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Quantitative Leaching of Spent Galvanized Zinc Ash by Hydrochloric Acid

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Abstract

Leaching is an extractive metallurgy technique widely used in converting metal into soluble salt in aqueous media. In this study, experiments on quantitative leaching of spent galvanized zinc ash in hydrochloric acid solution were examined. Experimental parameters such as acid concentration and reaction temperature were varied. In addition, reaction residues at optimal leaching were examined by scanning electron micrography (SEM) and the products of reaction were identified by energy dispersive X-ray (EDXRF) and X-ray diffraction (XRD). The leaching results showed that the amount of zinc ash powder dissolved increases with increasing acid concentration and temperature. At optimal conditions (4 mol/L HCl, 75°C, 0.1mm), the dissolution reached 98.5% within 120 minutes. Also, the leaching results conform to a rate limiting diffusion controlled reaction. The calculated activation energy of 25.96 kJ/mol is reasonable for a rate limiting surface reaction and supported the proposed dissolution mechanism.

Keywords: Galvanized zinc ash; leaching; hydrochloric acid; dissolution kinetic; diffusion control mechanism.

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1. Introduction

Zinc ash, a mixture of zinc oxide with varying quantities of entrained free metallic zinc is produced when floating debris is skimmed from the surface of a galvanized kettle (Hazardous Waste Act, 2001). It usually arises from hot dip galvanizing and zinc coating process. The oxidized zinc that forms on the surface of molten zinc metal consist of a powder material and solid metallic pieces of an irregular shape (Muzenda and Smate, 2002). Apparently, galvanization through the hot dip route makes it possible for a named material to be protected against various harsh elements or weather. It is the process of alloying steel so that it becomes a permanent part and thus enabling the metal to withstand corrosion including other circumstances such as saltwater or moisture (Alam *et al.,* 2020; Sparkwest Galvanization Manual, 2012). This practice may positively influence the Government Policy to regulate air emissions coming from secondary smelters and storm-water runoff emissions from open scrap yards (Wernick and Thermelis, 1998).

Most of the ash is formed by the disturbance of the bath surface during working as a result of which clean zinc oxidizes and particles of metallic zinc are entrained in the folds of the oxide. A considerable amount of metallic zinc may be entrained during the removal of the ash from the bath surface, if otherwise, the material may contain variable proportions of zinc in metallic form as low as 40, to as high as 90 percent, for example. The balance of the zinc, from 60 to 10 percent is zinc oxide and zinc ash is considered to be indispensable form because of the high zinc oxide content which could be classed to any of the following varieties:

- **Hard zinc smelter (92% Zn)** is obtained from galvanizing slab zinc bottom dross.
- **Galvanizing slab zinc top dross (>90% Zn)** is removed from the top of a continuous line galvanizing bath in slab form with a minimum zinc content of 90%.
- **Galvanizing slab zinc bottom dross (>92% Zn)** is removed from the bottom of a continuous line galvanizing bath, with minimum zinc content of 92%.
- **Zinc die casting dross (>85% Zn)** is apparently removed from the top of pot of molten zinc die-cast metal with minimum zinc content of 85%. This type is also synonymous to zinc skimming which are important in the recovery of the metallic values (Hazardous Waste Act, 2001; Sakamoto et al. 1995).

However, these varieties of zinc product from zinc ash are valuable base metal required for various applications in metallurgical, chemical and textile industries. Due to the aforementioned applications, there has been an increasing interest in developing processes for the recovery of zinc from secondary sources such as spent galvanized zinc ash. The developed process should produce a residue which could be recycled for further processing or safely disposed off without affecting the environment. It is evident from literature that pyrometallurgical and hydrometallurgical techniques are employed for treating such secondaries; but pyrometallurgical route is not economical due to high energy requirement as well as production of obnoxious dusts/gases such as Sulphur (IV) oxide.

Also, the presence of chloride and fluoride salts in the dust causes severe corrosion problems and necessitates use of expensive alloys as materials of construction. However, due to ease of material construction, economic and low energy considerations, hydrometallurgical options involving leaching, solvent extraction and precipitation for metal purification is often preferable in the treatment of low zinc containing materials on small scale (Baba and Adekola, 2011; Baba *et al.*, 2009; Jha *et al.*, 2001; Li *et al.*, 2020).

To date, some reported works (Barakat, 2003 Bright *et al.*, 2007; Jardova and Dvorak, 2006; Lupa *et al.*, 2006; Martha-de-Souza, Piroskova *et al.*, 2012; Tenorio, 2004) on zinc ash processing aiming at obtaining pure zinc are through reductive-roasting at elevated temperatures and thus energy intensive. Therefore, taking into consideration the aforementioned advantages of the hydrometallurgical method and due to the depletion of high grade ores/concentrates, the hydrometallurgical processing of secondary sources are gaining importance in the metallurgical industries for the recovery of metallic values (Gorgia *et al.*, 1995). This study was developed for possible optimization of leaching parameters for the establishment of kinetic mechanism for subsequent zinc extraction and purification from the zinc ash leach liquor by hydrochloric acid solution. The effects of acid concentration and temperature on the zinc ash dissolution were carried out with detailed morphological characterization.

