

Article

## Removal of Zn from Contaminated Sediment by FeCl<sub>3</sub> in HCl Solution

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**Abstract:** Harbor sediments contaminated with ZnS concentrate were treated by ferric chloride in HCl solution to remove Zn. The sediments were evaluated using Tessier's sequential extraction method to determine the different metal phase associations of Zn. Leaching tests were performed to investigate the effects of experimental factors, such as agitation speed, ferric ion concentration, temperature, and pulp density, on the removal of Zn. The sequential extraction procedure revealed that about 17.7% of Zn in the sediment was associated with soluble carbonate and oxide phases. The results of the leaching tests indicated that higher ferric concentration and temperature increased the leaching efficiencies significantly, while the agitation speed has a negligible effect on the removal of Zn. The removal ratio increased to more than 99% within 120 min of treatment at 1 kmol·m<sup>-3</sup> HCl solution with 1 kmol·m<sup>-3</sup> Fe<sup>3+</sup>, 10% pulp density, and 400 rpm at 90 °C. The dissolution kinetics of Zn were discussed by comparing the two shrinking core models. It was determined that the kinetic data followed the diffusion controlled model well compared to the surface chemical reaction model. The activation energies were calculated to be 76.9 kJ/mol, 69.6 kJ/mol, and 58.5 kJ/mol for 0.25 kmol·m<sup>-3</sup>, 0.5 kmol·m<sup>-3</sup>, and 1 kmol·m<sup>-3</sup> Fe<sup>3+</sup>, respectively.

**Keywords:** harbor sediments; ferric chloride; zinc sulfide; metal contamination

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## 1. Introduction

Operational or incidental spillage of materials during unloading activities of metal concentrates has caused contamination problems in some harbor areas in Korea. This has led to increasing concerns regarding metal-contaminated soils and sediments and their impacts on the environment. Various treatment methods have been proposed for remediating contaminated sites, such as gravity separation, phytoremediation, thermal processing, solidification/stabilization, electrokinetic remediation, and soil washing [1,2]. Gravity separation techniques have been considered to be cost-effective and environmentally friendly primarily because of the chemical-free process, but their effectiveness and applicability are rather difficult in the treatment of fine concentrates with particle sizes less than 75  $\mu\text{m}$  [2]. Since fine particles have high specific surface area, chemical treatment methods such as leaching generally are more suitable than physical treatment processes.

Zinc sulfide (sphalerite, ZnS) concentrates are normally subjected to roasting as a pre-treatment method before leaching to enhance the dissolution of Zn. After leaching, the released Zn ions are recovered as metallic zinc in the electrowinning process [3]. The emission of SO<sub>2</sub> during roasting is a serious environmental problem and is governed by strict environmental regulations. Due to this, the hydrometallurgical route has gained recognition as an alternative process to recover Zn from concentrates [3]. The leaching of sphalerite has been investigated using various leaching media, such as ferric sulphate and chloride with hydrogen peroxide or oxygen [3], ferric sulphate [4], hydrochloric acid with ferric chloride [5], and sulfuric acid with nitric acid [6]. These studies suggested the use of either ferric ions, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, or HNO<sub>3</sub> for ZnS oxidation using mineral grade sphalerite or concentrates. Only a few studies on the hydrometallurgical removal of Zn from ZnS-contaminated sediments with ferric ions are available in literature.

Harbor sediments contaminated with ZnS are exposed to natural environmental conditions and may undergo weathering over time and may change to a different chemical form. Metals accumulate in sediments from both natural and anthropogenic sources, thus making it difficult to identify and determine their origin. It is therefore important to evaluate the individual fractions of the metals not only to understand their actual and potential environmental effects but also to aid in the process design. However, metal concentrations in contaminated sediments are usually below the detection limit of the X-ray diffractometer (XRD), making their measurements difficult. To overcome this limitation, sequential extraction methods can be used [7,8]. One of the most widely used methods is the Tessier sequential extraction method which consists of five extraction steps: “bound to exchangeable”, “bound to carbonate”, “bound to oxide”, “bound to sulfide or organic matter”, and residue. A study conducted by Park *et al.* on the leaching of heavy metals (Cu, Zn, Pb) from contaminated soil using citric acid revealed that the metals in carbonate and oxide phases are easy to dissolve [2].

