Characterization of dross and its recovery by sulphuric acid leaching

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Abstract. This paper reports the characterization of dross from galvanizing process and its recovery using acidic leaching method. The diffraction profile of dross showed identical peaks with that of ZnO. The X-ray Fluorescence (XRF) analysis identified the content of following metals: Zn, Fe, Mn, Ga, Co, and W. The thermal behaviour examination revealed the existence of some volatiles within the initial sample. The acidic leaching at various concentrations of sulphuric acid was conducted to determine the optimum concentration for zinc recovery and the highest yield of zinc sulphate. It is concluded that the optimum concentration of H₂SO₄ for this kind of dross is 4 M with 71.9% yield of ZnSO₄. The result of leaching process was confirmed by infrared spectrum, where various absorptions corresponding to SO₄²⁻ and Zn-O bands were observed.

1. Introduction

In general, zinc can be obtained from primary source (i.e. natural mineral rocks) and secondary source (e.g. industrial waste such as galvanizing, smelting, and casting industries). Herein, the secondary source could be in the form of zinc ash, zinc dross, galvanizer dross, electric arc furnace dust (EAF Dust), and zinc flux. Regarding the content of metallic zinc, the galvanization process of metal sheet or metal tube can produce waste (in form of zinc ash, dross, and flux) with high zinc metallic content, e.g. 60 - 85% [1]. On the contrary, EAF Dust has low amount of remaining zinc species [2, 3]. Meanwhile, the highest content of zinc can be obtained from galvanizer dross with Zn and Fe content of 96% and 4%, respectively [4]. Those wastes can be recovered in order to obtain the alternative metal sources and to reduce environmental pollution.

Recently, study on waste recovery focuses on the development of novel and effective recovery process which is also environmental friendly. Basically, this can be carried out using either pyrometallurgy or hydrometallurgy approach. Pyrometallurgy uses thermal treatment to initiate chemical and physical transformations of metals species during recovery process. Unfortunately, this process requires high energy, costs, and pollution due to some mass loss during combustion stage [5, 6]. On the other hand, hydrometallurgy approach uses aqueous or organic solution which involves chemical reaction during the process [7]. This approach also generates some liquid pollutants. However, the handling is still much easier than that of the pollutant generated by pyrometallurgy approach. To date, various studies of hydrometallurgy approach have been conducted using various...
reagents such as hydrochloric acid [8], sulphuric acid [9], acetic acid [10], and sodium hydroxide with addition of hydrogen peroxide [11]. Yet, broad variation of waste sources still urges specific study of a recovery process to get industrially-optimized results.

Previous study conducted in The Warren Spring Laboratory of the UK concluded that zinc recovery from EAF Dust can be carried out using sulphuric acid with recovery percentage of 85 - 90% and 80% at pH of 2 and 3 - 4, respectively [12]. Nesbitt and Xue also reported that the use of sulphuric acid is best for metal recovery such as zinc, copper, and lead [13]. In another study, Nii and Hisamatsu found that sodium hydroxide can also be used for the recovery process. Yet, this lead to some difficulties during separation process [14].

This study is conducted to investigate the characteristic of the obtained dross and determine the laboratory-optimized recovery process of zinc as an initial basis for further scale-up recovery process. The study is expected to give some insights on the optimized recovery process of zinc from dross, especially from vehicle galvanizing industries.

2. Materials and methods

2.1. Dross preparation and characterization

Dross was obtained from vehicle galvanizing industries. Particularly, the material was produced during the burning process in electric arc furnace at temperatures more than 1400 °C under an oxidizing atmosphere. The initial structure and composition of the material was determined using X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF), respectively. Meanwhile, the thermal behaviour of the material was investigated using coupled Thermogravimetry - Differential Scanning Calorimetry (TG-DSC) analysis.

Based on the result of XRF analysis, the obtained dross contains zinc and iron of 96.25% and 3.60%, respectively. The remaining content, on the other hand, consists of trace metals such as gallium, manganese, tungsten, and cobalt, as described in table 1. The main impurity is iron, which could be in the form of hematite (Fe₂O₃), magnetite (Fe₃O₄), or zinc ferrite (ZnFe₂O₄).