2. Materials and Methods

2.1 Materials

The spent galvanized zinc ash used for this study was obtained from Sparkwest Industries, Sagamu, Ogun State, Nigeria. Prior to the leaching experiments, the zinc ash sample was initially subjected to physical processing by grinding using acetone-rinsed mortar and pestle, sieved to yield three particle distributions: 0.03 mm, 0.06 mm, and 0.09 mm. Unless otherwise stated, the particle size 0.03mm was used for all experiments in this study. Polished thin section of the 0.03 mm size was prepared and observed under the optical microscope (Rath *et al.,* 2003). The characterization of the raw galvanized zinc ash and the selected residues after optimal leaching were appropriately carried out by Scanning Electron Microscopy (SEM) and Electron Diffraction Spectrophotometry (EDS), respectively including the X-Ray Diffraction (XRD) for testing the material purity. All chemicals used were of analytical grade and de-ionized water was used for preparing all solutions.

2.2 Leaching tests

The leaching experiments were performed in a 250 ml glass reactor equipped with a mechanical stirrer. A leaching solution of 100 ml of appropriate HCl solution with the desired quantity of ash powder was used for each experiment. The stirring speed was maintained at 200 rpm, and thus enabled adequate dispersion of the sample particles without loss of the solution. The leaching temperature was evaluated in the range of 27 to 80 °C and the acid concentration between 0.1 and 4.0 mol/L were studied. At some selected time intervals, marking the end of the leaching process, the percent of the zinc ash dissolved was evaluated based on the leach liquor analysis. The material balance for zinc ash leaching was checked from the initial leached residue sample. Satisfactory mass balance was obtained (Baba *et al.,* 2020; Ha *et al.,* 2010; Rath *et al.,* 2003).

The HCl solution (2.0 mol/L) with highest zinc ash dissolution was used to investigate the effect of reaction temperature. At optimal conditions, estimation of activation energy (Ea) and reaction order for the dissolution process were achieved through appropriate Arrhenius plots for better understanding and prediction of kinetic mechanism for subsequent beneficiation studies. The dissolution reaction is consistent with the following stoichiometry:

$$ZnO + 2HCl \rightarrow ZnCl_2 + H_2O \qquad (1)$$

3. Results and discussion

3.1 Characterization of dry zinc ash powder

The results of chemical analysis by X-ray fluorescence (XRF) gave Zn (87.14%), Cu (6.13%), Mn (0.23%), Cr (0.03%), Pb (0.13%) and Co (0.021%). It is pertinent to note that Zn and Cu showed expressive amount and account for 93.27% of the total mass of the sample. Other elements or gangues not detected by XRF are likely to contain silica and they accounts for the remaining 6.15%. According to the X-ray spectrum (Fig. 1), *Zincite* (ZnO) is the main zinc compound detected in the dry powder along with *Tenorite* (CuO) which may be admixture of cuprite (Cu_2O). Other compounds found by XRD which occurred from low to trace levels are *Hausmanite* (Mn_3O_4) and *Piattnerte* (PbO).

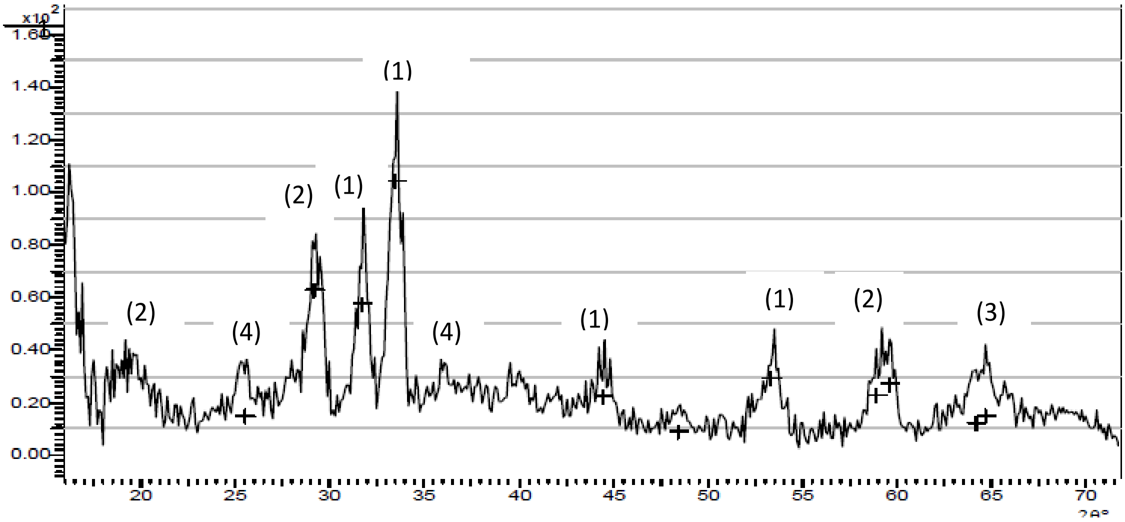

Figure 1: Xray diffraction of the zinc ash powder with various compounds detected. The Joint Committees on Powder Diffraction Standard (JCPDS) File Numbers for peaks attribution are in curl brackets: [1] ZnO: {05-0664}, [2] CuO: {05- 0667} / Cu_2O: {05- 0661}, [3] Mn_3O_4 : {24-0234}, [4] PbO: {25-0447}.

Photographic examination of the dried sample is depicted in Fig. 2. The plain section shows a silver grey surface **(A)** with black patches on it connotes zinc mineral with presence of associated gangue species including silica (SiO_2) **(B)**.

