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EFFECT OF ULTRASOUND ON ACIDIFIED BRINE LEACHING OF DOUBLE-KILN TREATED EAF DUST

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ABSTRACT

The U.S. steel industry produces approximately 500,000 tons/year of electric arc furnace (EAF) dust, which is classified as a hazardous waste. Increasing disposal costs of these dusts have encouraged studies to investigate treatment processes to render the material non-hazardous, and to possibly recover metal values. This research project was designed to examine the hydrometallurgical recovery of zinc from EAF dusts that have been treated by a double-kiln fuming process. The test work consisted essentially of acidified brine leaching of the pelletized calcine to determine the influence of traditional conditions, such as acid concentration, temperature and agitation, plus the application of ultrasound, on the zinc dissolution efficiency and selectivity.

Preliminary leaching tests using acidified calcium chloride indicated that selective leaching of zinc over iron could be attained if ultrasound was employed. The effect of air and nitrogen on the leaching process was investigated and it was established that selective leaching with ultrasound was not dependent upon external agitation or on the availability of oxygen. Without ultrasound, zinc dissolution was enhanced by the presence of oxygen, while iron dissolution was greatly retarded by the absence of oxygen. The role of surface area was examined by pellet grinding and it was demonstrated that selectivity was strongly time dependent and that zinc recovery and iron rejection were enhanced at finer particle sizes.

The results of the test work permitted possible mechanisms to be established for the acidified brine leaching process, and it is apparent from the results that ultrasound leaching can significantly improve the selective leaching of zinc from double-kiln treated EAF calcine.

Keywords

EAF dust; brine leaching; ultrasound; zinc

INTRODUCTION

The steelmaking process generates waste materials, which pose serious environmental and resource recovery problems [1]. Electric arc furnaces (EAFs) account for about 40% of the U.S. steel production, and produce some 500,000 tons of dust a year bearing up to 20% zinc [2]. Due to increasing environmental, space and economic restrictions, new handling and treatment methods for EAF dust will be needed, so that its metal content can be better utilized, and disposal problems lessened [1]. Recycling of EAF dust poses a number of problems due to (a) the build up of harmful volatile elements, such as zinc, lead and chloride, in the steelmaking process [3,4]; (b) difficulty with handling and assimilating the fine EAF dust particles ($-10\mu\text{m}$) into the process [1,5,6,7,8]; and (c) the variable chemical composition of the EAF dust [8]. It has been suggested that EAF dust should be treated to eliminate the troublesome elements, and to transform it into a stable product with a chemical composition suitable for either recycling or disposal [2,3,9].

Accordingly, a series of technologies has been tested with these purposes in mind [3,8]. Pyrometallurgical treatments [2,8,9,10] are attractive, but require high capital costs, while hydrometallurgical alternatives [3,4,11] are in a development stage. None of the above processes are widely accepted, but the trend indicates that EAF dust will probably be treated pyrometallurgically to produce condensed metallic zinc or zinc oxide fume, and a disposable or recyclable iron-rich by-product [3]. The impure zinc oxide could then be leached to produce a zinc electrolyte for zinc electrowinning.

A double-kiln pyrometallurgical process [12] has been developed by Horsehead Resource Development Co. Inc., in which a zinc oxide-rich calcine can be prepared. One of the purposes of this research is, therefore, to study possible hydrometallurgical alternatives to selectively separate zinc from calcine of this type, and to produce a solution capable of being assimilated into an electrowinning process.

The leaching of highly contaminated zinc oxides has not been extensively investigated, but it is generally accepted that, for furnace dusts and sludges, the major problems relate to recovery of zinc from ferrites and to the rejection of iron. To leach ferrites it is necessary to utilize high solvent concentrations at elevated temperatures. To accomplish iron rejection, it is considered that any iron taken into solution should be oxidized to the ferric state and allowed to precipitate at pH values of 2.8 or higher. Thus it is critical in leaching oxide dusts to ensure that oxidizing conditions are present to prevent iron contamination of the leach solutions. However it has been shown [13] that even under oxidizing conditions, the conversion of ferrous to ferric ions may not occur if insufficient gas/liquid/ solid contact is present in the leach reactor. It is therefore logical to consider the use of ultrasound to emphasize gas/liquid/solid contact to not only improve the dissolution of zinc, but also to retard that of iron from double-kiln treated EAF dusts.

