

The Effect of Zinc Ion Concentration and pH on the Leaching Kinetics of Calcined Zinc Oxide Ore

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ABSTRACT

Previous studies on the dissolution of zinc oxide have concentrated on the effects of temperature, reagent concentration, particle size and agitation rate, among other factors. However, there is dearth data on the effect of a combination of product concentration and pH on leaching rates. This work examines the effects of the concentration of pH and zinc ions on the dissolution kinetics of zinc oxide. The results showed that the rate of zinc dissolution was greatest at lower pHs. This is because at lower pH, the concentration of acid (H^+ ions) is also expected to be high ($pH = -\log_{10}[H^+]$), thus increasing the reaction kinetics in accordance with the kinetic molecular theory. The rate of reaction was found to increase with an increase in the concentration of zinc ions (Zn^{2+}), which is in contrast to established theories. This observation can be explained by the fact that since heat energy produced (via an exothermic reaction) was continuously being dissipated through a constant temperature water bath it favoured zinc oxide dissolution. Zinc oxide ore at 62.5% purity also comprised of other metal oxides (e.g., iron, copper, manganese, etc) which were simultaneously leached. Since the solution was recycled, the concentration of iron, for example, could have also increased. Since zinc is more reactive than iron, two reaction mechanisms could have possibly been occurring at the same time, i.e., the dissolution of zinc oxide ore by sulfuric acid and the displacement of iron in solution by zinc in zinc oxide forming iron hydroxide.

Keywords: dissolution kinetics; leaching; zinc ions; zinc oxide

1.0 INTRODUCTION

Zinc is an important base metal required for various applications in metallurgical, chemical and textile industries. It is usually found in nature as an ore with other metals and sulfur. Zinc is also found in wastes/ secondary materials such as zinc ash, dross, flue dusts, sludge, residue, etc., that are generated in various chemical and metallurgical industries. These waste/secondary materials contain different levels of impurities depending on the source (Jha *et al.*, 2000). A review by Jha *et al.* (2000) showed that zinc can be recovered from the different secondaries /wastes using different lixiviants. Usually, sulphuric acid, hydrochloric acid, ammonia/ammonium carbonate, ammonium chloride, caustic soda, carboxylic acid etc., were used as lixiviants for the dissolution of zinc. Based on the review made, they deduced that sulphuric acid and ammoniacal solutions are effective leaching reagents for various zinc containing secondaries given the eco friendly leach residues, economics, recovery of zinc and selectivity of the process. Dutra *et al.* (2006) investigated the effect that leaching method had on zinc recovery. They leached arc furnace steel dust with sodium hydroxide while varying the temperature and the sodium hydroxide concentration. These two parameters were subjected to, (1) conventional agitation leach, (2) pressure leach, (3) electric arc furnace dust pretreatment in microwave oven, and (4) leaching with ultra sonic agitation. Based on the information gathered, they concluded that the conventional agitated leaching method was the most effective since it displayed the highest zinc recovery of 74%.

Various other parameters have been studied by several researchers. Firstly, Jarupisitthorn *et al.* (2002) investigated the kinetics of zinc leaching from electric arc furnace dust by sodium

hydroxide by changing several factors (temperature, reagent concentration and solid-liquid ratio). They found that by increasing the temperature the leaching rate also increased. This was largely due to the fact that the reagents were on higher energy level and could overcome the effects of the activation energy required and electron repulsion forces much quicker. In the same study, Jarupisitthorn *et al.* (2002) reported that increasing reagent concentration increases kinetics until a certain point where the solution becomes viscous and the rate of leaching starts decreasing. This was because diffusion decreased as the solution became viscous. Jarupisitthorn *et al.* (2002) also observed the effect of solid-liquid ratio on leaching kinetics of electric arc furnace dust by sodium hydroxide. The study found that at a constant stirring speed of 850 rpm and a temperature of 95°C the rate of zinc leaching decreased as the percent solid increased. This resulted from depletion of initial concentration of sodium hydroxide in the leaching solution and the solubility limit of zinc in sodium hydroxide solution, which is lower at lower sodium hydroxide concentration. Secondly, in their study, Souza *et al.* (2009) investigated the effect of the agitation speed in the range of 360 - 720 rpm on zinc extraction for the high- and low-iron concentrates. It was found that the stirring rate did not affect the zinc extraction regardless of the iron content in both concentrates. Therefore, the dissolution process did not seem to be controlled by mass transfer through the liquid boundary film, despite the possible change in solution viscosity caused by silica gel formation. Jarupisitthorn *et al.* (2002) also observed similar results as they studied the effect of stirring speed. Finally, Abdel-Aal (2000) studied the effect of particle size on kinetics of sulphuric acid leaching of low grade zinc silicate ore. The results showed that decrease in particle size yielded an increase in reaction kinetics. This was due to the reduced particle radius which allowed shorter distance between the leaching reagent and the particle nucleus. This effect exposed the solid more which granted it an increased surface area.