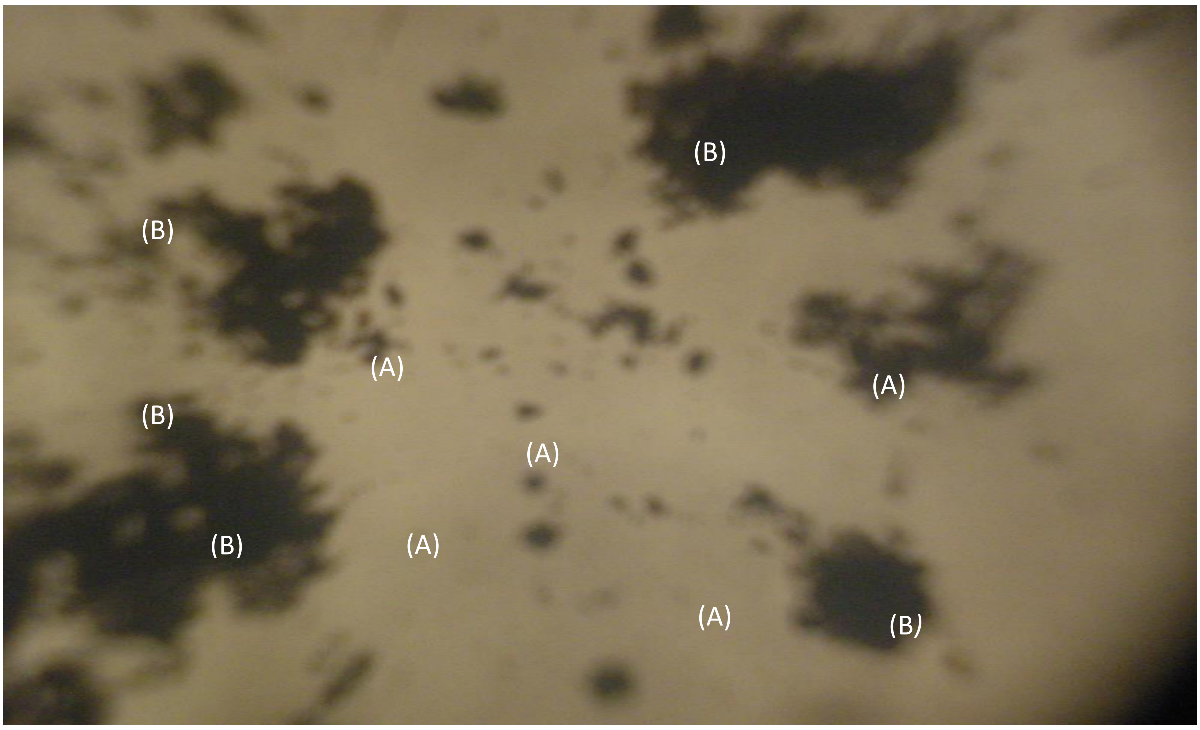

Figure 2: Photographic examination of zinc ash powder.

The morphological analysis by scanning electron microscopy (SEM) of the unleached zinc ash surface is depicted in Fig. 3. Here, the unleached powder showed a tough and porous surface generated by galvanization. Further, the quantitative analysis by EDS is depicted in Fig. 4. The EDS of the raw galvanized zinc ash gave zinc (97%), oxygen (2%) and carbon (1%) = 100%.