The use of ultrasound to enhance chemical reactivity is becoming a common and widely applicable technique [14,15,16]. Redox reactions are specifically affected by ultrasound, due to improved contact by cavitation, which in turn produces localized high pressures and temperatures. Secondary flows, known as acoustic streaming, can disrupt solid layers on particle surfaces, or break liquid film diffusion layers. Some previous attempts to intensify reactions by means of ultrasound have met with success [14,17,18] pointing to its use in this study.

Leaching rate can often be increased by controlling the traditional conditions such as temperature, agitation, reagent type and concentration etc. [19,20]. Possible leachants include sulfuric, hydrochloric and fluorosilicic acids, but based on industry experience with materials similar to the double-kiln treated dusts, acidified brine was selected for the test work.

There are numerous models available to describe the leaching process, and of particular interest to this research, are the film diffusion control and chemical reaction control equations for a shrinking core model [21]. The enhancing potential of ultrasound lies in the fact that it can destroy or disrupt layers of products, transport components, activate intermediate steps of a chemical reaction [14,16] and accelerate the flow of liquid through a porous media [22]. Thus, this research will assess the acidified brine leaching of zinc from the double-kiln calcine as a function of several factors, including ultrasound. The effect of ultrasound on the controlling mechanism of the leaching will also be investigated.

EXPERIMENTAL

Material

A representative sample of a double-kiln calcine in the form of pellets was obtained from the Horsehead Resource Development Co. Inc. of Monaca, PA. In Horsehead's first kiln operation, zinc and other volatile elements and oxides are fumed from EAF dusts, leaving an iron-rich slag. In the second kiln treatment, very volatile compounds, such as chlorides,

are removed from the first kiln fume, and the remaining material is agglomerated as pellets. The chemical analysis and size distribution of the as-received pellet sample were determined, together with X-ray, scanning electron microscopy, and optical microscopy characterization data.

Equipment

The leaching tests were undertaken in glass reactors, which were immersed in temperature controlled ultrasound baths, and a single pellet was added to the leach reactor. Two ultrasound baths were utilized for the leaching operations, and these were a 14x14x14 cm single-generator Cole Parmer model 8850, and a 24x13.5x10 cm double-generator Buehler model Ultramet-II. The single-generator gave 265 w/m², and the double-generator 687 w/m², with a nominal constant frequency of 55 kHz.

Pellet Leaching Tests

The preliminary study consisted of leaching whole and ground pellets with acidified calcium chloride (Tests (a)1-4), with and without the application of ultrasound. The acidified chloride leachant was selected because previous leaching tests utilized this mix to treat other zinc-bearing waste materials, and promising results had been obtained. The use of brine as a leachant does permit increased chloride ion concentrations without excessive acidity. The experimental conditions for the preliminary tests are given in Table 1.

TABLE 1 Experimental conditions for preliminary leach tests

Pellet Wt. 1-3g : Leachant Volume 10-30ml						
Test	Acid	[Conc.] M	Temp. °C	Gas Flow (cc/s)		Pellet Size
				Air	Nitrogen	
1	Cl/HCl	1.2/1.8	40	0	0	Whole
2	Cl/HCl	1.2/1.8	40	20	0	Whole
3	Cl/HCl	1.2/1.8	50	0	20	Whole
4	Cl/HCl	1.2/1.8	40	0	0	-150/+75µm
5	Cl/HCl	1.2/1.8	40	0	0	-38µm

During the leach tests, solution samples were taken at time intervals of 15, 30, 60, 90 and 150 minutes, and then diluted and analyzed for zinc and iron by atomic absorption. To determine the role of oxygen, either air or nitrogen was bubbled into the leaching solution in several tests ((a)2,3) using a capillary. In addition, several calcine pellets were ground and screened to produce size fractions to permit the examination of the role of particle size on the leaching behavior of the calcine (test (a) 4).

To permit direct comparisons of the test results, a leaching selectivity index was used. This index contrasted the zinc recovery in the leach solution and iron rejection in the residue. The selectivity index (SI) was defined as:

$$SI_{Zn-Fe} = [(RS_{Zn}RP_{Fe})/(RP_{Zn}RS_{Fe})]^{0.5} \quad (1)$$

where R is the distribution of the metal in either the solution (S) or solid phase (P). Thus the parameter indicates the effectiveness of a separation of two components into two phases. As can be seen from its definition, higher values indicate better separation or leach selectivity.

