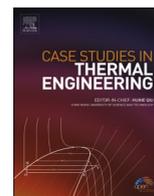




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The utilization of carbonized coffee in purifying zinc dross waste by pyrometallurgy method

Perdinan Sinuhaji^{a,*}, Agus Sukarto Wismogroho^{b,**}, Gokma Sahat Tua Sinaga^b,
Indra Kisanta Siregar^a

^a Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Sumatera Utara, Medan, 20155, Indonesia

^b Research Centre of Physics, Indonesia Institute of Sciences, Serpong, 15314, Tangerang Selatan, Banten, Indonesia

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ABSTRACT

The purification of zinc oxide has been carried out from zinc dross waste by pyrometallurgy method. The amount of zinc dross waste was cleansed by using aqua DM liquid with ratio of 1:10, then this amount was characterized using XRF to determine chemical compounds contained within the 90% of zinc dross waste, while impurity compositions of Fe, Al, and Mg were found. Hence, the amount of zinc dross waste was mixed to carbonized coffee within two ratios, i.e. 87.5%wt: 12.5%wt, and 75%wt: 25%wt. Carbonized coffee is obtained from carbonization of coffee grounds waste from the coffee industry. The mixture samples were then dissolved by aqua DM, followed by milling treatment by performing Planetary Ball Mill for 40 min, so that the muddy-phase was obtained. This sample was then filtered and it was heated inside an oven at 100 °C for 24 h to powder. The mixture powder of zinc dross and carbon was then placed in pyrolysis vessel at 1200 °C for 2.5 h. The obtained amount of zinc oxide powder was characterized by using XRF, and this has 98% of purity with impurities element i.e. Al₂O₃, Fe₂O₃, MgO, and SiO₂. Thermal testing was performed for ZnO sample by using DT instrument to investigate the effect heating to the reaction events. The analysis of DTA showed that the mixture sample of zinc dross and carbon had reaction sequences at 800 °C. The morphological analysis conducted by SEM and OM depicted that ZnO has agglomeration characteristics with uniformity shape among particles. The size of the particles is between 1900 μm and 9378 μm.

1. Introduction

Anti-corrosive coating on iron and steel can be done in electroplating, however the most common technique that has been used widely now is hot-dip galvanisation, or it is popular as galvanisation [1,2]. In galvanic industries, iron or steel materials products yield zinc ashes waste and zinc dross [3–5]. The number of zinc percentage obtained from these wastes is in between 10% and 27% from the total of zinc that has been used for the metal coating processes [4–6]. Industrial wastes produced from hot dip galvanic system are floating zinc which is termed as zinc dross [7,8]. The composition of this waste is floating particles on the zinc coating process in galvanic industries [6] which has immense percentage of zinc; S. A. Rahman has reported that the proportion of zinc in this dross waste is from 90% to 98%, with average percentage accounted for 96.25% [9–11]. Untreated zinc inside zinc dross waste is recyclable

* Corresponding author.

** Corresponding author.

E-mail addresses: perdinan@usu.ac.id (P. Sinuhaji), agussukarto@gmail.com (A.S. Wismogroho).

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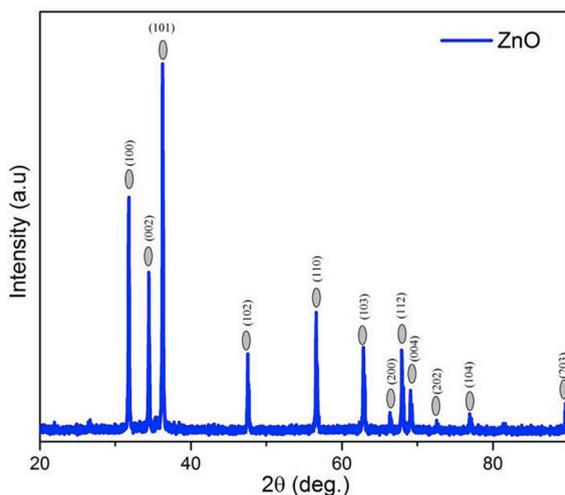
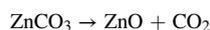
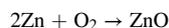


Fig. 1. Diffraction patterns of zinc dross.

material, so that it can be re-used as iron or steel coating, implying to one of the promising features [8,12–15].