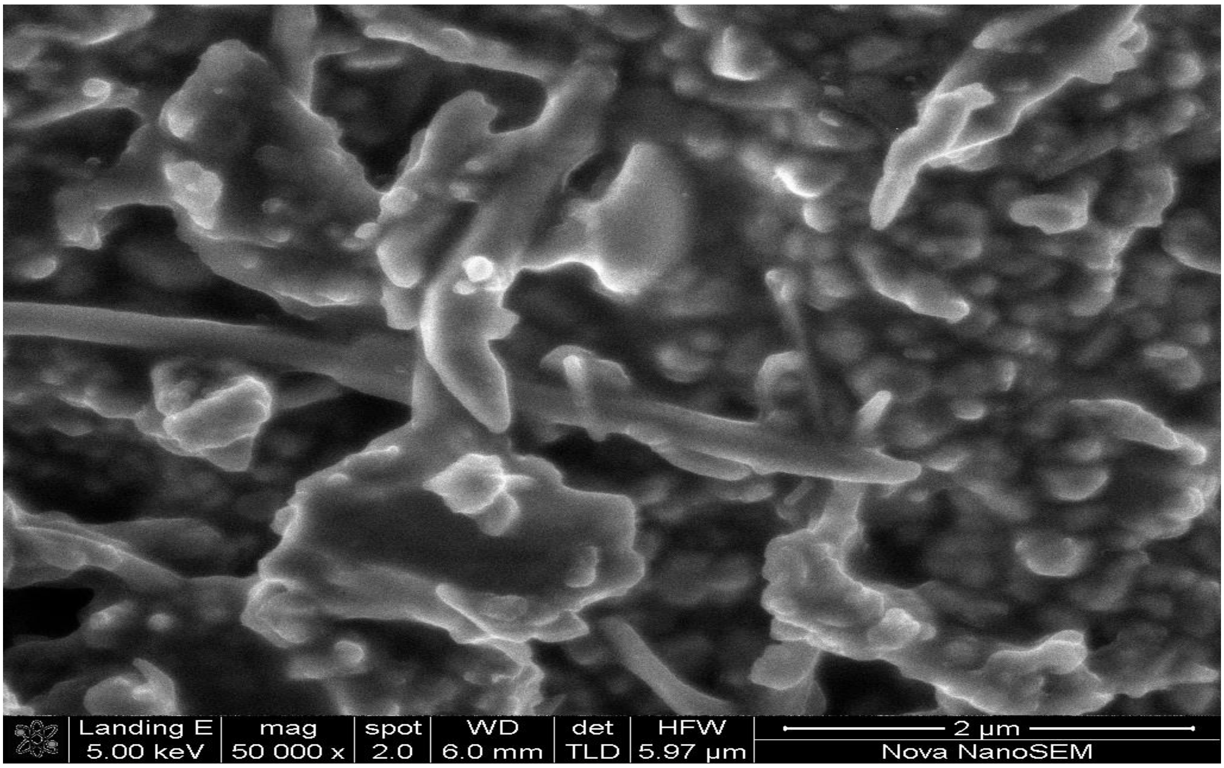

Figure 3: Morphological structure of zinc ash

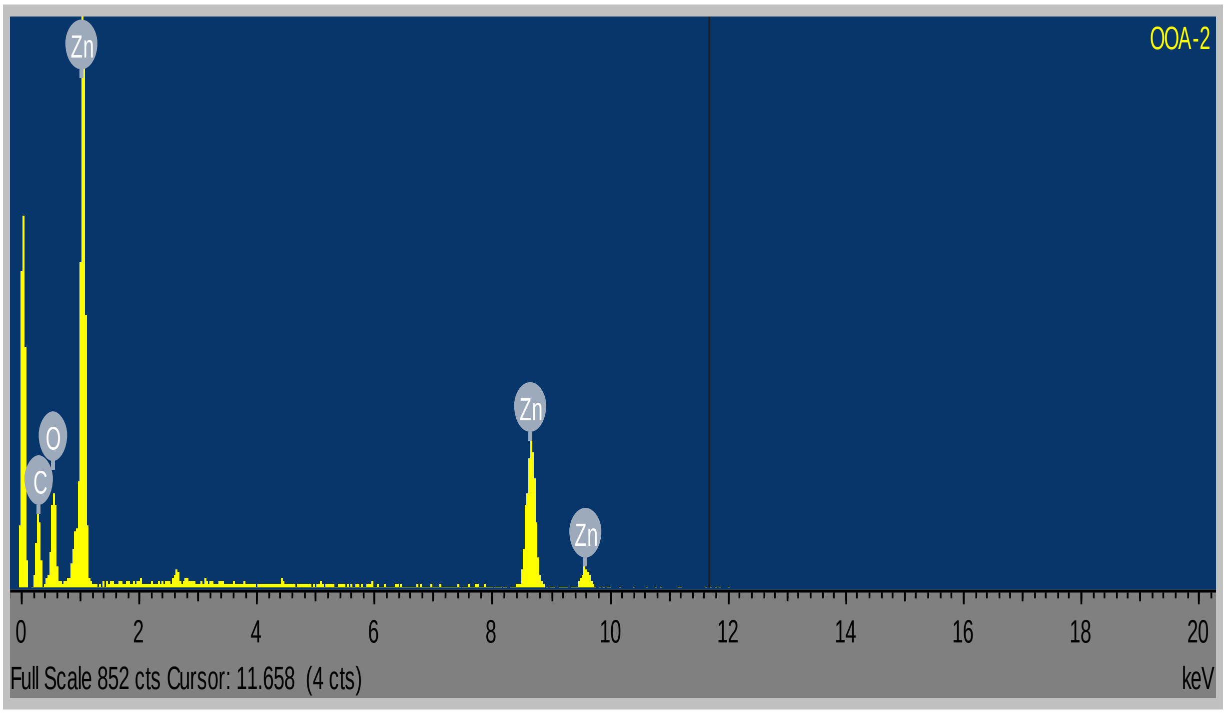

Figure 4: EDS of the raw zinc ash powder by EDS.

powder by SEM.

3.2 Leaching studies

3.2.1 Effect of HCl concentration

The effect of HCl concentration on the rate of zinc ash dissolved has been examined for particle size 0.03 mm. The result of the zinc ash dissolved as a function of contact time at various HCl concentrations are presented in Fig. 5.

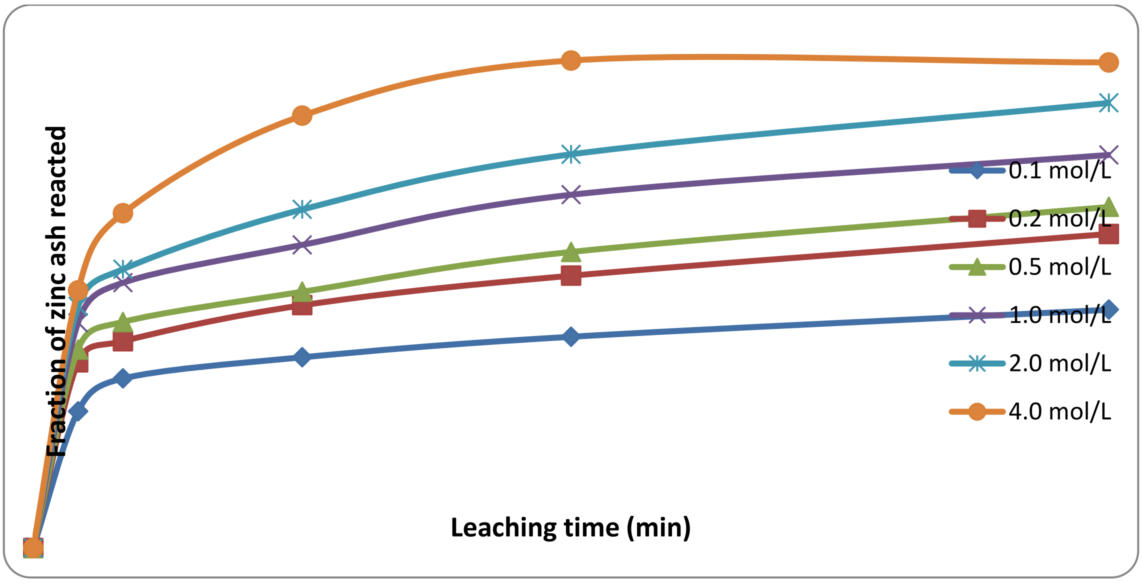

Figure 5: Fraction of zinc ash dissolved vs leaching time at different HCl concentrations.