In the present study, the sediments contaminated with ZnS concentrate were evaluated using Tessier’s sequential extraction method. Ferric chloride leaching tests were performed to investigate the effects of leaching factors such as agitation speed, ferric chloride concentration, temperature, and pulp

density on Zn removal. The dissolution kinetics were discussed and interpreted by comparing the two shrinking core models.

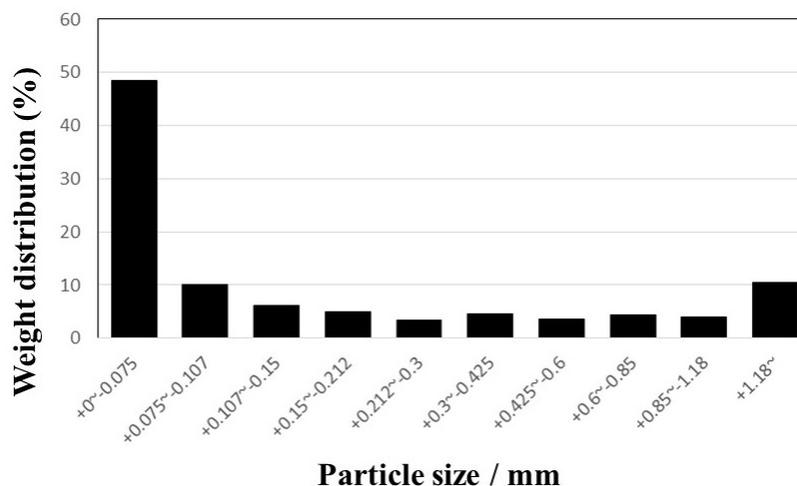
## 2. Experiments

### 2.1. Materials

Sediments contaminated with ZnS were collected from a harbor site that has been used for the unloading of Zn concentrate. The samples were washed three times with distilled water and then dried overnight at 105 °C. The particle size distribution of the sediment as shown in Figure 1 reveals that 48.5% of the sample has a particle size <75 µm. This size fraction was used in the leaching tests. The zinc content of the sample was determined to be 5287 mg/kg by aqua-regia digestion. All chemicals used in this study were of reagent grade.

### 2.2. Leaching Procedures and Analytical Methods

The leaching tests were performed in a 500 dm<sup>3</sup> three-necked Pyrex glass reactor using a heating mantle to maintain the desired temperature to within ±2 °C. This reactor was fitted with a stirrer and a reflux condenser to prevent solution loss at high temperatures. Leach solutions were prepared with FeCl<sub>3</sub> concentrations of between 0.25 kmol·m<sup>-3</sup> and 1 kmol·m<sup>-3</sup> in 1 kmol·m<sup>-3</sup> HCl solution. For every batch of leaching test, 200 cm<sup>3</sup> of leach solution was introduced into the reactor. Once the solution reached thermal equilibrium (40–90 °C), 20–60 g of the fine sediment powder was added and agitated at 200–600 rpm. During these tests, a 2 cm<sup>3</sup> aliquot solution was withdrawn periodically over the desired time interval (5–240 min) for analysis.