As noted above, the effects of temperature, reagent concentration, particle size and agitation rate on zinc recovery from various sources have been intensively researched. However, limited literature is available on the effect of product concentration on leaching rates. The aim of the study is to investigate the effect of pH and zinc ions concentration and on leaching rates.

2.0 MATERIALS AND METHODS

2.1 Apparatus used

Two steel reactors of the same volume were used. They were submerged in water to maintain the temperature constant and were fitted with agitators which had the same size, current supply and material of construction. Tap water and 98% sulphuric acid were used as the solvent while calcined zinc oxide was the solute. The reagents were prepared in 800 mL glass beakers. A scale was used to measure the mass of the calcined zinc oxide required and the mass of sulphuric acid required to prepare a 100 g/L solution of sulphuric acid. This concentration of acid (i.e., 100 g/L) was prepared to avoid large pH variations during acid additions.

Samples were taken every 30 minutes using a syringe. The syringe was also used for acid additions. Bugna filter was fitted with filter paper to filter the sampling and the rest of the solution after leaching process was completed. An atomic absorption spectrophotometer (AAS) was used to analyse the samples for zinc.

2.2 Experimental Procedure

Three tests were conducted under different pH ranges. The first test was conducted under a pH of 1, the second under a pH of 2 and the last under a pH of 3. Each test had a series of three tests - first, second and third test in which Zn concentration was varied. The same procedures were followed for all the tests, only that the acid additions were dependant on the pH range.

First Test

Four liters of tap water was added into a reactor. Approximately 100 g/L of sulphuric acid solution was prepared by adding 80g of sulphuric acid into 800mL of tap water. The acid solution was added to the water in the reactor and the pH was adjusted according to the desired pH value. Approximately 4g of calcined zinc oxide was weighed and fed to the reactor and the agitator was started. pH readings were taken every 10 minutes and was adjusted accordingly by adding 100g/L sulphuric acid. Periodically at 30 minutes interval, 30mL samples were taken, filtered and stored in a sample container. The process was left to run for 90 minutes. After running the process, the solution was filtered; its volume was measured, sampled and used for the second test.

Second Test

The solution obtained from the initial test was used for the second test. Where the solution was less than 4L, tap water was added to adjust the volume to 4L. A sample was then taken to determine the concentration of zinc present and the pH was adjusted accordingly by adding 100g/L sulphuric acid. Thereafter, 4g of calcined zinc oxide was added and the same procedure was followed as the first test.

Third Test

The solution obtained from the second test was used for the third test, and the procedure was similar to the second test. After running the process, the solution was filtered; its volume was measured and disposed of properly.

After the entire tests were conducted, the samples were taken for analysis. Table 1 and 2 show the chemical composition and particle size distribution, respectively, of the ore used in this study.

Table 1: Chemical composition of zinc oxide ore

Mineral	ZnO	Fe ₂ O ₃	SO ₃	SiO ₂	CaO	Al ₂ O ₃	MnO	CuO	others
Mass %	62.6	9.5	6.0	3.0	1.1	1.0	0.9	0.9	15%

Table 2: Particle sizes of zinc oxide ore

Size (µm)	75	106	150
Mass (g)	230.5	45.2	45.3

3.0 RESULTS AND DISCUSION

3.1 Effect of pH

Figures 1, 2 and 3 show the zinc recovered over different initial zinc concentrations. It was observed that the rate of zinc dissolution was greatest for pH 1 when compared to the other pH ranges (pH 2 and pH 3). Similar effects of leaching under different concentrations of H⁺ were observed by Souza et al (2009), and Espiara et al (2006), who also observed that the increase in acid concentration also increased the rate of reaction. This observation confirmed the kinetic molecular theory that when the concentrations of reactants are increased, reaction kinetics also increases.