From Fig. 5, it was observed that an increase in HCl concentration leads to increasing amount of galvanised zinc ash reacted at various contact times up till 120 minutes, respectively. Hence, concentration of the leachant apparently has a significant effect on the leaching of the dry powder in order to release zinc ion (Barakat, 2003). For instance, dissolution by 4 mol/L HCl solution at temperature of 55 ^{0}C at 60 and 120 minutes gave 75.9% and 75.6%, respectively. These values are almost equal and these affirmed that dissolution has reached optimal at this concentration. Further, increase in acid concentration beyond 4 mol/L apparently decreases the dissolution rate due to possible precipitation phenomena (Baba *et al.*, 2009) as evidenced from the dissolution data of 60 and 120 minutes, respectively. Hence

4 mol/L HCl was fixed as optimal acid concentration and was used for optimizing other leaching parameter such as reaction temperature.

3.2.2 Effect of temperature

It has been reported by several workers that increase in reaction temperature of a given material promotes or increases the dissolution of that material (Adebayo *et al.*, 2003; Gogia *et al.*, 1995). Thus, experiments were carried out to study the effect of temperature on the rate of zinc ash powder dissolution under temperatures between 27^0C and 75^0C by 4 mol/L HCl solution. It was observed that where about 43.6% to 98.5% dissolution was achieved within 120 minutes respectively (Fig. 6).

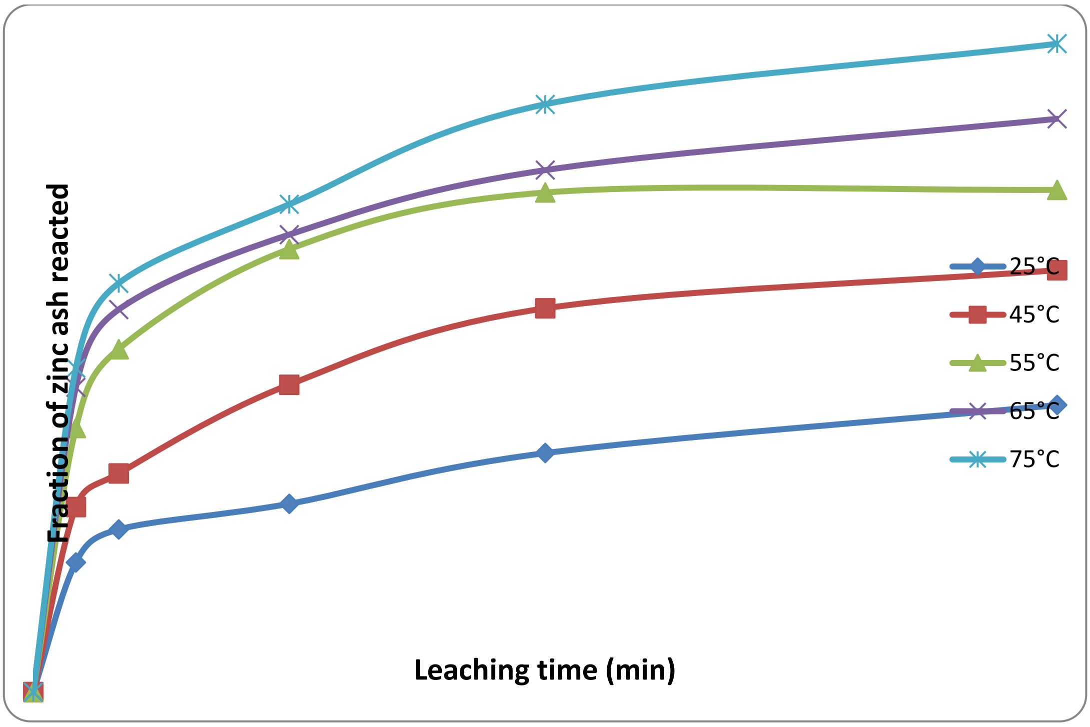

Figure 6: Fraction of zinc ash dissolved vs leaching time at different temperatures

3.2.3 Characterization of residual product at optimal leaching

The SEM morphological characterization of the leached products at the beginning (27 °C) as compared to optimal leaching temperature (75 °C) within 120 minutes by 4 mol/L HCl solution where about 43.6% and 98.5% dissolution were recorded are shown in Fig. 7a and 7b, respectively.