RESULTS AND DISCUSSION

Characterization

The kiln calcine was determined to consist of porous, hard, spherical pellets, which were dark brown to black in color. The pellet size distribution was essentially $-10\text{mm} + 1\text{mm}$. The average composition of the pellets was found to be 54.4% Zn and 10.1% Fe, and this is in good agreement with the supplier's analysis, which also indicated 2.0% Pb, 0.2% Cd and 0.3% F. A mineralogical examination revealed that the pellets consisted essentially of zincite plates with intergrown magnetite and ferrite particles, and a fully detailed description is given elsewhere [21]. The maximum water soluble chloride was found to be 1.05% by weight by using a chloride ion probe. Ultrasound was found to increase the soluble chloride removal for both whole pellets and ground pellets with almost 100% removal being obtained.

Pellet Leaching with Acidified Chloride Solutions

1. Air without bubbling

Plots of zinc and iron recoveries versus leaching time, in the presence of air, and with and without ultrasound, are illustrated in Figure 1. It can be seen that the metal recoveries increase with time in all cases, and that the zinc and iron recovery curves for leaching without ultrasound are very similar, attaining final recoveries of approximately 35%. This similarity obviously reflects a very poor selectivity, as evidenced by a SI value of 0.9. However with ultrasound, the zinc recovery was enhanced to 72.2%, and the iron dissolution retarded to 6.4%. The application of ultrasound to the leach process actually increased the selectivity index from 0.9 to 6.2.

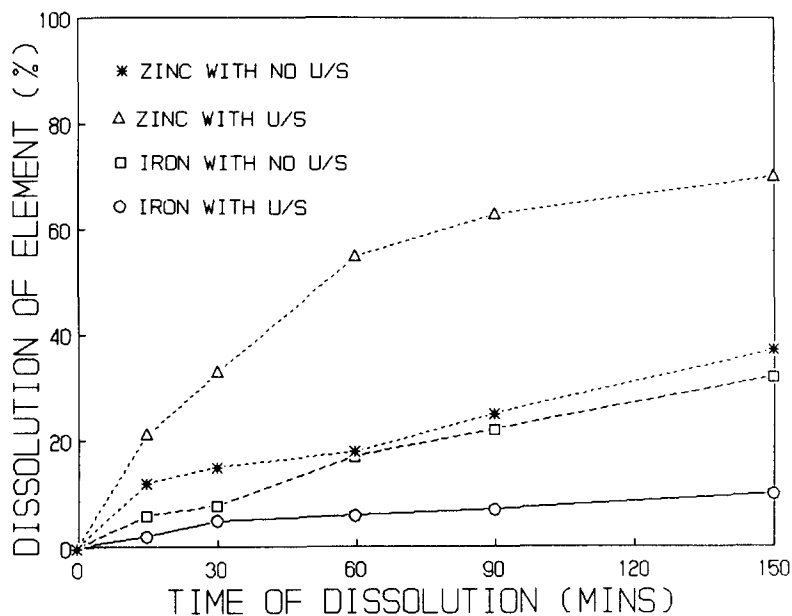


Fig.1 Acidified Chloride Leaching of Kiln Treated EAF Dust.
[1.8M HCl, 1.2M CaCl₂, 40°C]

This increase in zinc dissolution with ultrasound {36% to 72%} may have been induced by an increase in the reaction surface area, due to the ability of the ultrasound to drive the leachant into the pellet pores and to enhance film disruption. Zincite is known [23] to have a higher specific reaction rate than ferrite and magnetite, and hence it would be expected that zinc dissolution would occur preferentially. This was not the case without ultrasound, possibly because of the pellet geometry preventing effective contacting of the acid with the particles within the pellet. With ultrasound the weakly attached calcine particles near the surface of the pellets were possibly detached, creating more solid-liquid interface area. In

addition, microstreaming and cavitation could have destroyed or minimized the liquid film around the zincite particles, and raised the localized temperature, thus increasing the reaction rate. Possibly, a combination of superficial pellet disintegration, liquid penetration into the pellet, and microstreaming and erosion of the zincite particles, is the mechanism by which ultrasound increases the zinc recovery. This can be supported by the fact that the reaction of this calcine produced many loose black particles giving evidence of superficial breaking of the pellet.

