006). Both

hydrometallurgical and pyrometallurgical methods have been used for extraction of zinc from ore or residual (Chen et al., 2009). Recently there are some reports stating that zinc oxide ores can be treated by flotation (Onal et al., 2005; Ejtemaei and Irannajad, 2008; Irannajad et al., 2009; Ejtemaei et al., 2011) and by biohydrometallurgical methods (Meshkini et al., 2011b). Although the results obtained by these methods showed that the efficiency is comparable with usual methods the technology certainly needs further follow-up.

Many studies on leaching of zinc oxide ores by acid and basic solution have been published. In recent years the leaching of zinc ores containing oxidized minerals such as carbonates or silicates with sulfuric acid and its kinetics have been investigated. He et al. (2010) Cun-xiong et al. (2010) and Xu et al. (2010) focused on pressure leaching. The amount of zinc extraction in sulfuric acid solution is high in comparison with other methods and the concentration of silica and other unwanted elements are low. In these studies, the effects of temperature, concentration of sulfuric acid, ore particle size, air pressure, leaching time and solid to liquid ratio were investigated and optimum conditions were established. Espiari et al. (2006) studied the zinc dissolution kinetics of smithsonite and hemimorphite in the lead flotation tailings by sulfuric acid. Zhao and Stanforth (2000) produced zinc powder by use of the alkaline leaching process on smithsonite. They extracted over 85% of both Zn and Pb, and less than 10% of aluminum using 5 M NaOH solution as a leaching agent in which zinc, lead and aluminum come into solution as  $\text{Zn}(\text{OH})_4^{-2}$ ,  $\text{Pb}(\text{OH})_4^{-2}$ , and  $\text{Al}(\text{OH})_4^{-1}$ . Similarly to this study Chen et al. (2009) investigated the parameters affecting the process like ore particle size, temperature, leaching time, alkali concentration and solid to liquid ratio to leach refractory hemimorphite  $[\text{Zn}_4(\text{Si}_2\text{O}_7)(\text{OH})\cdot\text{H}_2\text{O}]$  zinc oxide ores with NaOH solution. The optimum conditions determined were: particle size of 65–76  $\mu\text{m}$ , 2 h leaching time at 85 °C in the presence of 5 mol/dm<sup>3</sup> sodium hydroxide and solid to liquid ratio of 1:10. The maximum zinc extraction in optimum conditions was reported to be 73% of zinc content of ore. Ju et al. (2005) studied the dissolution kinetics of smithsonite ore in ammonium chloride solution. The effect of stirring speed, ore particle size, reaction temperature, and concentration of ammonium chloride on zinc dissolution rate was investigated. The results showed that at the optimum leaching conditions about 91.2% of zinc could be recovered under conditions: ore particle size of 84–110  $\mu\text{m}$ ; reaction temperature of 90 °C, 240 min reaction time and ammonium chloride concentration 5 mol/dm<sup>3</sup>. In recent years the studies on zinc oxide leaching by organic acids were initiated. Hursit et al. (2009) studied the dissolution kinetics of smithsonite ore in aqueous gluconic acid solutions using the parameters such as temperature, acid concentration, ore particle size and stirring speed. On the other hand organic acids can be produced by microbial processing (Papagianni et al., 1999; Sankpal et al., 2001). There are many studies showing that zinc oxide sources were treated by organic acids produced by microorganism (Schinner and Burgstaller, 1989; Burgstaller et al., 1992; Castro et al., 2000; Meshkini et al., 2011b).

Moreover, there are few reports on leaching of zinc oxide ores with organic acid reagents. The aim of this work was to investigate the extraction of zinc from Iranian low grade zinc ore by hydrometallurgical techniques using organic acid as a leaching agent. The effect of important variable parameters such as solid to liquid ratio, acid concentration, reaction time, temperature and particle size on zinc leaching has been investigated.