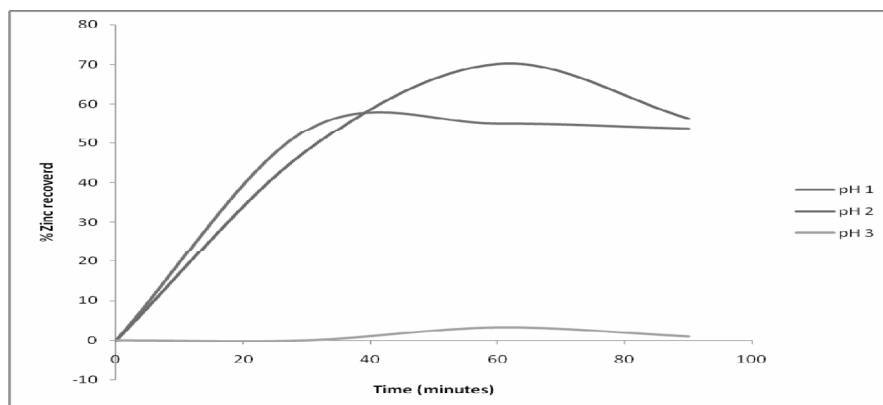


Figure 1: Recovery of Zinc for first run tests.

The test of pH 3 on Figure 1 shows that almost no zinc reacted. This was attributed to the fact that pH readings were taken every 10 minutes. Since small acid additions were required to maintain the pH at 3, the acid was almost completely consumed as it is observed by the pH spikes in Figure 8. That meant that there was almost no reaction taking place up until the next acid addition. Figures 1 and 2 also show that the difference between the initial rates of zinc dissolution for pH 1 and 2 was not large until when the reaction time reached 30 minutes when the difference started to increase. This was attributed to the fact that at this time there was need to add acid so as to maintain pH 1. Since the addition of the acid required the agitation to be temporarily stopped due to the nature of the equipment used, the rate of zinc recovery also dropped for pH 1.

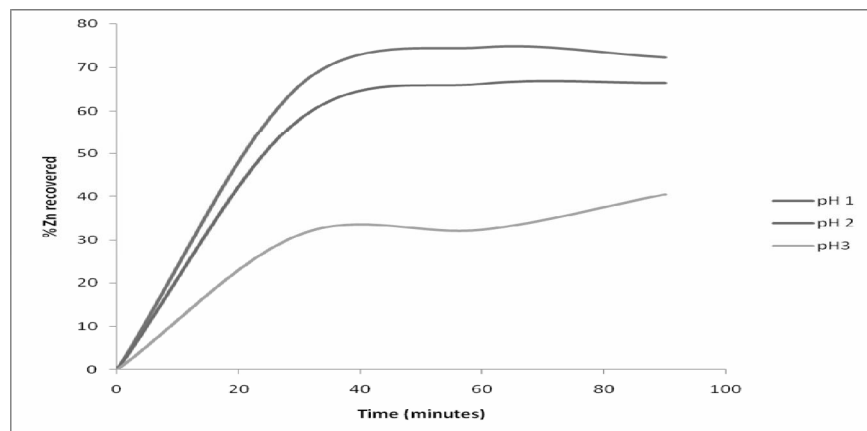


Figure 2: Recovery of zinc for second run test.

3.2 Effect of Zn^{2+}

Figures 4, 5 and 6 illustrate the effect of increasing Zn^{2+} at various H^+ concentrations. The figures show that the initial Zn^{2+} concentration for test 1 is higher than in test 2, and test 2 is higher than test 3 for Figures 4, 5 and 6. It can be observed from these three figures, except that for test 3 in Figure 5 that by increasing the concentration of Zn^{2+} , the rate of reaction also increased. These were found to be unorthodox since it is expected that rate of reaction would decrease as the Zn^{2+} increases. The theory behind the expectation was related to the fact that the concentration gradient decreases between the surface of the calcined zinc ore and the solution as the concentration of Zn^{2+} was increased.

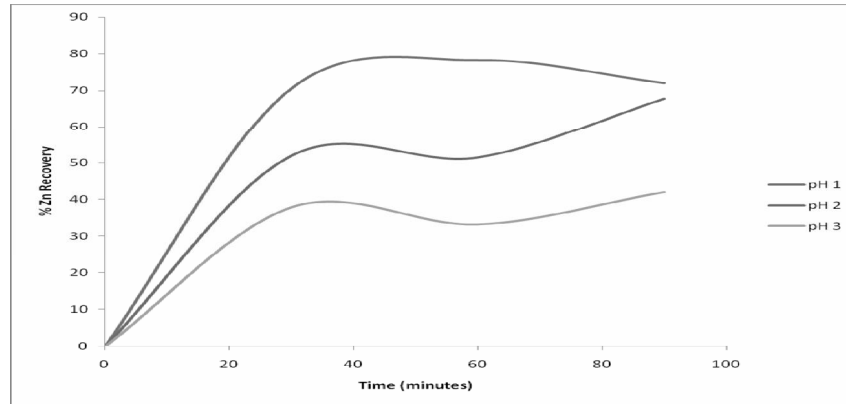


Figure 3: Recovery of zinc for third run test.