**Figure 1.** Particle size distribution of the contaminated sediment.

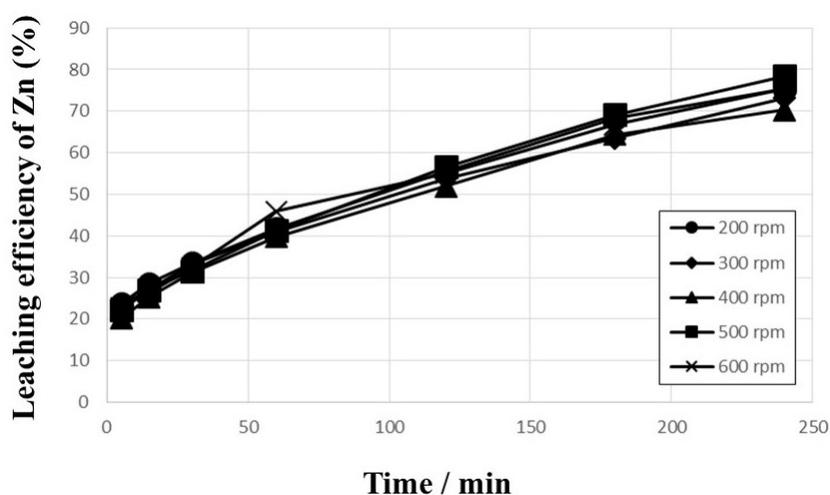
The sequential extraction method used in this study was originally developed by Tessier *et al.* (1979) [7] and later modified by Li *et al.* (1995) [8]. The extraction method used 1 g of dried sample and was performed under the following conditions and reagents: (1) 8 cm<sup>3</sup> of 1 kmol·m<sup>-3</sup> MgCl<sub>2</sub> (adjusted to pH 7) for 1 h at room temperature in the shaking bath; (2) 8 cm<sup>3</sup> of 1 kmol·m<sup>-3</sup> CH<sub>3</sub>COONa (adjusted to pH 5) for 5 h at room temperature in the shaking bath; (3) 20 cm<sup>3</sup> of 0.4 kmol·m<sup>-3</sup> NH<sub>2</sub>OH·HCl (in

25% CH<sub>3</sub>COOH) for 6 h at 96 °C in a heating block; (4) 3 cm<sup>3</sup> of 0.02 kmol·m<sup>-3</sup> HNO<sub>3</sub> and 5 cm<sup>3</sup> of 30% H<sub>2</sub>O<sub>2</sub> (adjusted to pH 2) for 2 h at 85 °C in a heating block, followed by 3 cm<sup>3</sup> of 30% H<sub>2</sub>O<sub>2</sub> (adjusted to pH 2) for 3 h at 85 °C in a heating block, and, finally, 5 cm<sup>3</sup> of 3.2 kmol·m<sup>-3</sup> CH<sub>3</sub>COONH<sub>4</sub> (in 20% HNO<sub>3</sub>) and about 4 cm<sup>3</sup> deionized water for 30 min at room temperature in the shaking bath; (5) 20 cm<sup>3</sup> of aqua regia for 20 min. All solid/liquid separations were done by centrifugation for 30 min at 10,000 rpm (1065× g), designated amounts of supernatant were taken and then diluted with 5% HNO<sub>3</sub> solution. The concentration of Zn was determined with AA-7000 atomic absorption spectrophotometer (Shimadzu Scientific Instrument, Ltd., Kyoto, Japan).

### 3. Results and Discussion

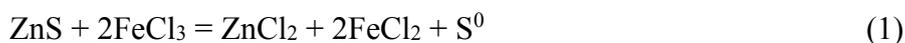
Zinc concentrate is usually imported to Korea in the form of ZnS (sphalerite) and due to operational or incidental spillage during unloading, this concentrate has become the source of Zn contamination in harbor sediments. The chemical association of Zn in this sediment was examined using Tessier's sequential extraction method to understand its characteristics, through which it was found that 7.9% and 9.8% of the Zn was in the "bound to carbonate" and "bound to oxide" phases, respectively. The rest of the Zn content was found to be associated with the "bound to sulfide" phase. This result indicates that 17.7% of Zn is bound to the weathered forms, such as carbonates and oxides, which can be dissolved easily in HCl solution.