To support the XRF results, XRD characterization was also conducted. As depicted in figure 1, the prominent peaks at 31.770°, 34.436°, 36.25°, 47.537°, 56.589°, 62.842°, and 67.944° are clearly observed, which is identical with the pattern of ZnO. This is in line with the XRF result, where the dominant species is Zn species in oxide form. However, another unidentified metal phase was also observed. This can be attributed to the poor crystallinity of the phase or the insignificant amount of the phase so it cannot reach the detection limit of XRD. It is then confirmed that the main species of the dross is zinc oxide.

Figure 2 shows the TG-DSC analysis result of dross under nitrogen atmosphere. At first, the water content of the sample evaporates as the temperature increases to 200 °C. The process is followed by the evaporation of volatiles as the temperature increases to 350 °C. Above this temperature, the first stage decomposition of dross begins, which is denoted by the increase of the heat flow. At this stage, the mass loss exceeds 12%. At elevated temperature (around 900 °C), the melting phase started to occur. In addition, the increase of mass can be observed at about 1200 °C, which is likely due to the atmospheric reaction of the sample.
2.2. Acidic leaching and iron precipitation
At first, the as-received dross was washed using hot deionised water to dissolve the water-soluble impurities (e.g. Cl⁻, OH⁻). The recovery process was carried out in two steps, which are acidic leaching using sulphuric acid and iron precipitation using ammonia. The high-grade sulphuric acid (Merck, purity 95-97%) was used to prepare 2 M, 4 M, 6 M, and 8 M sulphuric acid solutions for acidic leaching. The leaching step was conducted by dissolving 2 g of dross into sulphuric acid with a certain concentration at 60 °C for 2 hours, with solid to liquid ratio of 10:1. The leaching reaction can be described as follows [15]:

\[
\text{ZnO (s) + H}_2\text{SO}_4(aq) \rightarrow \text{ZnSO}_4(aq) + \text{H}_2\text{O (l)}
\]  

(1)

\[
\text{Fe}_2\text{O}_3(s) + 3\text{H}_2\text{SO}_4(aq) \rightarrow 2\text{Fe}_2(\text{SO}_4)_3(aq) + 3\text{H}_2\text{O(l)}
\]  

(2)

After solid-liquid separation, the remaining leaching solution was characterized using Atomic Absorption Spectroscopy (AAS). The iron species was precipitated by adding ammonia into the
leaching solution until pH of 9 is reached and ammonium jarosite \( \text{NH}_4[\text{Fe(SO}_4\text{)}_2(\text{OH})_6] \) is formed. After separating the ammonium jarosite, the solution that contains zinc sulphate was heated up until the water and \( \text{NH}_3 \) gas vaporized, while leaving out the clear zinc sulphate crystal. The obtained crystal was analyzed using Fourier Transform Infrared Spectroscopy (FTIR) analysis. FTIR measurement was conducted using KBr pellet in the wavelength region of 400 cm\(^{-1}\) to 4000 cm\(^{-1}\).

3. Results and discussion

3.1. Atomic Absorption Spectroscopy (AAS) analysis
The effect of sulphuric acid concentration on the yield of either zinc or iron was investigated using AAS analysis. Figure 3 reveals that highest yield of zinc and iron (i.e. 19600 ppm and 796 ppm, respectively) can be obtained when concentration of 4 M was used.

