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Bioleaching of Zinc and Iron from Steel Plant Waste using *Acidithiobacillus Ferrooxidans*

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Abstract The bacterial leaching of zinc and iron from solid wastes at the Isdemir iron and steel plant has been investigated using *Acidithiobacillus ferrooxidans* as the bacterial agent. The effects of a range of operational parameters, including particle size, solids concentration and pH, on the efficiency of the bioleaching process were investigated. In each test, several variables were determined to assess the efficiency of leaching, including slurry pH and redox potential, temperature, bacteria population and concentrations of zinc and iron in solution. Experimental results demonstrated that pulp solids concentration, slurry pH and solids particle size were all important parameters in the bacterial leaching process. Maximum extraction was achieved at pH values around 1.3 and a solids concentration of 1% *w*/*v*, with 35% of the Zn content and 37% of the Fe being dissolved.

Keywords Iron ores · Tailings · Bacteria · Bioleaching · Recycling · Waste processing · *Acidithiobacillus ferrooxidans*

Introduction

The production of steel in integrated iron- and steel-making plants generates large quantities of solid waste materials, mainly blast furnace and steel furnace slags, electric arc furnace

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(EAF) dusts and various sludges [1, 2]. It has been reported that a typical plant produces over 400 kg of solid waste per tonne of steel output [3, 4].

This paper reports on a study into a sample of the 10–15 million tonnes of solid wastes accumulated by the Isdemir steel-making plant in Turkey. Initially, the waste solids from the plant (mostly produced as sludges) were dewatered and recycled (as an additional source of iron) into the sinter mix. However, since 2004, the Zn content of the waste has increased to over 1.6%, and it is no longer possible to recycle this material, since the quality of the steel is significantly reduced if the Zn content is higher than 0.03%. Consequently, the solid waste is currently dewatered and accumulated at a waste yard near the plant.

Dusts, scale and sludges produced by the steel industry can either be recycled back to the iron and steel process (blast furnace, basic oxygen furnace or electric arc furnace) or used externally as raw materials in other industries (known as industrial ecology). Concentrations of metals such as iron, zinc, chromium, nickel and molybdenum in these wastes can vary significantly, depending on the process from which the waste is generated, and these variations often limit the use and recycling of the material. In some cases, pre-treatment may be required before the waste can be recycled.

Zn ferrites are present in various solids such as electric arc furnace dusts or leaching residues from roasting. This compound is formed at temperatures ranging from 800 to 1,300°C in an oxidising atmosphere and there are two options for managing solid materials containing Zn ferrite-hydrometallurgical or pyrometallurgical processing. Currently, hydrometallurgical processes based on selective leaching do not offer total extraction of Zn in the ferrite form, whereas in pyrometallurgical processes zinc can be easily extracted, owing to the high temperature used [5, 6]. The resulting product is a mixture of oxides (mainly ZnO), which must then be treated by a hydrometallurgical route. Improvements in the efficiency of these processes may be possible by the addition of suitable bacteria to the leach solution, and this aspect is reported in the current study.

The use of microbial processes by the mineral industry (known as biohydrometallurgy) predates the understanding of the role of microorganisms in metal extraction, commonly referred to as bioleaching [7]. Traditionally, the removal of metals from wastes has been carried out predominantly by acid leaching at low pH (1.5–2.0), and techniques have recently been developed to effect the removal of heavy metals such as Pb, Cd, Cr and Ni contained in EAF dusts [8], although careful continuous control is often required.

An effective alternative to the acid-leaching system may be offered by microbial leaching. It is already known that some bacteria, particularly those belonging to the *Acidithiobacillus* genus, can markedly enhance the leaching of metal sulphides. *Acidithiobacillus ferrooxidans* is an acidophilic bacterium which can either grow on reduced sulphur compounds or on ferrous species. It utilises energy obtained from the oxidation of sulphide minerals (e.g. FeS_2, $CuFeS_2$) as well as ferrous iron dissolved in a liquid medium. Fe^{2+} is oxidised to Fe^{3+} in acidic medium by means of *A. ferrooxidans*, while its chemical oxidation by means of oxygen is extremely low. The bioleaching process has been widely reported [9–21] and the technique has been applied to the extraction of metals from various ores and concentrates [22].