Leaching tests using the contaminated sediments were carried out at agitation speeds in the range of 200–600 rpm to examine the effect of liquid film boundary diffusion surrounding the solid particles on the leaching efficiency at the following conditions: 1 kmol·m<sup>-3</sup> HCl with 1 kmol·m<sup>-3</sup> Fe<sup>3+</sup>, 10% pulp density, and 50 °C. Figure 2 shows that the leaching efficiencies of Zn are independent of the agitation speeds. Therefore, in all subsequent leaching tests, a working agitation speed of 400 rpm was selected to ensure effective particle suspension in the solution. It was also observed that the leaching efficiency of Zn increased rapidly to more than 20% within 5 min and then gradually increased afterwards. This can be attributed to the initial dissolution of Zn present in the "bound to carbonate" and "bound to oxide" phases.



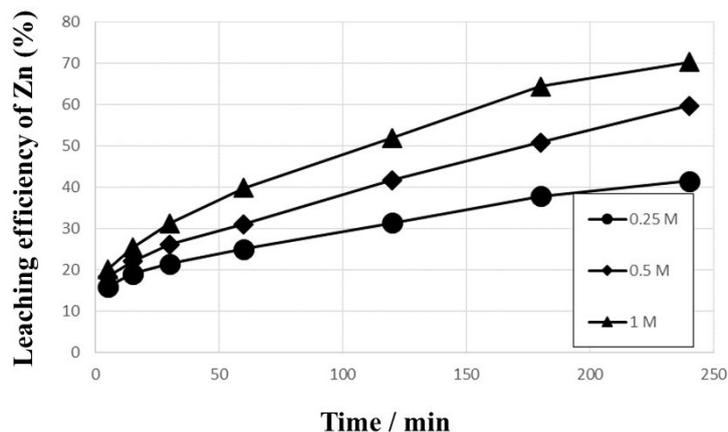
**Figure 2.** The effects of agitation speed on the leaching efficiency of Zn at 1 kmol·m<sup>-3</sup> HCl with 1 kmol·m<sup>-3</sup> Fe<sup>3+</sup>, 10% pulp density, and 50 °C.

Figure 3 shows the effect of  $\text{Fe}^{3+}$  concentration on the dissolution of Zn from the contaminated sediment at  $1 \text{ kmol}\cdot\text{m}^{-3}$  HCl solution, 10% pulp density,  $0.25\text{--}1 \text{ kmol}\cdot\text{m}^{-3}$   $\text{Fe}^{3+}$ ,  $50 \text{ }^\circ\text{C}$ , and 400 rpm. The leaching efficiencies of Zn increased gradually with leaching time and improved significantly with higher  $\text{Fe}^{3+}$  concentrations. A ferric ion was used as an oxidant in this study, and the oxidation of ZnS was promoted by the ferric ion according to the following equation [9]:



The sediments contain  $5287 \text{ mg/kg}$  of Zn, which is equivalent to  $8 \text{ mol}\cdot\text{m}^{-3}$  in a 10% pulp density solution. However, although  $250 \text{ mol}\cdot\text{m}^{-3}$   $\text{Fe}^{3+}$  is already almost 15 times more than the stoichiometric requirement of  $16 \text{ mol}\cdot\text{m}^{-3}$   $\text{Fe}^{3+}$  to oxidize  $8 \text{ mol}\cdot\text{m}^{-3}$  of ZnS, the leaching efficiency of Zn was only 41.4% at 240 min as shown in Figure 3.

Figure 4 shows the effect of temperature on the leaching efficiency of Zn at  $1 \text{ kmol}\cdot\text{m}^{-3}$  HCl solution, 10% pulp density,  $1 \text{ kmol}\cdot\text{m}^{-3}$   $\text{Fe}^{3+}$ ,  $40\text{--}90 \text{ }^\circ\text{C}$ , and 400 rpm. Higher temperatures yield higher Zn leaching efficiency and it increased to more than 99% within 120 min and 180 min at  $90 \text{ }^\circ\text{C}$  and  $80 \text{ }^\circ\text{C}$ , respectively. These results also show that the Zn content decreased to less than  $200 \text{ mg/kg}$ , which is the environmental standard for Zn in Korea, and indicate that Zn could be removed successfully. The effect of pulp density on the leaching of Zn from the sediments was investigated under the following conditions:  $1 \text{ kmol}\cdot\text{m}^{-3}$  HCl,  $1 \text{ kmol}\cdot\text{m}^{-3}$   $\text{Fe}^{3+}$ , 10%–30% pulp density,  $50 \text{ }^\circ\text{C}$  temperature, and 400 rpm agitation speed, but the results showed no apparent differences in leaching efficiency (data not shown).