## Materials and methods

The sample of the ore came from mining tailings of Angoran lead-zinc mine, Iran. X-ray diffraction analysis indicated that the mineralogical constituents were smithsonite, small amounts of other zinc minerals such as hemimorphite, gangue minerals of quartz and some clay minerals (Meshkini and Irannajad, 2011a). Results of XRF analysis are given in Table 1. Citric acid was purchased from Merck and used without further purification.

Table 1. Chemical analysis of the ore sample

Component	Wt%
ZnO	16.1
Al <sub>2</sub> O <sub>3</sub>	8.0
SiO <sub>2</sub>	21.2
CaO	21.3
Fe <sub>2</sub> O <sub>3</sub>	3.59
Impurities	5.37
L.O.I	24.44

Ore samples were crushed and sieved to size fractions of  $-400+300 \mu\text{m}$  ( $350 \mu\text{m}$ ),  $-300+180 \mu\text{m}$  ( $240 \mu\text{m}$ ),  $-180+88 \mu\text{m}$  ( $134 \mu\text{m}$ ),  $-88+44 \mu\text{m}$  ( $66 \mu\text{m}$ ) and  $-44+37 \mu\text{m}$  ( $40.5 \mu\text{m}$ ). The entire experiment was performed in a  $500 \text{ cm}^3$  round-bottomed flask with a condenser and was placed in a thermostatically controlled water bath to prevent evaporation loss. For each experiment  $100 \text{ cm}^3$  volume of citric acid was poured into the flask at a definite concentration and heated to the required temperature. Then the ore sample of required size fraction was added and agitated with the stirrer at 350 rpm. At the end of each experiment the solution was analyzed by Atomic Absorption Spectrometry (AAS) to determine the zinc content. Zinc recovery ( $R_{\text{Zn}}$ ) was calculated according to the following equation:

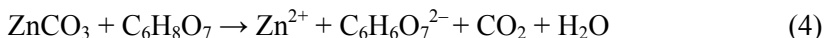
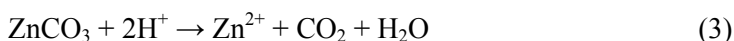
$$R_{\text{Zn}} = \frac{c \cdot v}{c_0} \cdot 100 \quad (1)$$

where,  $c$  ( $\text{mg}/\text{dm}^3$ ) is the metal concentration of leaching solution,  $v$  (l) the leaching solution volume and  $c_0$  (mg) is the amount of zinc in the ore sample.

X-ray diffraction (XRD) spectra and X-ray fluorescence analysis of the sample were obtained using a Philips X-ray diffractometer 1140 ( $\text{Cu}_\alpha=1.54 \text{ \AA}$ , 40 kV, 30 mA, calibrated with Si-standard) and a Philips X-ray fluorescence apparatus Xunique II (80 kV, 40 mA, calibrated with Si-standard), respectively. Determination of zinc concentration was done using a Unicam Atomic Absorption Spectrometry (AAS).

## Results and discussion

The reaction between citric acid and smithsonite ore can be presented as follows:



The sum of reactions (2) and (3) is reaction (4). Citric acid is a weak acid and it seems that the coordination of citrate with zinc ions causes the increase of smithsonite solubility.

### Effect of solid to liquid ratio

Figure 1 presents the results of leaching with different solid to liquid ratio that was studied in the range of 1:5 to 1:30. The leaching rate of the ore sample increased with the decreasing solid to liquid ratio. According to a definite concentration of initial citric acid, the increasing of solid to liquid ratio reduces the zinc recovery. It decreases from 67% at S/L= 1:30 to 20% at S/L= 1:5. When solid to liquid ratio was increased,