The oxidation of Fe^{2+} by *A. ferrooxidans* is responsible for the large increase in the slurry redox potential. Precipitation of Fe^{3+} as sulphate, iron hydroxide or jarosite may explain the sludge acidification. According to Wong and Smith [23], the reaction mechanisms can be described as follows:

$$FeSO_4 + 2H_2SO_4 + O_2 \xrightarrow{A.\ ferroxidans} 2Fe_2(SO_4)_3 + 2H_2O \qquad (1)$$

$$Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4 \tag{2}$$

$$3Fe_2(SO_4)_3 + 12H_2O \rightarrow 2HFe_3(SO_4)_2(OH)_6 + 5H_2SO_4 \tag{3}$$

The equilibrium of reactions (2) and (3) is shifted to the right by precipitation of Fe^{3+} compounds and this is responsible for the sulphuric acid production utilised in the metal-leaching process. The aim of this current study was to evaluate the application of this bioleaching technique to recover Zn and Fe from the Isdemir steel-making waste, thereby making it suitable for recycling again.

Materials and Methods

Materials

A solid waste sample of EAF steel-making dust from the ısdemir steel-making plant in Iskenderun-Hatay, Turkey, was used in this study. Table 1 shows the chemical and mineralogical composition of the sample. The sample was analyzed by X-ray diffraction (XRD) using a Philips X Pert SW-binary diffractometer with CuKα radiation (40 kV, 50 mA), equipped with automatic divergence slit, sample spinner and a graphite secondary monochromator. XRD analysis indicated that magnetite (Fe_3O_4), calcite ($CaCO_3$) and hematite (Fe_2O_3) were the dominant phases present. Elemental analysis of the sample by a wet chemical method involving hydrofluoric acid digestion and measurement by atomic absorption spectrophotometry (AAS; Perkin Elmer, Model 3100) indicated that the major constituent of the sample was Fe. The particle size distribution of the sample was measured

Table 1 Chemical and mineralogical composition of waste material from the Isdemir plant.

Component	Weight %	Mineralogical composition
Zn	1.23	Magnetite (Fe_3O_4)
Fe	54.73	Calcite ($CaCO_3$)
Cu	0.04	Hematite (Fe_2O_3)
Cr	0.03	
Ni	0.04	
SiO_2	0.47	
Al_2O_3	0.28	
TiO_2	0.02	
Cr_2O_3	0.06	
CaO	7.32	
MnO	2.98	
MgO	2.07	
K_2O	0.41	
Na_2O	0.56	
P_2O_5	0.10	
V_2O_5	0.06	
SO_3	0.39	
SrO	0.02	
PbO	0.17	

by the laser radiation scattering on a Laser Particle Sizer (Malvern Mastersizer 2000). The mean particle diameter, d_m, was calculated from granulometric data. Several sub-samples of differing particle size (d_{90}=0.063 mm, d_{90}=0.045 mm and d_{90}=0.038 mm) were prepared from the main sample by dry grinding in a ceramic ball mill, and these were used to study the effects of particle size on various operational parameters.

A strain of mesophilic iron oxidizing bacterium (*A. ferrooxidans*, DSM 583) provided by Deutsche Sammlung von Mikroorganismen und Zellkulturen (DSMZ) was used throughout the investigations. *A. ferrooxidans* is a gram-negative bacterium, characterised by non-sporulating rods, 0.5–0.6 µm wide and 1.0–2.0 µm long with rounded ends, and occurring singly or in pairs, or rarely in short chains. The bacteria are also known to be motile by means of a single polar flagellum [24]. All of these characteristics were observed during the isolation of the strain used. The composition of the nutrient growth medium (9K) and maintenance of cells was 33.4 g/L $FeSO_4{\cdot}7H_2O$, 0.4 g/L $(NH_4)_2SO_4$, 0.4 g/L $MgSO_4{\cdot}7H_2O$ and 0.4 g/L K_2HPO_4 [25, 26].