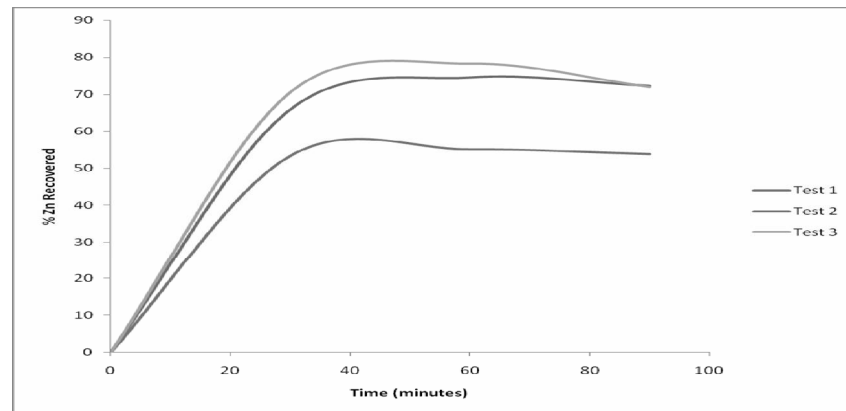


Figure 4: Recovery of zinc at an average pH of 1.

This unorthodox observation can be explained by the fact that heat energy produced (via an exothermic reaction) was continuously being dissipated through a constant temperature water bath thus favouring zinc oxide dissolution. As can be seen from Table 1, the zinc oxide ore at 62.5% purity also comprised of other metal oxides (e.g., iron, copper, manganese, etc) which were simultaneously leached. Since the solution was recycled, the concentration of iron, for example, could have also increased. Since zinc is more reactive than iron, two reaction mechanisms could have possibly been occurring at the same time, i.e., the dissolution of zinc oxide ore by sulfuric acid and the displacement of iron in solution by zinc in zinc oxide forming iron hydroxide as shown in Equation 1 (Reghavan et al., 1998).

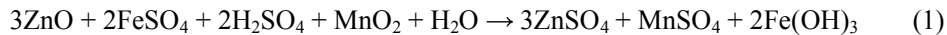


Figure 7 depicted the concentration profile of zinc for different H^+ concentrations over a given time. The concentration directly indicated the amount of zinc leached as a function of time over a given time. Cumulative zinc leached at pH 3 was the lowest after 270 minutes. The reason being the same as those discussed above. Linear trend lines were fitted for the concentration profile of various pH ranges and it was found from the slope of the equation of pH 1 and 2 that the variance of the rate of the reaction was insignificant. The amount of zinc leached was similar for both the pH's. This observation indicated that the acid concentration can be increased to a certain point up until any further increase would not have any effect on the leaching rate and the recovery of zinc.

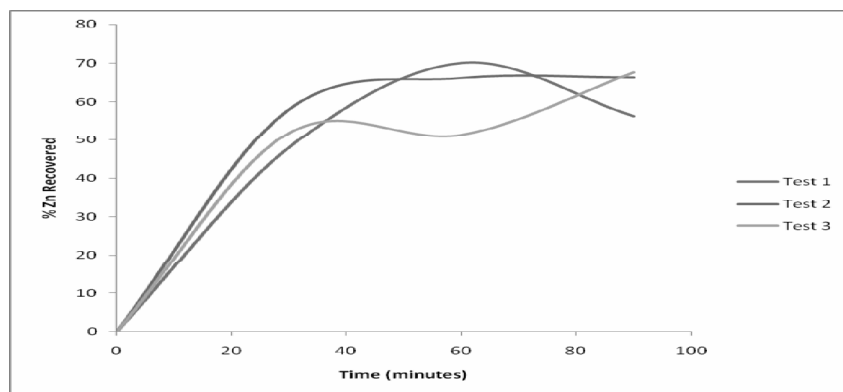


Figure 5: Recovery of Zinc at an average pH of 2.

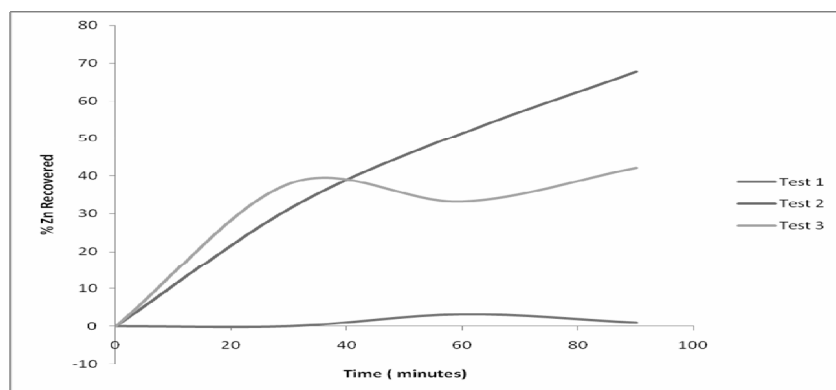


Figure 6: Recovery of Zinc at an average pH of 3.