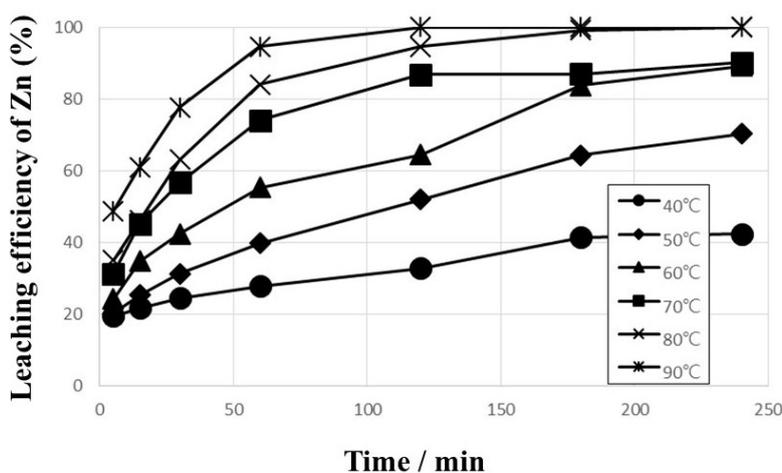
**Figure 3.** The effects of  $\text{Fe}^{3+}$  concentration on the leaching efficiency of Zn at  $1 \text{ kmol}\cdot\text{m}^{-3}$  HCl, 10% pulp density,  $50 \text{ }^\circ\text{C}$ , and 400 rpm.

Studies on the dissolution kinetics of ZnS were reported previously and investigations were carried out using pure sphalerite crystals [9,10], low-grade calcareous sphalerite [11], and ZnS concentrate [4,5]. Activation energy values were calculated using the shrinking core model and the Dickson and Heal model [4,5,9–11] and were determined to be  $27.5 \text{ kJ/mol}$  in sulfuric acid [4] and  $42\text{--}49.2 \text{ kJ/mol}$  in hydrochloric acid [5,9–11], respectively. The shrinking core model could be expressed by [5,12]:

$$1 - (1 - x)^{\frac{1}{3}} = k_r t \quad (2)$$

$$1 - \left(\frac{2}{3}\right)x - (1-x)^{\frac{2}{3}} = k_d t \quad (3)$$

Equation (2) represents the shrinking core model based on surface chemical reaction (reaction-controlled model), while Equation 3 is based on diffusion reaction (diffusion-controlled model). The value for  $x$  in the equations represents the fraction reacted and is obtained from the leaching efficiencies, while  $k_r$  and  $k_d$  are rate constants.



**Figure 4.** The effects of temperature on the leaching efficiency of Zn at  $1 \text{ kmol}\cdot\text{m}^{-3}$  HCl with  $1 \text{ kmol}\cdot\text{m}^{-3}$   $\text{Fe}^{3+}$ , 10% pulp density, and 400 rpm.

The leaching efficiency of Zn increased to more than 90% at 80 °C and 90 °C within 120 min, so the leaching data within 60 min were fitted to the models as shown in Figure 5 (reaction-controlled model) and Figure 6 (diffusion-controlled model), respectively. Based on the calculations, the correlation coefficients ( $R^2$ ) for the diffusion-controlled model are higher compared to that of the reaction-controlled model. Previous studies on ZnS leaching with  $\text{FeCl}_3$  reported that the leaching behavior of Zn followed the reaction-controlled model [5,9,10] while others proposed that the reaction was controlled by both the reaction- and diffusion-controlled model [4,11]. In the current study, the kinetic model parameters indicated that the diffusion-controlled model is more suitable to explain the kinetic behavior of Zn removal. This result can be attributed to the low Zn content of the test sample (about 0.5%) as compared to the 48%–67% Zn contents of the samples used in previous studies [4,5,9–11].