Chemical Leaching Experimental Procedure

Preliminary chemical leaching tests were undertaken in order to evaluate the effectiveness of sulphuric acid and to compare the effectiveness of bioleaching of the Isdemir steel-making waste. A 250-mL flask was taken. Three different concentrations—5%, 10% and 15% (*w*/*v*)—of sulphuric acid were shaken with 10% (*w*/*v*) of solids for 10 h. Liquid samples were taken at set intervals up to 10 h, filtered and analyzed for dissolved Zn and Fe by AAS. The rate of agitation (120 rpm) was kept constant for all the experiments. A clock glass was fitted to the flask to prevent evaporation.

Bioleaching Experimental Procedure

The culture of *A. ferrooxidans* was incubated in a 500-mL Erlenmeyer flask containing 200 mL of the medium and 10% (*v*/*v*) inoculum on a rotary shaker at 150 rpm at a constant temperature of 30±2°C. The initial pH of the culture was adjusted to 1.5 using 0.5 M H_2SO_4. The cells were harvested towards the end of the logarithmic phase by centrifugation at 15,000 rpm for 10 min at 4°C. The cells were then washed with dilute sulphuric acid at pH 1.5 and were finally re-suspended in the same solution. The stock and pre-inoculum culture were maintained in the same medium under similar conditions. The cultures used were sub-cultured at 2-week intervals through several transfers in solid waste medium as the energy source of bacterial strain in the bioleaching experiments to adapt the bacteria to the experimental conditions. Initial bacterial populations in inoculum were counted at about 2×10^7 cells/mL using a Petroff–Hausser counting chamber.

Bioleaching experiments were carried out in 250-mL Erlenmeyer flasks. The pH of the slurry was initially basic and 5% *w*/*v* H_2SO_4 was added to lower the pH to create a favourable environment for the microbial strain. Masses of 1–5 g of the ground solid waste sample (corresponding to 1–5% *w*/*v* solid concentration) was added. The flasks were inoculated under aseptic conditions with a 10 mL aliquot of the selected culture to produce a final slurry volume of approximately 100 mL. To facilitate mixing of the contents and transfer of O_2 and CO_2, the flasks were agitated on an orbital shaker controlled at a growth temperature of 30±2°C. Each flask was sampled daily by removing a 1 mL aliquot of the leach solution, which was then used for analysis of Zn and Fe by atomic absorption spectrophotometry and for monitoring pH and redox potential. The water lost due to evaporation was compensated for by adding distilled water and the reduced volumes due to sampling were made up with the same volume of ferrous-free 9K nutrient matrix at pH 2.0 to maintain a constant pulp density in the suspension. In all experiments, chemical grade reagents and distilled water were used, except in the chemical analysis where double distilled water was used. All experiments were conducted at least in duplicate and results were reproducible to within 5%.

Only *A. ferrooxidans* in pure culture was used in this study, since a mixed culture of microorganisms did not give better results in preliminary experiments.

Kinetic Study

For the bioleach treatment, a kinetic model [27, 28] was employed, the equations of which are:

$$-d\,C_{\mathrm{Fe}}/\mathrm{d}t = k(C_{\mathrm{Fe-max}} - C_{\mathrm{Fe}}) \tag{4}$$

$$-d\,C_{\mathrm{Zn}}/\mathrm{d}t = k(C_{\mathrm{Zn-max}} - C_{\mathrm{Zn}}) \tag{5}$$

where C_{Fe} and C_{Zn} are dissolved iron and zinc concentrations; k is the kinetic coefficient; $C_{\mathrm{Fe\text{-}max}}$ and $\mathrm{C}_{\mathrm{Zn\text{-}max}}$ are the maximum attainable iron and zinc concentrations with values limited by the bioleaching capacity or by available iron in the solid; t is the leaching time.