Zinc dross waste treatment throughout hydrometallurgy method has been reported to be able in obtaining zinc oxide (ZnO), yielding for 62.45%, while in other study 81.73% of ZnO [9,13] has been obtained. The ZnO is produced throughout pyrolysis of zinc carbonate, which is described chemically in the following equation:



Zinc oxide can be produced from different methods, i.e.: (1) The oxidation of zinc oxide metal, (2) The reduction based on re-oxidation system, (3) The deposition of metal oxide and carbonate. Moreover, zinc oxide is also synthesized from industrial wastes from hydrometallurgy and pyrometallurgy methods. In hydrometallurgy method, acid and base solvent are performed, while in pyrometallurgy, high temperature heating process is carried out [10,16]. Zinc oxide is applied to several functions, such as ceramic glaze, lubricants, adhesive, sealants, and dried cell (battery) [9,17]. Although hydrometallurgy process and chemical stabilization method requires relatively low energy [18], pyrometallurgy is conducted in metal recovery with high potential, relatively ease of residual treatment, which is considered as promising technique to recycle and commercialization.

This research aims to investigate the effects of carbonized coffee as treatment agent in zinc dross waste for zinc oxide purification, and to identify the ZnO characterisation resulted from zinc dross purification by pyrometallurgy process. It is expected that zinc dross which has been exported as waste can be treated, so that the sale value can be increased or become one of the sources of ZnO to meet domestic needs.

2. Materials and methods

Sample materials used were zinc dross waste, which was resulted from Galvanic Industry at Cikarang. Glacial acetic acid, nitric acid, zinc standard solution and distilled water were analytical pure. This research was carried in three steps, and firstly, they were zinc dross particle reduction which is followed by extraction process, and finally was results analysis. In the first step, which was particle reduction, zinc dross was placed into a crusher, followed by sieving on 150 mesh. Next, samples were analysed to obtain its concentration by performing the Atomic Absorption Spectrophotometer (AAS). As many as 20 g of zinc dross was extracted by adding glacial acetic acid solution throughout open hydrometallurgy system. In this process, several variables were employed, such as time of extraction for 30; 60; 90; 120 min. Meanwhile, extraction temperatures were employed from 150 °C, to 170 °C, and 190 °C, and the concentration of glacial acetic acid was 20%. The precipitation resulted from the reaction was analysed by AAS instruments to determine the zinc concentration within zinc oxide. X-ray Diffraction was performed to identify the crystallinity of zinc oxide resulted. Instrumentations that were used in this study were crusher, filter, glasses apparatus, oven memmert, electrical heating Selecta multimat 5 N, magnetic stirrer Magsuda SM 60 N, timer Seiko, analytical balance Satorius BSA 2245-CW, stirrer, thermometer, Atomic Absorption Spectrophotometer (AAS) Shimadzu, X-Ray Diffraction (XRD) GPC type Emma X-Ray Fluorescence (XRF).

3. Results and discussion

3.1. X-ray Diffraction analysis of zinc dross element

The amount of zinc dross was purified by analysing the elements or compound composed within throughout XRD analysis. The

Table 1
Zinc dross composition analysed by XRF.

No	Elements	Percentage (%wt)
1.	Zn Dross	90
2.	Fe	4.09
3.	Mg	2.03
4.	Al	0.48

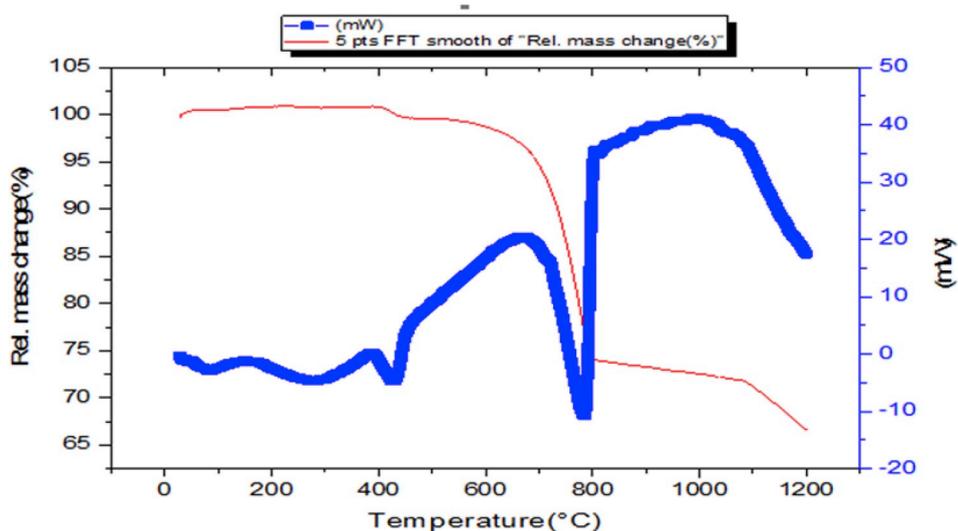


Fig. 2. DTA spectrum of zinc dross and carbonized coffee.

diffraction pattern of zinc dross is illustrated by following Fig. 1.