Rate constants for different temperatures were calculated from Figure 6, and the Arrhenius plots of  $\ln K$  vs.  $T^{-1}$  for leaching data are shown in Figure 7. From the Arrhenius plots, the activation energies of 76.9 kJ/mol, 69.6 kJ/mol, and 58.5 kJ/mol were calculated for the sphalerite dissolution in  $0.25 \text{ kmol}\cdot\text{m}^{-3}$ ,  $0.5 \text{ kmol}\cdot\text{m}^{-3}$ , and  $1 \text{ kmol}\cdot\text{m}^{-3}$   $\text{Fe}^{3+}$ , respectively. The results indicate that the reaction is controlled by the diffusion of  $\text{Fe}^{3+}$  ions.

This study confirmed that the removal of Zn could be achieved by ferric chloride leaching in HCl solution, and the Zn content decreased to less than 200 mg/kg, satisfying the Korean environmental standard. During leaching, ferrous ( $\text{Fe}^{2+}$ ) ion is generated and the  $\text{Fe}^{2+}$  ion could be oxidized electrochemically or biologically into  $\text{Fe}^{3+}$ , which can be reused as an oxidant in the process. Further study will be required to optimize the re-oxidation.

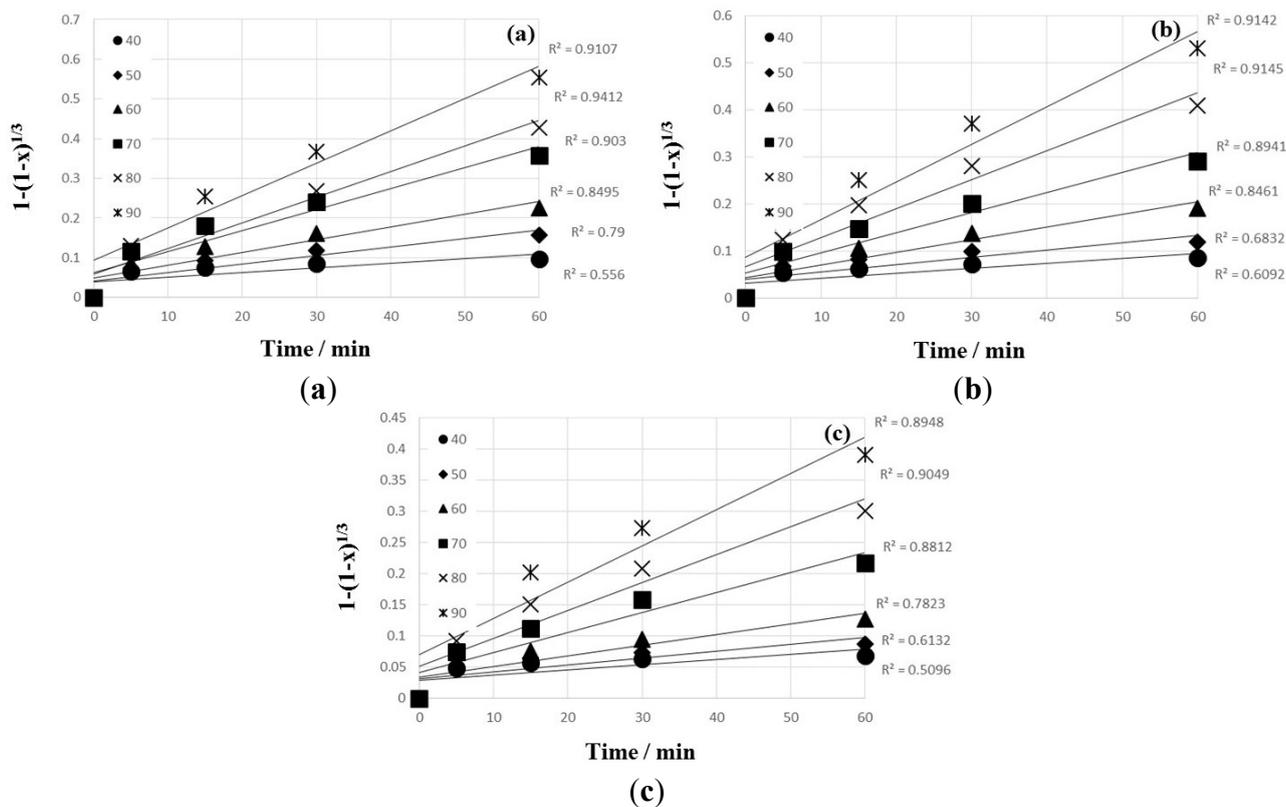


Figure 5. Plot of  $1 - (1 - x)^{1/3}$  vs.  $T$  for different temperatures ( $[Fe^{3+}]$ : (a) 1.0 M; (b) 0.5 M; (c) 0.25 M; 10% pulp density; 400 rpm agitation speed).

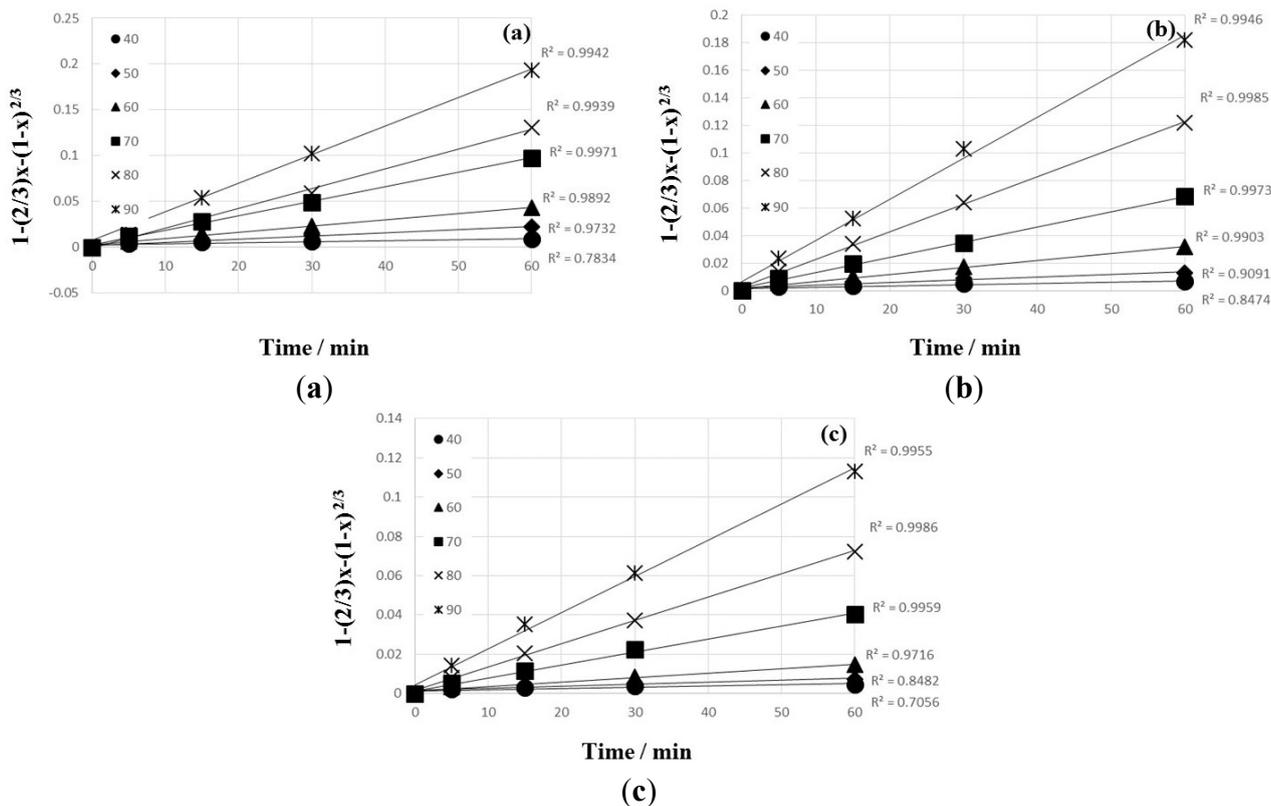
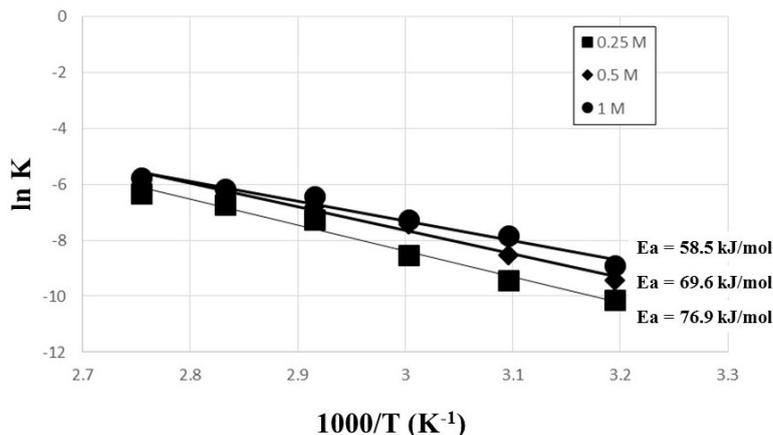