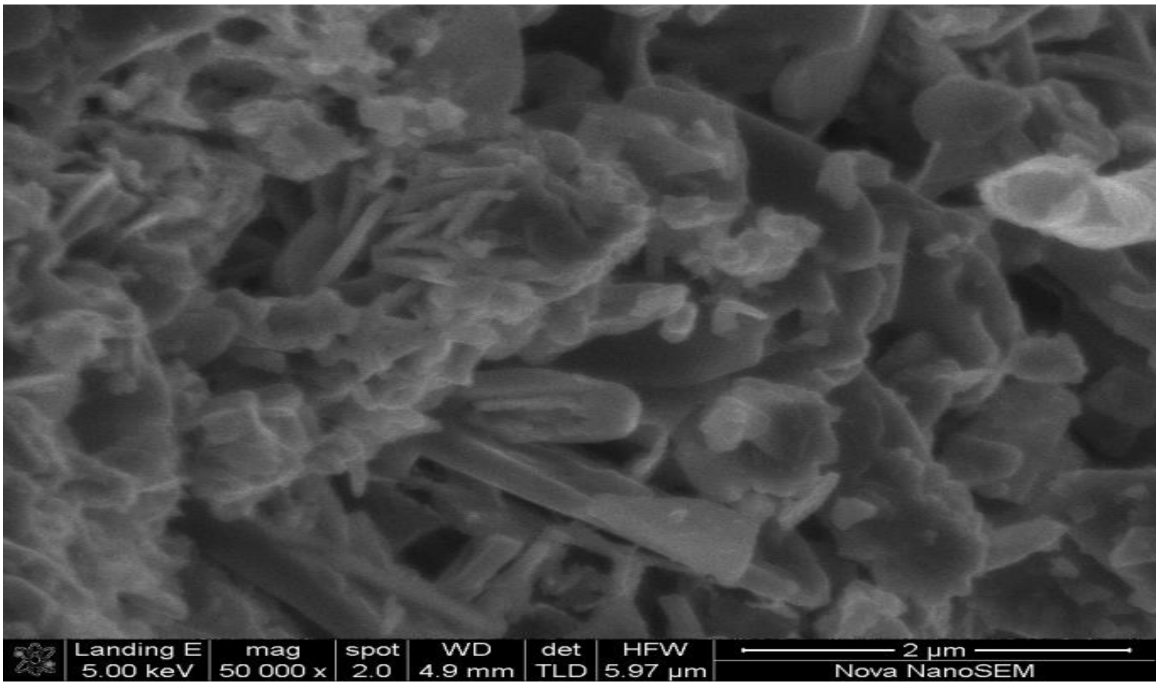

Figure 7a: Leach residue: 27 °C, 120 min.

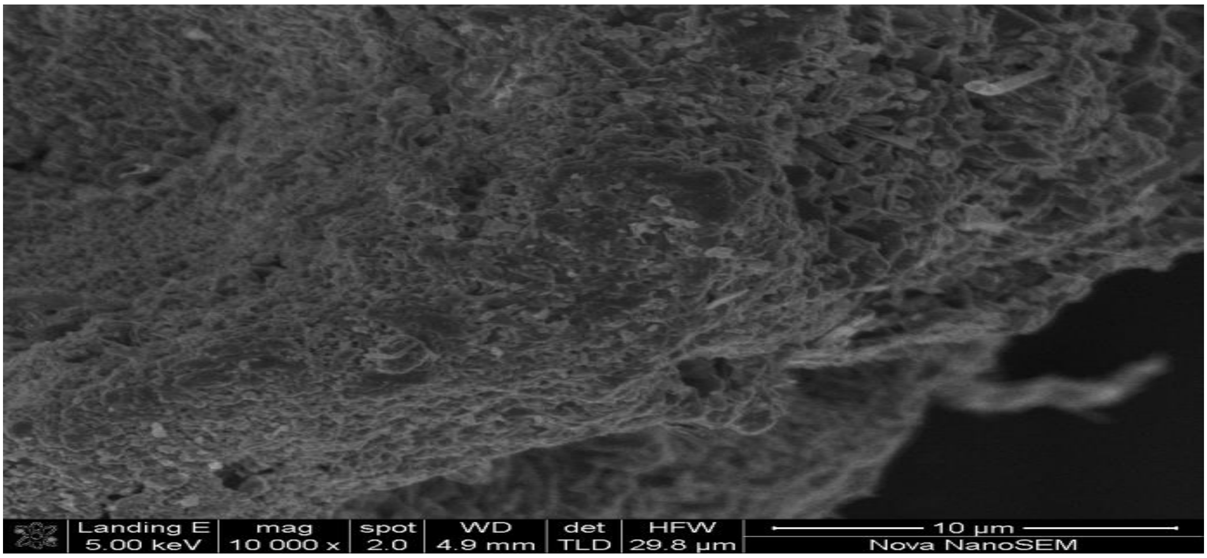

Figure 7b: Leach residue: 75 °C, 120 min.

It is evident that the leached sample surface shows relatively smooth network (Fig. 7a) with clusters of the porous surface and roughness, bump shape (Fig. 7b) observed and indicates the possible presence of silica as the un-leached product. The quantitative examination of these products at optimal condition by EDS is depicted in Fig. 8.