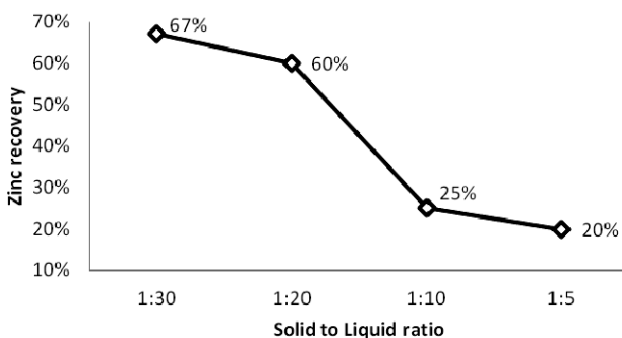


Fig. 1. Effect of solid to liquid ratio on zinc recovery at 25 °C, 0.5 M citric acid and 60 min reaction time

the amount of dissolved ore per unit liquid increase consequently the recovery decreases (Bayrak et al., 2010). Those are consistent with the results of Chen et al. (2002) and Espiari et al. (2006) in the treatment of the zinc oxide ore by alkaline and acidic leaching respectively.

### Effect of acid concentration

The effect of acid concentration was investigated for a leach time of 60 min at 25 °C for solid to liquid ratio of 1:10, 1:20 and 1:30. As observed in Fig. 2, by increasing acid concentration the zinc recovery is increased in both 1:20 and 1:30 solid to liquid ratios. In the 1:10 solid to liquid ratio experiments showed that the zinc recovery increases by increasing the acid concentration up to 0.5 M of citric acid concentration and further increase in the acid concentration causes the decrease of zinc recovery. These results are partly similar to the results obtained by Hursit et al. (2009) using the gluconic acid as leaching reagent. It seems that the increase in acid concentration in the leaching medium caused the acid saturation near the solid particles (Hursit et al., 2009). Conversely, this behaviour cannot be seen in alkaline or non-organic acid leaching of zinc oxides. For this reason the constant concentration value was fixed as 0.5 M in the experiments. Additionally, for economy reasons the solid to liquid ratio was maintained constant at 1:10.

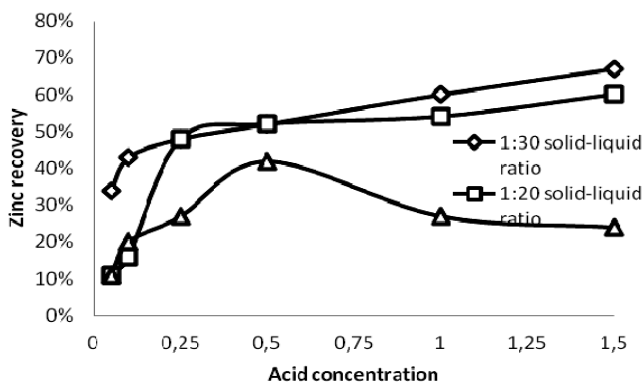


Fig. 2. Influence of acid concentration at various solid to liquid ratios on zinc recovery at 25 °C

### Effect of reaction time

The results obtained in leaching tests under different reaction times at temperature of 25 °C using 0.5 M citric acid and 1:10 solid-to-liquid ratio are presented in Fig. 3. The reaction time does not affect zinc recovery positively. These results are similar to the results of alkaline and acidic leaching of zinc oxide ore studied by Chen et al. (2002), He et al. (2010) and Xu et al. (2010), respectively.

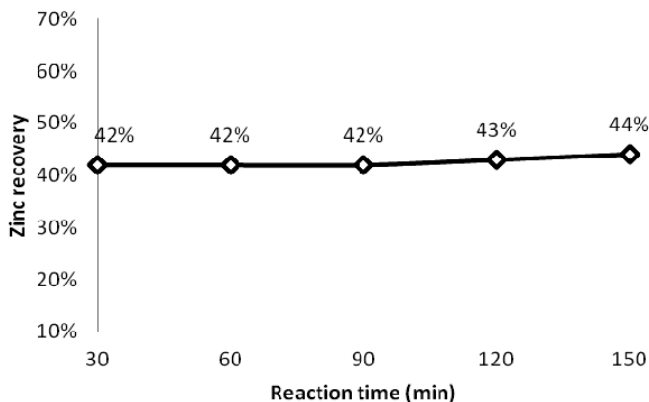


Fig. 3. Effect of reaction time on zinc recovery at 25 °C, 0.5 M citric acid and 1:10 solid-to-liquid ratio

### Effect of temperature

Four batch leach tests were performed to determine the optimum temperature of zinc extraction. The effect of temperature was investigated in the range of 25–80 °C for a reaction time of 60 min in 0.5 M citric acid and 1:10 solid-to-liquid ratio. As observed in Fig. 4, the zinc recovery increased as the temperature increased. This is similar to the previous results reported by Santos et al. (2010) investigating the leaching of a zinc silicate ore. He reported that increasing the temperature from 70 °C to 90 °C caused the increase in zinc extraction from 36 to 90%.