One intriguing aspect of these results is the significant decrease in the iron dissolution resulting from the application of ultrasound. This is probably related to the enhancement of the zincite dissolution rate, which causes increased consumption of the available leachant, such that the slower reacting magnetite had less chance to dissolve. Alternatively it is possible that, for any iron taken into solution, the experimental conditions favored the formation of ferric ions and subsequent precipitation of ferric hydroxide, as the enhanced zincite dissolution caused an increase in pH. This possible mechanism requires an oxidizing environment to ensure the presence of the ferric ion, and if this did occur, it must have happened continuously in localized pockets within the pellet, as Figure 1 does not display evidence of iron dissolution and re-precipitation. As found previously [13], intimate mixing of gas, liquid and solids is necessary to permit the iron precipitation mechanism to occur and ultrasound would be instrumental in providing such conditions.

2. Air bubbling

To investigate the possible role of oxygen and agitation in the dissolution process, air was bubbled in to the leach vessel through a capillary. It is apparent from Figure 2 that the aerated, acidified chloride leach of the pellets without ultrasound is not selective, although both zinc and iron recoveries in solution increased compared with the first test. These increases in recovery are possibly due to increased mixing in the leach vessel resulting from the air bubbling. It should also be noted that the selectivity index did increase slightly to 1.4. In the presence of ultrasound, zinc was very selectively dissolved ($SI=14.8$), with a 90% zinc recovery compared to a 4% iron recovery. This selectivity enhancement resulting from the use of ultrasound can be explained in general terms in the same manner as outlined above, but it is apparent that the presence of excess air has further increased zinc dissolution and decreased iron dissolution. This would appear to indicate that general solution agitation, or oxygen, or both, play a role in the dissolution process.

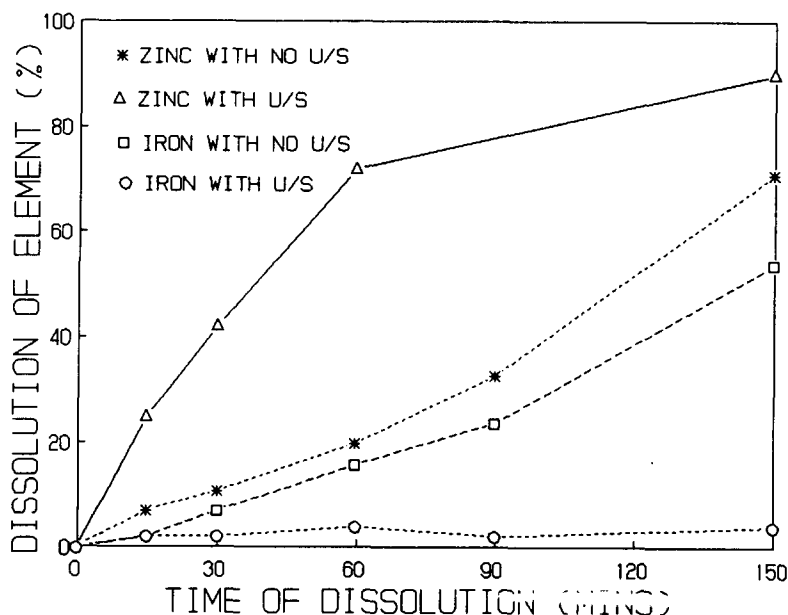


Fig.2 Acidified Chloride Leaching of Kiln Treated EAF Dust with Air Bubbling.
[1.8M HCl, 1.2M CaCl₂, 40°C]

3. Nitrogen bubbling

To separate the effect of oxygen and agitation, nitrogen was bubbled through the leach solution. It can be seen from Figure 3, that the dissolution of zinc and iron was inhibited, with the effect being far more significant for the leach without ultrasound and for iron. Both tests displayed a selective zinc dissolution, with selectivity indices of 3.6 without ultrasound, and 15.6 with ultrasound.