The diffraction pattern of zinc dross from Fig. 1 above showed that zinc dross waste contained ZnO. According to the analysis, the ZnO compounds were able to be purified. Based from Fig. 1, the single phase composition is ZnO. The secondary phase at 26.5° and 35° shows the presence of other compositions.

3.2. X-ray fluorescence element analysis

The analysis of element from zinc dross was performed by using x-ray fluorescence (XRF). The element compositions which are contained within zinc dross were demonstrated by the following Table 1 in form of percentage.

From Table 1 above, it can be seen that the analysis showed four elements within zinc dross waste. The main four metals are zinc (Zn) with 90 %wt, iron (Fe) with 4.09 %wt, magnesium (Mg) with 2.03 %wt, and aluminium (Al) with 0.48 %wt followed by small percentage of impurities. The presence of Fe and Mg impurities because this zinc waste is a waste from the iron galvanis plate which is melted, so that most of the Fe and Mg components in the galvanis plate come flying into liquid waste.

3.3. Thermal analysis of zinc dross with Differential Thermal analysis (DTA)

The thermal characterisation of zinc dross was performed by DTA to investigate the effect of heat expansion to the reaction events. From the analysis, the DTA data was demonstrated in ratio between real mass changes (%), heat flow (mW) to the temperature (°C). The zinc dross material was heated from room temperature (± 25 °C) to 1200 °C with heat rates around 1 °C per minute. The chemical reactions which were occurred can be recognized throughout the extreme changes of temperatures [19–23]. The sensors installed to the instruments detected the change of heat flow which indicates the exothermic and endothermic reactions.

Thermal analysis of zinc dross and carbonized coffee showed the alteration of real mass change (%) in form of spectrum peaks resulted from DTA machine. The change of spectrum peaks are caused by the extreme alteration of chemical reactions followed by temperature shifting of the mixture samples of zinc dross and carbonized coffee. The following Fig. 2 below illustrates the DTA analysis of zinc dross and carbonized coffee.

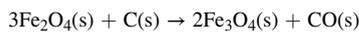
From Fig. 2 above, the mixture of zinc dross and carbonized coffee showed thermal activities. It can be interpreted from Fig. 2, thermal characteristics of zinc dross and carbonized coffee which was heated from 25 °C to 1200 °C had dehydrated event. The first exothermic reaction occurred at 392 °C, which is the reduction reaction of carbon, and oxidation reaction for ferrite oxide. The following equation shows the reaction:

Table 2
The composition of ZnO powder attached to thermocouple.

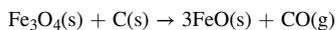
No.	Compounds	Percentage (%wt)
1.	ZnO	98.1
2.	Al ₂ O ₃	0.61
3.	Fe ₂ O ₃	0.1
4.	SiO ₂	0.03
5.	MgO	0.34

Table 3
The composition of ZnO powder attached on the surface of the wall.

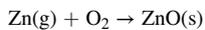
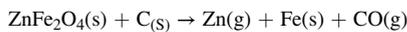
No.	Compounds	Percentage (%wt)
1.	ZnO	96.5
2.	Al ₂ O ₃	0.34
3.	MgO	0.34
4.	Fe ₂ O ₃	0.06
5.	SiO ₂	0.48



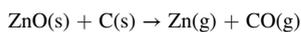
The reaction above was continuously followed by the loss mass around 3% at 392 °C. Moreover, at 410 °C, the endothermic reaction occurred which showed the end point of these first two reactions. Second exothermic reaction appeared at 670 °C which was indicated by second peak in Fig. 2. At this temperature, the reaction as it is illustrated by the following equation:



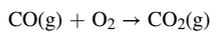
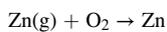
Above reaction expired at 791 °C. In this reaction, carbon transformed from solid to carbon dioxide gas, airborne to the air, and this reaction was indicated by the loss mass accounted for 25% in exothermic reaction. Furthermore, at 791 °C was the peak melting temperature implying to the starting reactions of ZnO in second endothermic reaction. Chemically speaking, the following equation demonstrates the formation of ZnO at 791 °C:



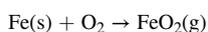
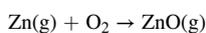
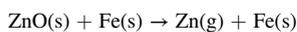
This reaction involved zinc ferrite (ZnFe₂O₄) and carbon solid was converted into carbon dioxide gas airborne. The Zn that came out exposed to heat was given oxygen gas, so the reaction produced pure ZnO. The exothermic reaction ended in between 791 °C to 1000 °C which is marked at the third peak on Fig. 2, and no mass was lost in this reaction. At the temperature of 1000 °C, the following reaction occurred:



The amount of Zn which was separated during the process was in oxygen condition, and no pristine ZnO was obtained. On the other hand, the carbon dioxide gas which was placed in oxygen condition produced no precipitation. The following reaction describes the reaction occurred in oxygen condition:



Continuously, at 1200 °C, the Zinc Oxide (ZnO) was yielded highly due to higher temperatures and the number of this metal oxide emerged, followed by a small number of Fe that reacted at 1200 °C. These two metals (zinc and ferrite) were flowed with oxygen gas to obtain the formation of pure ZnO, while in Fe there were no results, as in the reaction below:



In the above reaction zinc (Zn) turned into gas and oxygen gas was reduced from zinc oxide (ZnO) until the test ends in this reaction.

Table 4
The composition of residual waste powder.

No.	Compounds	Percentage (%wt)
1.	ZnO	85.2
2.	Fe ₂ O ₃	7.36
3.	SiO ₂	3.19
4.	MgO	2.63
5.	Al ₂ O ₃	0.8

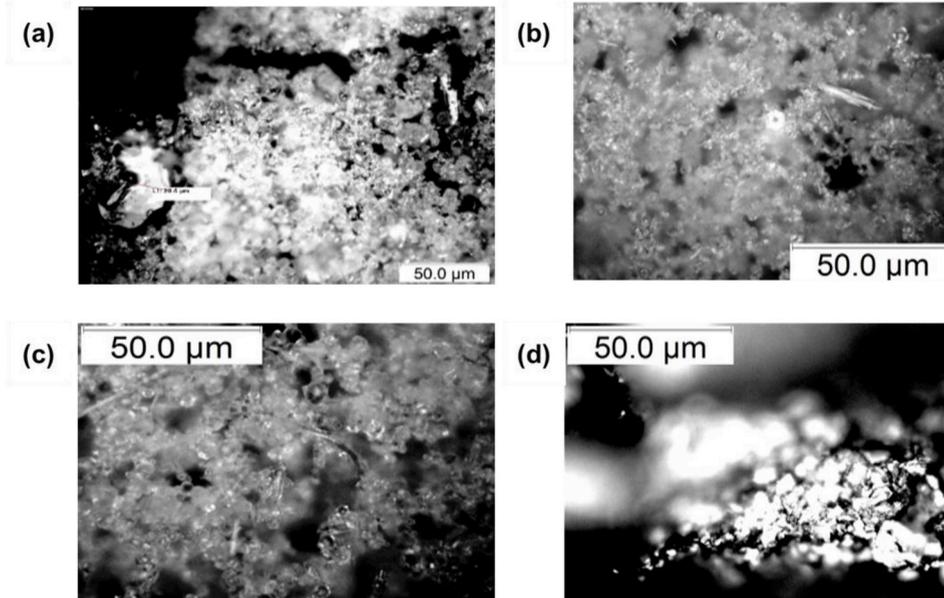


Fig. 3. Microstructure Image from Optical Microscopy of ZnO powder on (a) furnace cover tube, (b) furnace wall tube (c) thermocouple (d) residual waste.