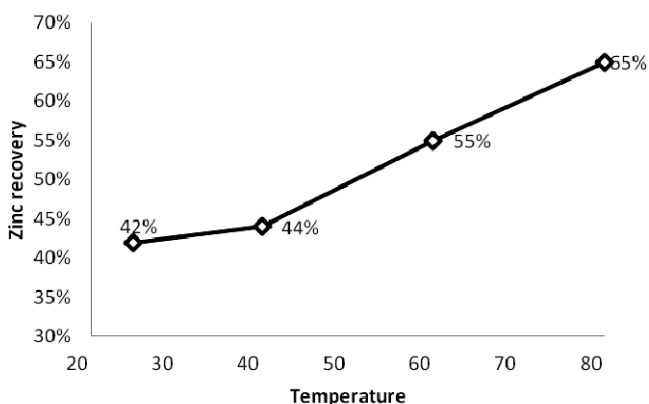


Fig. 4. Effect of temperature on zinc recovery at 0.5 M concentration of citric acid, 1:10 solid-to-liquid ratio and 60 min reaction time

### Effect of particle size

The experiments were performed with different particle size at 25 °C using 0.5 M citric acid and 1:10 solid-to-liquid ratio. Figure 5 shows that particle size had not a significant effect on zinc recovery. However the increase in particle size increases zinc recovery and the best results were obtained with particle size of 350  $\mu\text{m}$ . The result is similar to one obtained in the work by Chen et al. (2002) in which zinc was extracted by alkaline leaching. However other works (Santos et al., 2010; Hursit et al., 2009) showed that the increase of particle size caused the decrease in zinc recovery attributed to the decrease of the contact surface in the case of larger particle size.

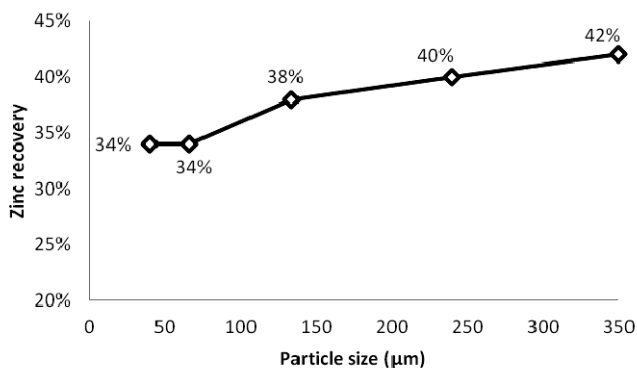


Fig. 5. Effect of particle size on zinc recovery at 25 °C, 0.5 M citric acid, 1:10 solid to liquid ratio and 60 min reaction time

### Final optimisation experiment

By optimizing the leaching parameters as summarized in Table 2 the final tests showed that it was possible to extract 82% of zinc content.

Table 2. The results of leaching under optimum process conditions at a solid-to-liquid ratio of 1:10

acid concentration (M)	reaction time (min)	Temperature (°C)	particle size (micron)	Recovery (%)
0.5	60	80	350	82

### Conclusions

This study demonstrates that zinc can be successfully recovered from mining tailings by citric acid leaching. Particle size and reaction time had an insignificant effect on the leaching recovery of zinc from smithsonite in the size range of 40–350  $\mu\text{m}$ . When the ore sample of 350  $\mu\text{m}$  size were leached for 60 min at 80° C in the presence of 0.5 mol/dm<sup>3</sup> citric acid and 1:10 solid-to-liquid ratio, more than 80% of zinc from the oxide ore can be extracted.

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