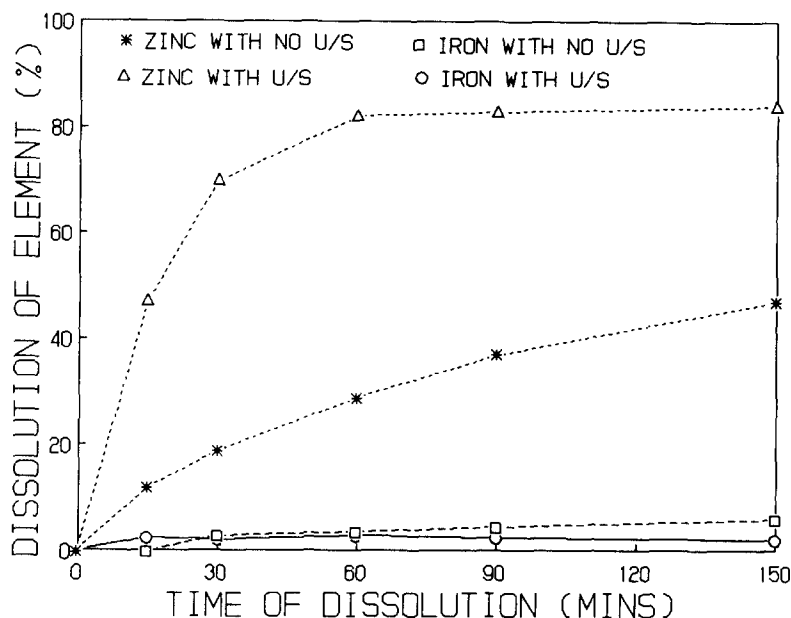


Fig.3 Acidified Chloride Leaching of Kiln Treated EAF Dust with Nitrogen Bubbling.
[1.8M HCl, 1.2M CaCl₂, 50°C]

Without ultrasound, although nitrogen bubbling produced a more selective leach than either of the two previous tests, both the zinc and iron recoveries were substantially below the values obtained with air bubbling. Thus it would appear that oxygen is necessary for the leaching of both zincite and magnetite, and that it is more critical for magnetite. The mechanism by which oxygen may influence the leaching of the zinc and iron oxides is not clear, but oxidation/reduction reactions are possibly involved, although the oxygen may play a role in modifying localized conditions within the pores of the pellets, away from the reacting surface layers.

With ultrasound there is little difference between the air bubbling and nitrogen bubbling results, which suggests that ultrasound produces the overriding effect. This would indicate that the presence of ultrasound is sufficient to enhance zinc dissolution, due to improved transport, film disruption and localized heating, and to retard iron dissolution, due to localized conditions either not favoring iron leaching or permitting ferric hydroxide precipitation. It appears that the zinc not recovered in the leach may well be in the form of ferrite.

4. Particle size

To investigate the role of the complex, porous nature of the pellets, leaching tests were carried out using ground pellets. The effect of particle size, or surface area available for reaction, on the recoveries of zinc and iron from two ground pellet fractions is illustrated in Figures 4 and 5. It is apparent that all the tests have a high zinc recovery and a low iron recovery, and that the shape of the iron dissolution curves has changed considerably.

Without ultrasound, the effect of increasing surface area is to increase zinc recovery, decrease iron dissolution, and hence increase the overall selectivity index (4.2 to 9.4). These

results may be explained simply in terms of surface available for reaction, but it should be noted that initially iron was taken into solution, and then precipitated. This resulted in a time dependant selectivity index, and hence it appears that the precipitation mechanism explaining low iron recoveries is valid. The effect of decreasing particle size was to enhance the initial iron recovery and to reduce the final iron content of the leach solution.