![Figure 3. Content of zinc (left) and iron (right) in leaching solution.](image)

3.2. Fe precipitation
The formation of zinc sulphate crystal from liquid is difficult to occur when iron is still present in the leaching solution. Thus, iron precipitation must be carried out beforehand. Iron can be precipitated by adding ammonia and iron sulphate into the leaching solution to initiate the formation of jarosite. First, ammonia will react with the excess of sulphuric acid as follows:

\[
2\text{NH}_4\text{OH (aq)} + \text{H}_2\text{SO}_4 (aq) \rightarrow (\text{NH}_4)_2\text{SO}_4 (aq) + 2 \text{H}_2\text{O (aq)} \]  

Ammonium sulphate is involved in iron precipitation after the completion of leaching reaction. At low concentration of sulphuric acid, the hematite and magnetite could not dissolve and remain as the residue. When the concentration is increased, zinc ferrite dissolves easily as the bond between zinc oxide and hematite breaks. After addition of ammonia, the formed iron sulphate is then reacted with ammonium sulphate, forming ammonium jarosite. Below is the detail of the reaction:

\[
3 \text{ZnO (s)} + 3 \text{Fe}_2\text{O}_3 (s) + 12 \text{H}_2\text{SO}_4 (aq) \rightarrow 3 \text{ZnSO}_4 (aq) + 3 \text{Fe}_2\text{SO}_4 (aq) + 12 \text{H}_2\text{O (l)} \]  

\[
3 \text{Fe}_2\text{SO}_4 (aq) + (\text{NH}_4)_2\text{SO}_4 (aq) + 6 \text{H}_2\text{O (l)} \rightarrow 2 \text{NH}_4[\text{Fe(SO}_4\text{)}_2(\text{OH})_6] (\text{s}) + 6 \text{H}_2\text{SO}_4 (aq) \]  

Giving overall reaction:

\[
3\text{ZnO (s)} + 3 \text{Fe}_2\text{O}_3 (s) + 6 \text{H}_2\text{SO}_4 (aq) + (\text{NH}_4)_2\text{SO}_4 (aq) \rightarrow 3\text{ZnSO}_4 (aq) + 2\text{NH}_4[\text{Fe(SO}_4\text{)}_2(\text{OH})_6] (\text{s}) + 6 \text{H}_2\text{O (l)} \]
The obtained zinc sulphate solution is then crystallized by evaporating the water at room temperature to get zinc sulphate crystal.

3.3. Fourier Transform Infrared Spectroscopy (FTIR) analysis

Figure 4 depicts the absorption of various functional groups of the zinc sulphate crystal. There is no single trace of N-H bond, which implies that the obtained zinc sulphate crystals are NH$_4^+$ ions free. The broad vibration band of symmetric stretching mode of –OH group from water molecule was observed at 3134.99 cm$^{-1}$. The wavelength region of 400 – 600 cm$^{-1}$ is the range for metal oxide vibration bands. Hence, the band observed at 460.07 cm$^{-1}$ is expected to be Zn-O vibration. The bands observed from 1000 – 400 cm$^{-1}$ are expected to be SO$_4^{2-}$ ion vibrations. The bands observed at 618.22 and 978.99 cm$^{-1}$ are attributed to the $\nu_2$ and $\nu_3$ of SO$_4^{2-}$ mode, respectively, while the bands observed at 1108.53 and 1397.99 cm$^{-1}$ are attributed to the $\nu_1$ of SO$_4^{2-}$ mode [16, 17].

3.4. Effect of concentration of sulphuric acid

Figure 5 plots the effect of sulphuric acid concentration on the yield of zinc sulphate. The %yield is calculated as follows:

$$\text{% Yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\% \quad [7]$$

The concentration of 4 M gives the highest yield of zinc sulphate crystal (i.e. 2.73 g or 71.9% of initial mass). This result is in line with the AAS result which estimates the optimum concentration of sulphuric acid for zinc recovery to be 4 M. The crystallization of zinc sulphate was expected to reach more than 80% after iron precipitation. This could be attributed to the insufficient crystallization time of zinc sulphate. Another issue is the possibility of precipitation of some dissolved zinc into ammonium jarosite. Hence, factors affecting the optimum crystallization time should also be investigated for further study.

4. Conclusions

The main compound of the dross is zinc oxide with iron as the major impurities. The dross can be recovered using sulphuric acid with optimum concentration of 4M, wherein the yield exceeds 71.9% (in the form of zinc sulphate crystal).
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