By integrating Eqs. 4 and 5 between the initial moment (t=0, C_{Fe}=0) and the conditions corresponding to a time t, Eqs. 6 and 7 were obtained, from which the value of the kinetic constant can be deduced:

$$\ln\left[C_{\mathrm{Fe-max}}/C_{\mathrm{Fe-max}} - C_{\mathrm{Fe}}\right] = kt \tag{6}$$

$$\ln\left[C_{\mathrm{Zn-max}}/C_{\mathrm{Zn-max}} - C_{\mathrm{Zn}}\right] = kt \tag{7}$$

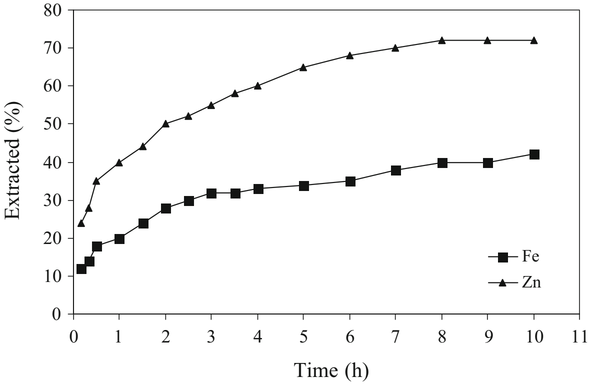


Fig. 1 Influence of leach time on Zn and Fe extraction (d_{90}=0.045 mm, 10% *w*/*v* H_2SO_4, 10% *w*/*v* solids, reaction temperature 60°C, 150 rpm)

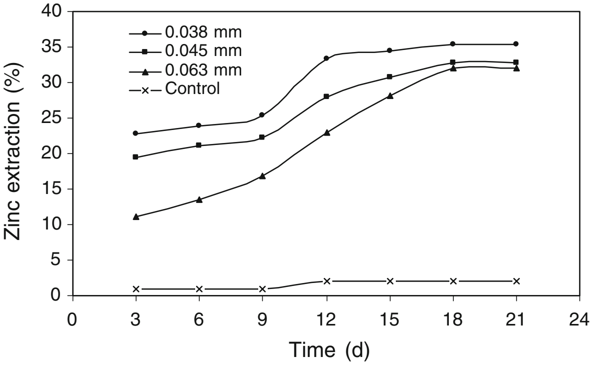


Fig. 2 Influence of particle size on Zn extraction with varying leach time (1% *w*/*v* solids, reaction temperature 30°C, pH 2, 150 rpm)

Results and Discussion

Chemical Leaching

Figure 1 shows the time dependency of Zn and Fe extraction using 10% (*w*/*v*) sulphuric acid and solids with a particle size of 0.045 mm. As expected, both Zn and Fe dissolution increased with time, with Zn being significantly higher than Fe, especially at longer leach times, reaching over 70%. This is due to Zn solubilisation being more dependent on the presence of H^+ ions, so an acidic environment with lower pH dissolves more Zn. In contrast, the maximum Fe extraction was much lower at around 40%. The concentrations of Fe^{2+} and Fe^{3+} were 160 mg/L and 1,790 mg/L, respectively, in solution after 10 h leaching.

Bioleaching

Comparison of Adapted and Non-Adapted Bacteria

Experiments with adapted and non-adapted bacteria were carried out in a ferrous-free 9K nutrient medium. In the presence of non-adapted bacteria, the extraction of Zn and Fe was less than 6% and 2% after 21 days leaching, respectively. However, in the presence of bacteria, rates for both Zn (25%) and Fe (16%) increased markedly. Therefore, in all subsequent bioleaching experiments, adapted bacteria were used. The percent extraction of

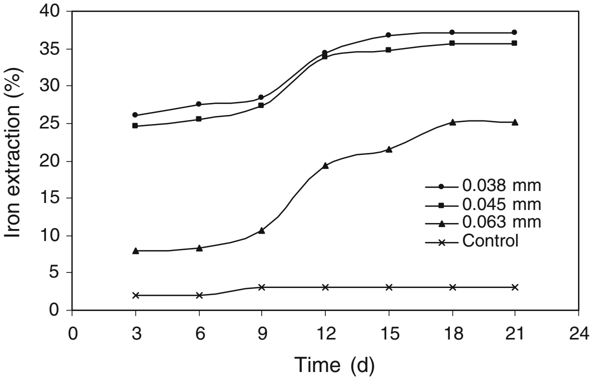
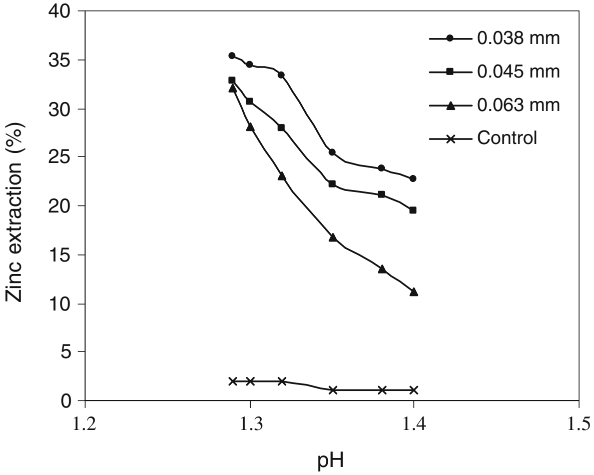