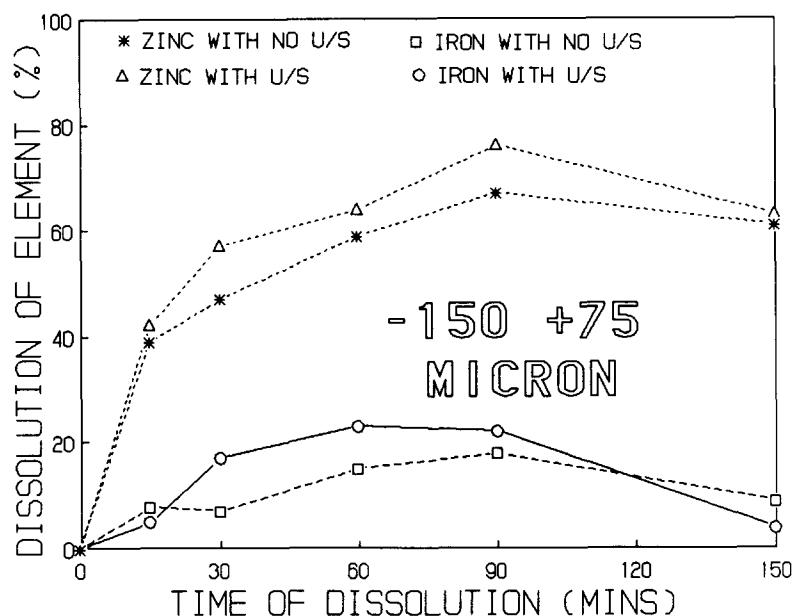


Fig.4 Acidified Chloride Leaching of Kiln Treated EAF Dust Fraction (-150+75micron) [1.8M HCl, 1.2M CaCl₂, 40°C]

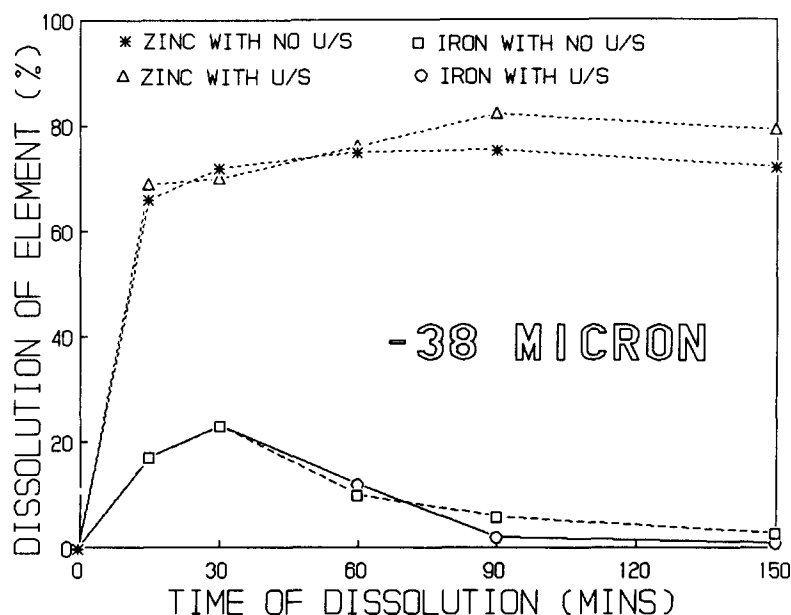


Fig.5 Acidified Chloride Leaching of Kiln Treated EAF Dust Fraction (-38 micron). [1.8M HCl, 1.2M CaCl₂, 40°C]

With ultrasound the major effect of increasing surface area is an increase in overall selectivity index (7.1 to 18.3), due mainly to a reduction in iron recovery in the leach solution. The 150 minute leach results for the finer fraction are better than any of the previous tests, but the selectivity index is obviously very time dependant, and it can be seen to increase rapidly towards the end of the leach period. This is possibly due to the

continuing dissolution of zinc consuming the acid and permitting the pH to rise and cause ferric hydroxide precipitation. The previous tests with whole pellets were slightly time dependant, with the selectivity decreasing with time, as the zinc dissolution reached a plateau, while the iron dissolution continued to increase slowly.

It appears that the leaching of whole and ground pellets can be effectively achieved with acidified calcium chloride in the presence of ultrasound. The key feature of the leach is the rejection of iron, which is clearly achieved in the case of ground pellets by precipitation of dissolved iron. For whole pellets the rejection mechanism for iron is not evident, and is probably linked with the constraints imposed on the process by the porous nature of the pellets.

CONCLUSIONS

Ultrasound has been demonstrated to be very beneficial in the selective acidified chloride leaching of zinc from pellets produced by the double-kiln treatment of EAF dusts. Zinc recovery was found to be enhanced by ultrasound, possibly through a combination of leachant pore penetration, boundary and product layer breakdown and localized temperature increases. Iron recovery was inhibited in the presence of ultrasound, and this may be due to enhanced zincite dissolution at the expense of the iron dissolution or to the precipitation of any dissolved iron. The absence of oxygen was shown to also decrease the iron dissolution. In addition any agitation of the leach solution appeared to improve the process possibly by aiding in transport and diffusion of reactants and products.