Figure 6. Plot of  $1 - 2/3x - (1 - x)^{2/3}$  vs.  $T$  for different temperatures ( $[Fe^{3+}]$ : (a) 1.0 M; (b) 0.5 M; (c) 0.25 M; 10% pulp density; 400 rpm agitation speed).



**Figure 7.** Arrhenius plots. (1 kmol m<sup>-3</sup> HCl; 0.25 kmol m<sup>-3</sup>–1 kmol m<sup>-3</sup> Fe<sup>3+</sup>; 400 rpm agitation speed; 10% pulp density; 40 °C–90 °C temperature).

#### 4. Conclusions

The leaching behavior of Zn from sediment contaminated with ZnS concentrate using Fe<sup>3+</sup> ions in HCl solution was investigated. The chemical associations of Zn in the sediment were also evaluated using Tessier's sequential extraction method. By fitting the leaching data to two shrinking core models, the following conclusions were made:

1. The removal of Zn was achieved by ferric chloride leaching in HCl solution. The removal ratio increased to more than 99% within 120 min under the following leaching conditions; 1 kmol·m<sup>-3</sup> Fe<sup>3+</sup>; 1 kmol·m<sup>-3</sup> HCl; 400 rpm agitation speed; 90 °C leaching temperature; 10% pulp density. More importantly, the results obtained meet the Korean environmental standards for Zn of 200 mg/kg.
2. About 17.7% of Zn in the sediment was associated with the soluble carbonate and oxide phases as determined by the sequential extraction procedure. The leaching efficiency of Zn increased quite rapidly in the first 5 min and then gradually in the succeeding treatment time. The rapid increase can be attributed to the dissolution of Zn in carbonate and oxide fractions. These results confirm the importance of evaluating the different metal phase associations through sequential extraction to understand the leaching behavior.
3. The kinetic data indicated that the leaching behavior followed the diffusion-controlled model well rather than the surface chemical reaction model. As ferric ion concentration increases, the calculated activation energy decreases. The results also suggest that higher ferric ion concentration and temperature could enhance the leaching efficiency of Zn.

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## Author Contributions

Lee and Yoo wrote the paper and contributed to all activities. Kwon conducted leaching tests and analyses. Alorro contributed to interpretation and discussion of the kinetics data.

## Conflicts of Interest

The authors declare no conflict of interest.

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