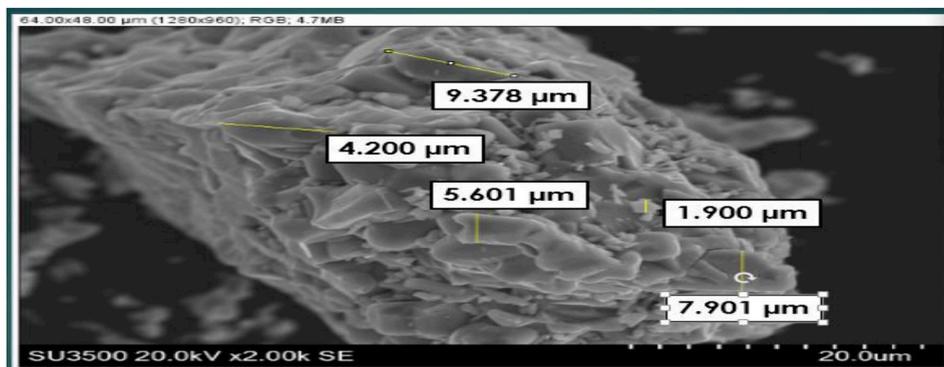


Fig. 4. ZnO microstructure image.

3.4. Analysis of zinc dross powder with XRF

Sampling preparation was done by mixing each material with a ratio of zinc dross powder and carbonized coffee powder, 87.5% wt: 12.5% wt. This mixture then was added as many as 200 ml of aqua DM, followed by dimilling process by using Planetary Bill Mill (PBM) for ± 40 min. The samples were place inside a furnace for 2.5 h at 1200 °C. The composition of ZnO powder elements attached to the thermocouple and attached to the wall as well as the residual combustion powder were analysed to determine the composition, which was shown in the following [Table 2](#), [Table 3](#), and [Table 4](#) below.

Based on the tables above, it can be seen that the largest percentage of weight comes from zinc metal (Zn). In [Table 2](#), zinc oxide

reached to 98.1%, in Table 3, zinc oxide reached 96.5%, and in Table 4, the residual waste powder had 85.2% of ZnO. On the other hand, the impurity that had the largest percentage were from Table 2, Aluminium oxide (Al_2O_3) accounted for 0.61%, in Table 3, silica (SiO_2) accounted for 0.48%, and from the combustion of ferrous metal (Fe_2O_3) reached 7.38%. The magnesium had the lowest percentage among the compositions.

The ZnO powder microstructure obtained can be analysed by using an optical microscope with 40 times magnification. Sample ZnO + Carbonized coffee which were placed at 1200 °C for 2.5 h were analysed. The zinc oxide powder attached at (a) cover the furnace tube, (b) wall of the furnace tube, and (c) thermocouple. On these two planes, some zinc oxide powder was agglomerated on the surface of the planes, which had non-uniformity. From Fig. 3, it can be seen that the light section of microstructure at the top is clumped powder so that the finer purity of ZnO results were found on the part of the powder. In the combustion residue, surface analysis was performed, the ZnO powder which had a low content was found due to the presence of other impurities content such as Fe_2O_3 , MgO, Al_2O_3 , and SiO_2 .

3.5. ZnO powder microstructure observation

The ZnO sample was observed by using SEM to analyse the microstructure, with magnification 2000 times. The following Fig. 4 displays the microstructure photographic image of ZnO sample.

From Fig. 4 above, it can be seen that the powder formed ZnO depicted non-uniformity features. All samples could be considered were agglomerated, so that the shape is non-uniform creating agglomerations. Particle size distribution of ZnO is in between 1900 μm and 9378 μm . Agglomeration among the ZnO powders and the presence of non-uniformity occurred due to the influence of polarity. The ZnO electrostatic power and the large energy on the surface of the particles which usually occurs during the synthesise process became one of the reason. The results of ZnO powder size measurements carried out by SEM had differences when it was compared by using PSA.

4. Conclusion

Based on the results and analysis, conclusions can be drawn, namely: zinc oxide (ZnO) from zinc dross has been successfully purified by pyrometallurgical process using furnaces at 1200 °C for 2.5 h. The use of carbonized coffee as a mixture in the purification of zinc oxide (ZnO) produced a fairly high percentage of yields, and it can purify ZnO through the reduction that actively began at temperatures of 1000 °C. The Differential Thermal Analysis/Thermal DTA/TG Gravimetry Analysis of Zn dross and Carbonized Coffee samples that have been given Heat Treatment showed that the Zinc Oxide started the reaction at 791 °C. The results of characterization with XRF obtained that purified ZnO powder from Zn dross and carbonized coffee samples in before and after pyrolysis at 1200 °C, for 2.5 h, 90%–98.1% purified results were obtained. Optical microscopy (OM) results and SEM-EDX test results on the morphology of ZnO powders had non-uniform shape and particle agglomerations with sizes from 1.900 μm to 9.378 μm .

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