Fig. 3 Influence of particle size on Fe extraction with varying leach time (1% *w*/*v* solids, reaction temperature 30°C, pH 2, 150 rpm)

Fig. 4 Influence of slurry pH on Zn extraction after 21 days leaching (1% *w*/*v* solids, reaction temperature 30°C, 150 rpm)



Zn and Fe did not show significant differences when the inoculation cell population reached 2×10^7 cells mL^{-1}. Therefore, the cell population was fixed at this value in suspensions.

Effects of Particle Size and Solids Concentration

The effects of particle size were studied using three different size fractions of material (d_{90}=0.063 mm, d_{90}=0.045 mm and d_{90}=0.038 mm) at a slurry pH of 2.0. Results in Fig. 2 show that particle size was significant in terms of percent Zn extraction during the early stages of leaching, but much less so when the leach time reached 18–21 days, such that there was little difference over the particle size range studied. In the case of Fe (Fig. 3), extraction rates for 0.038- and 0.045-mm materials were very similar, but those for the 0.063-mm material were significantly lower, again, all reaching a maximum after 18–21 days leaching.

The percent extraction for both metals increased below approximately pH 1.4, reaching 35% for Zn and 37% for Fe at pH 1.3 with a particle size of 0.038 mm, as indicated in

Fig. 5 Influence of slurry pH on Fe extraction after 21 days leaching (1% *w*/*v* solids, reaction temperature 30°C, 150 rpm)

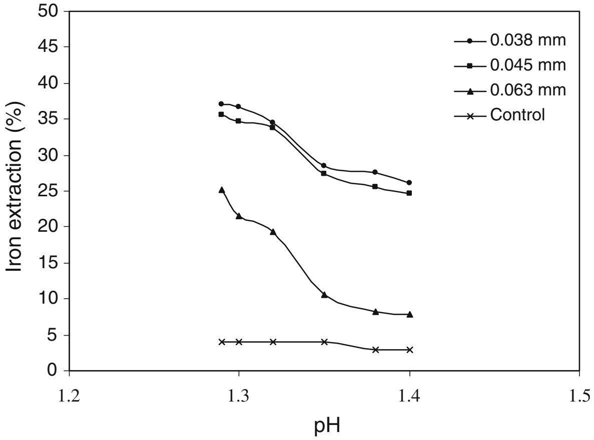
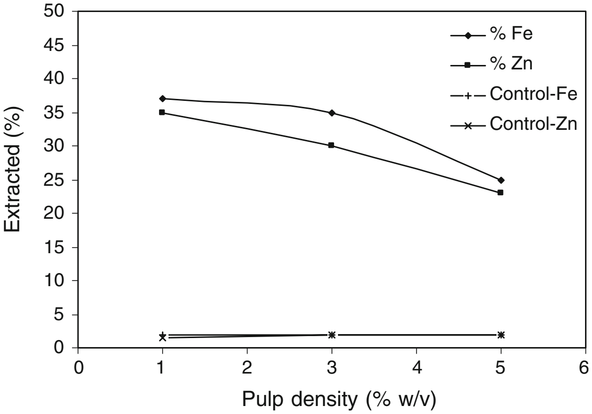


Fig. 6 Influence of solids concentration on Zn and Fe extraction (d_{90}=0.045 mm, reaction temperature 30°C, pH 2, 150 rpm)



Figs. 4 (for Zn) and 5 (for Fe). This confirms that the biological activity is dependent on pH, while measured redox potential showed an increasing trend during the process, thus indicating that the production of sulphuric acid due to bacterial activity is responsible for the progressive metal solubilisation.