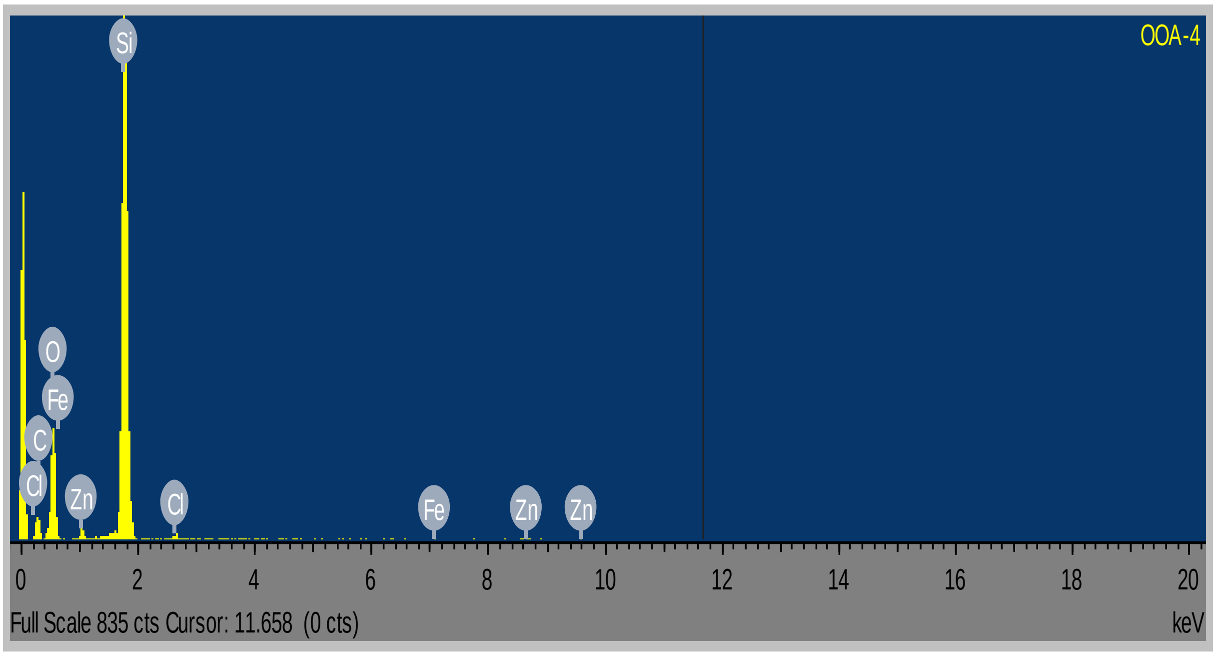

Figure 8: Quantitative examination of the residual product at optimal leaching by EDS.

From Fig. 8, the composition of the residual product consists of silicon (95%) with admixtures of other impurities such as iron, oxygen and carbon occurred from low to trace levels (<5%). This shows that substantial amount of zinc ash powder containing zinc has been quantitatively dissolved in HCl solution when compared to the initial zinc ash sample prior to beginning of the reaction (Fig. 4).

3.3 Discussion

3.3.1 Dissolution kinetic analysis

For better understanding of the dissolution mechanism, the rates of zinc ash reacted in this study were assessed with the shrinking core model based on the assumption that the zinc ash powder is a homogeneous spherical solid phase (Levenspiel, 1972). The kinetic analysis was tested according to the unreacted core model which apparently account for the diminishing surface area of the solid. If a reaction such as:

$$aA_{\text{fluid}} + bB_{\text{particle}} \rightarrow \text{Products} \tag{2}$$

is controlled by diffusion through semi-permeable product layer, then the dissolution mechanism is given as:

$$1 - 2/3\ \alpha - (1 - \alpha)^{2/3} = k_1 t. \tag{3}$$

However, if the reaction given in equation (2) is chemically controlled, the rate equation becomes (Adebayo *et al.*, 2003):

$$1 - (1 - \alpha)^{1/3} = k_2\, t, \tag{4}$$

where α is the molar fraction of zinc ash reacted; t, the leaching time (min.); k_1, k_2 are apparent reaction constants for the diffusion and chemical reactions, respectively. It is important to note that data in this study were appropriately fitted to the model equations (3) and (4); and found that the model equation (3) gave better average correlation of approximately 0.92 as compared to 0.64 obtained from using equation (4). Hence, the model equation (3) was used to evaluate the experimental data of Fig. 5 to obtain the following plots (Fig. 9) used in determining the reaction order for the dissolution process.

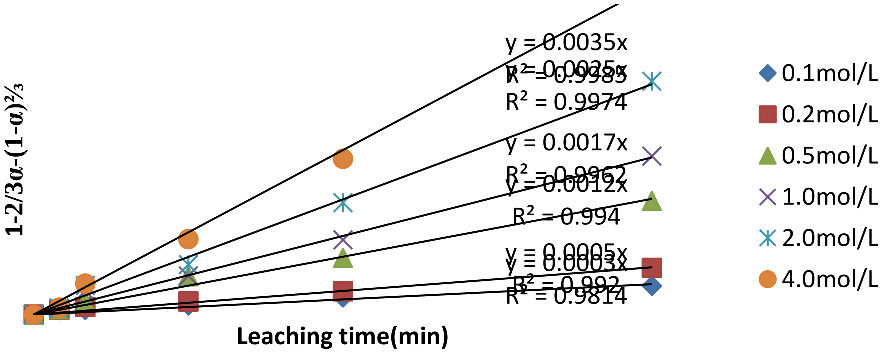

Figure 9: Plot of $1 - 2/3\alpha - (1 - \alpha)^{2/3}$ vs leaching time at different HCl concentrations.

From Fig. 9, the apparent rate constants, k, were calculated from slopes of the straight lines. By using these values, the plot of lnk vs ln[HCl] was made (Fig. 10), where a reaction order of 0.72 ≈ 1 was obtained from the Arrhenius plot. This slope is proportional to the reaction order for the dissolution process and apparently indicates that the reaction is a first order with respect to HCl concentrations between 0.1 mol/L and 4.0 mol/L, respectively.