The effect of pellet grinding was shown to be beneficial to leaching with very high selectivities being achieved with finely ground material. As the leach progressed, the pH rose due to the consumption of acid by metal dissolution, and in turn iron precipitation occurred. This resulted in the leach selectivity being time dependent, and hence an optimal time did exist for maximum leach selectivity.

It is apparent that further work utilizing constant acid concentration leaching is warranted to determine the mechanisms of dissolution. In addition larger scale tests are necessary to permit electrolytes to be evaluated for impurity content and electrowinning properties.

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REFERENCES

1. Fosnacht, D.R., Disposal, Recycling and Recovery of Electric Furnace Exhaust Dust., *Iron and Steel Soc. Inc.*: 15-19 (1987).
2. Higley Jr, L.W. & Fine, M.M., *U.S. Bureau of Mines. RI No 8209.* (1977).
3. Morris, A.E., O'Keefe, T.J., Cole, E. & Neumeier, L., Disposal, Recycling and Recovery of Electric Furnace Exhaust Dust., *Iron and Steel Soc. Inc.*: 35-50 (1987).
4. Frenay, J., Ferlay, S. & Hissel, J., Disposal, Recycling and Recovery of Electric Furnace Exhaust Dust., *Iron and Steel Soc. Inc.*: 171-175 (1987).
5. Engelleitner, W.H., Disposal, Recycling and Recovery of Electric Furnace Exhaust Dust., *Iron and Steel Soc. Inc.*: 69-76 (1987).

6. Krishnan, R. & Kemmer, W.F., Disposal, Recycling and Recovery of Electric Furnace Exhaust Dust., *Iron and Steel Soc. Inc.*: 77-87 (1987).
7. Evans, L.G. & Hogan, J.C., Disposal, Recycling and Recovery of Electric Furnace Exhaust Dust., *Iron and Steel Soc. Inc.*: 89-94 (1987).
8. Kaltenhauser, R, Disposal, Recycling and Recovery of Electric Furnace Exhaust Dust., *Iron and Steel Soc. Inc.*: 31-34(1987).
9. Kern. P.L. & Mahler Jr, G.T., *TMS Technical Paper No. A88-5*. TMS-AIME (1988).
10. Pusateri, J.F., Chew, R. & Stanze, A.E., Disposal, Recycling and Recovery of Electric Furnace Exhaust Dust., *Iron and Steel Soc. Inc.*: 97-101 (1987).
11. Eacott, J.G., Robinson, M.C., Busse, E, Burgener, J.E. & Burgener, P.E., *CIM Bulletin* 77, (869) 75-81 (1984).
12. Bounds, C.O. & Pusateri, J.F., *CIM Annual Meeting*, Halifax, (1989).
13. Sato, T. & Lawson, F., *Hydrometallurgy*, 11, 371-388 (1983).
14. Suslik, K.S., Casadonte, D.J., Green, M.L.H., & Thompson, M.E., *Ultrasonics*, 25 (1), 56-59 (1987).
15. Pugin, B., *Ultrasonics*, 25 (1), 49-55 (1987).
16. Henglein, A., *Ultrasonics*, 25 (1), 6-16 (1987).
17. Pandey, A.D., Mallick, K.K. & Pandey, P.C., *Ultrasonics*, 18 (3), 115-119 (1980).
18. Slaczka, A., *Ultrasonics*, 24 (1), 53-55 (1972).
19. Levenspiel, O., *Chemical Reaction Engineering* 2nd ed. John Wiley & Sons, New York, NY. (1972).
20. Doraiswamy, L.K. & Kulkarni, B.D., *Chemical Reaction and Reactor Engineering*, J.J. Carberry and A. Varma (Eds): 293-371 (1987).
21. Barrera-Godinez, A.J., *PhD Thesis*, University of Missouri-Rolla, (1989).
22. Fairbanks, H.V. & Chen, W.I., *Chem. Engr. Progr. Symposium Ser.*, 67 (109), 108-116 (1976).
23. Terry, B., *Hydrometallurgy*, 11, 315-344 (1987).