Woznick and Huang [29] have indicated that the efficiency of metal dissolution is strongly influenced by the solids concentration of the leach slurry. Figure 6 demonstrates this trend, in which an increase in pulp density results in a decrease in percent extraction for both Zn and Fe, with maximum extraction occurring at just 1% *w*/*v* solids concentration. A more marked decrease in the percent extraction with increasing solids concentration was observed for Zn at values higher than 3% (*w*/*v*). It may be that increasing the pulp density created a condition with higher toxicity and shear stress and decreased the mass transfer that could result in slowing down the percent extraction of Zn.

Kinetic Study

The kinetic model (Eqs. 4 and 5) was used to describe the leaching of iron and zinc for chemical leaching and bioleaching. Figure 7 shows the fitting of the results from experiments at the optimum chemical leaching conditions (d_{90}=0.045 mm, 10% *w*/*v* H_2SO_4, 10% *w*/*v* solids, reaction temperature 60°C, pH 2.0, 150 rpm). The values for

Fig. 7 Kinetic modeling to Eqs. 4 and 5) of chemical leaching (d_{90}=0.045 mm, 10% *w*/*v* H_2SO_4, 10% *w*/*v* solids, reaction temperature 60°C, 150 rpm)

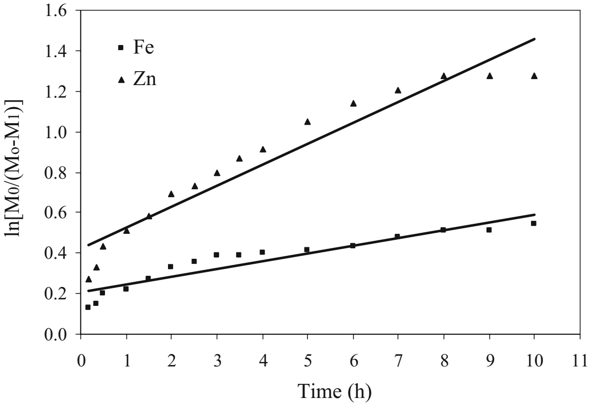
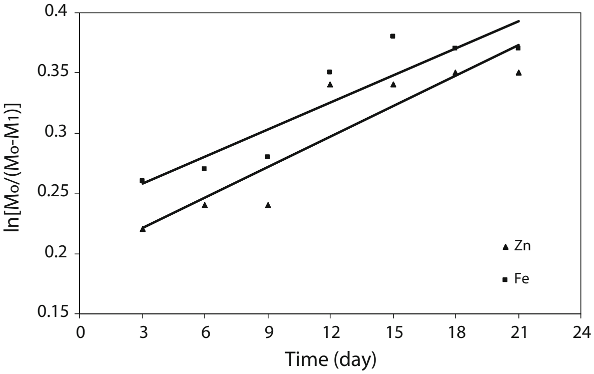


Fig. 8 Kinetic modeling to Eqs. 4 and 5 of bioleaching (d_{90}=0.045 mm, 1% *w*/*v* solids, reaction temperature 30°C, pH 2, 150 rpm)



coefficient (k) and correlation parameter (R^2) were determined as 0.038 h^{-1} and 0.8823 for iron, and 0.104 h^{-1} and 0.924 for zinc, respectively.

From the results of bioleaching experiments at optimum conditions (d_{90}=0.045 mm, 1% *w*/*v* solids, reaction temperature 30°C, pH 2.0, 150 rpm), the kinetics of the process with *A. ferrooxidans* were studied. The values for coefficient (k) and correlation parameters (R^2) were determined as 0.0075 day^{-1} and 0.835 for iron, and 0.0085 day^{-1} and 0.828 for zinc, respectively (Fig. 8).

Conclusions

The extraction of Zn and Fe from iron- and steel-making plant waste using a bioleaching technique involving *A. ferrooxidans* has been investigated. Experimental results demonstrated that pulp solids concentration, slurry pH and solids particle size were all important parameters in the bacterial leach process. Maximum extraction was achieved at pH values around 1.3 and a solids concentration of 1% *w*/*v*, with 35% of the Zn content and 37% of the Fe being dissolved.

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