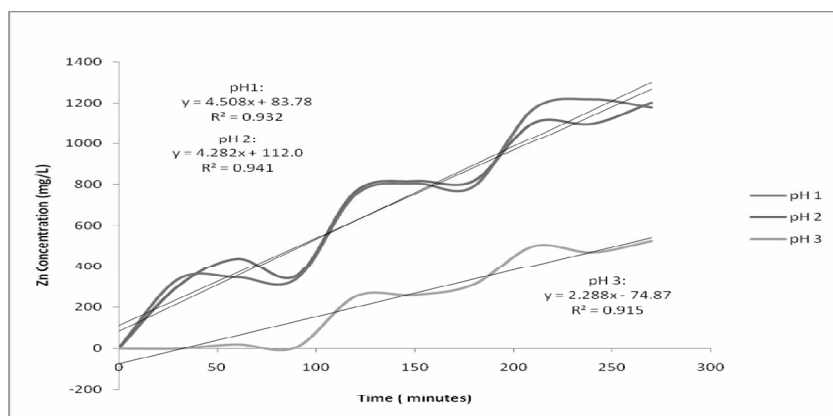


Figure 7: Zn concentration versus time.

3.3 pH control

Figure 8 illustrated the acid addition required to maintain the pH at a desired values. It was observed from the spikes on pH 3 and 2 that the pH control was not at an optimum. Since the pH was monitored at intervals, figures where spikes were observed indicated the system was deprived of H^+ ions. That was attributed to the human error factor of the experiment. Figure 9 illustrated the acid required to maintain the desired pH over the entire period of leaching for various pH readings. It was observed that the acid requirements for pH 1 were three times those for pH 2 even though the yield and reaction rate were similar for both the tests.

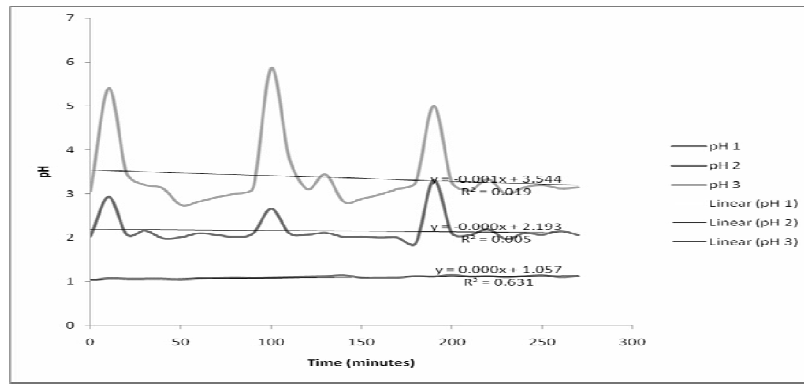


Figure 8: pH control over time.

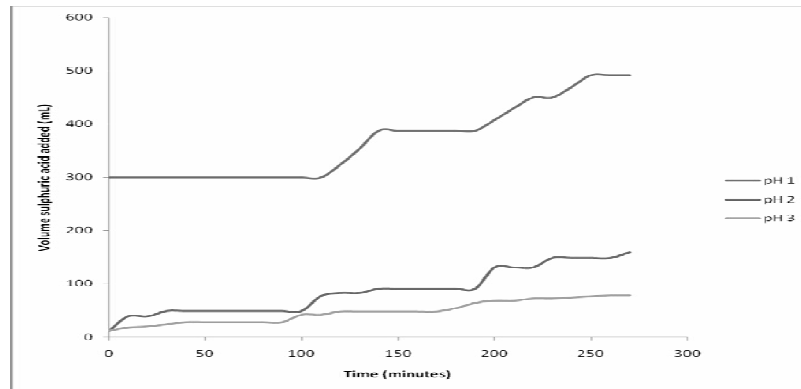


Figure 9: Cumulative acid addition for different pH ranges.

4.0 CONCLUSIONS

The following conclusions can be made from this study:-

- (1) Leaching rate of the calcined ZnO ore increases with increasing acid concentrations.
- (2) An increase in Zn^{2+} concentration increases the rate of leaching ZnO.

5.0 REFERENCES

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