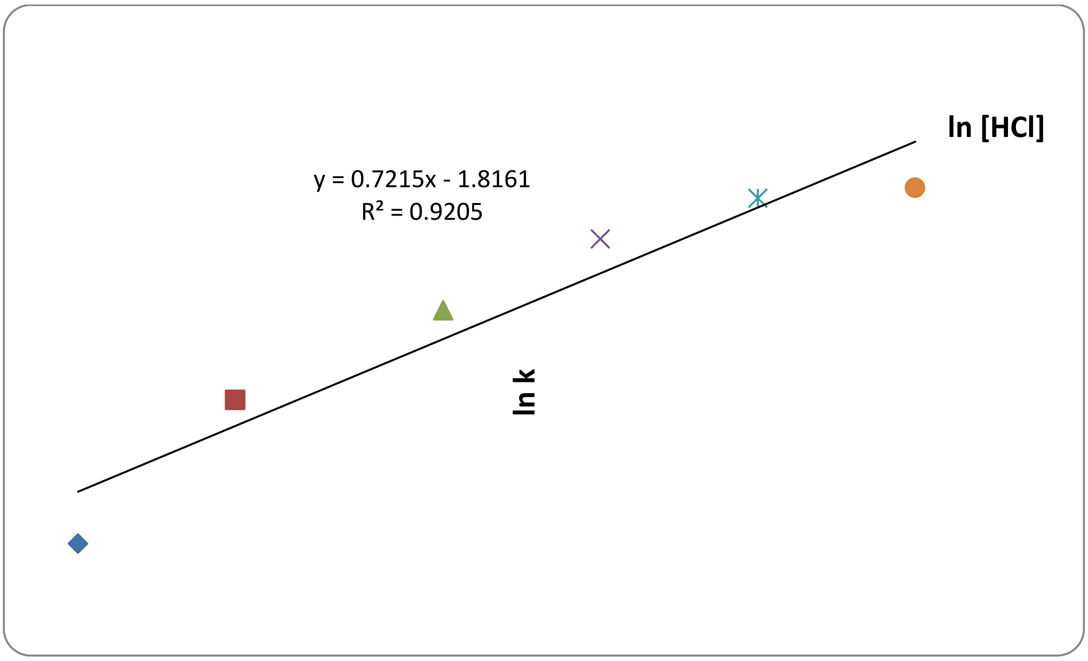

Figure 10: Plot of lnk vs. ln[HCl].

Also, the linearization of the experimental data of Fig. 6 according to equation (3) as previously established was carried out to obtain straight line reactions. Evaluation of the apparent rate constants at different temperatures were obtained and the values were used in the construction of the following Arrhenius relation (Fig. 11) from which the activation energy, E_a of 25.96 kJ/mol was calculated for the dissolution process. This value of E_a suggested that diffusion reaction at the zinc surface was the rate determining step in the dissolution of zinc ash powder by 4 mol/L HCl solution at a given temperature. The result of this study proved more economical when compared to other reported work by Souza et al. 2007 on zinc containing material where high value of E_a of 51.9 kJ/mol was obtained, for example.

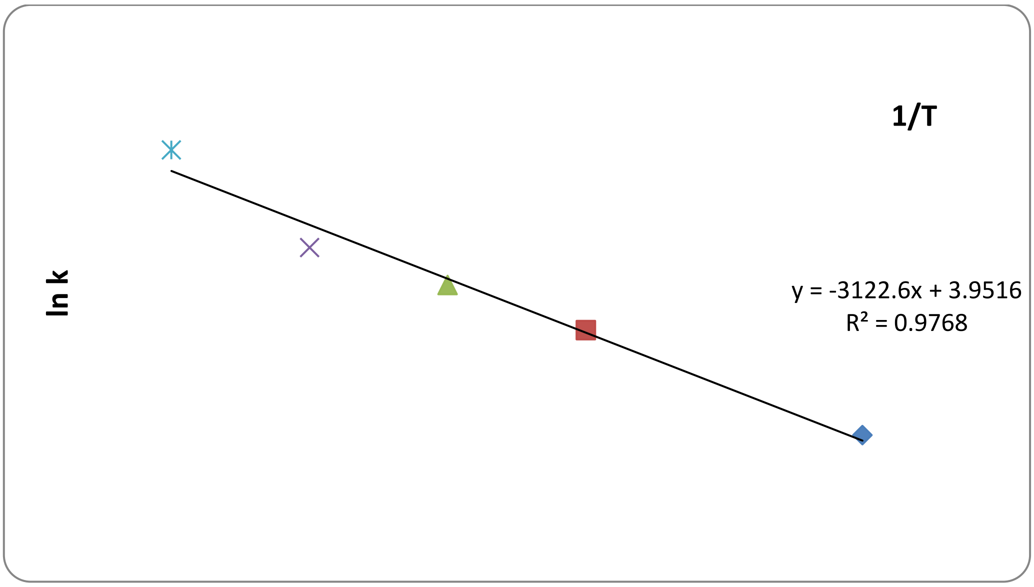

Figure 11: Activation energy Arrhenius plot of lnk vs 1/T.

4. Conclusion

Experiments on the extent of dissolution of zinc ash powder in hydrochloric acid solution has been examined and observed to depend on acid concentration and reaction temperature. At optimal leaching conditions, (4mol/L HCl, 75 °C), the extent of dissolution reached 98.5% within 120 minutes. The kinetic analysis for the dissolution process was found to follow a shrinking core model with the diffusion control reaction as the rate determining step. The value of the activation energy (25.96 kJ/mol) supported the proposed mechanism. Morphological characterizations before and after leaching were provided as the supportive evidence.

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