INNOVATIVE PROCESSES FOR ZINC OXIDE RECOVERY FROM ELECTRIC ARC FURNACE DUST

[1]SUREERAT POLSILAPA, [2]CHANWIT THITITANAGUL

[1]Department of Materials Engineering, Faculty of Engineering, Kasetsart University, 50 Ngamwongwan Rd., Chatuchak, Bangkok, Thailand, 10900
[2]Interdisciplinary Graduate Program in Advanced and Sustainable Environmental Engineering, Department of Chemical Engineering, Faculty of Engineering, Kasetsart University, 50 Ngamwongwan Rd., Chatuchak, Bangkok, Thailand, 10900
E-mail: [1]fengsrsn@ku.ac.th

Abstract - Electric arc furnace (EAF) dust, iron scale, and eggshell are by products from steel making and food industries respectively.EAF dust is generated from steel making process and normally collected in the bag house filter during steel scrap smelting. Zinc ferrite ($ZnFe_2O_4$) is the main compound mostly found in EAF dust. It is a very stable compound led to difficult extraction of zinc. Innovative processes used to decompose zinc ferrite by using byproducts obtained from steel deformation and food industries were investigated in this study. Iron powder (for iron scale), lime and eggshell were materials selected as reducing agents to transform zinc ferrite to zinc oxide using low temperature pyrometallurgical processes. The EAF dust was mixed with each of the reducing agents and the effects of the molar ratio of zinc ferrite in EAF dust to each ofthe reducing agents, temperature and time on the decomposition were studied. It was found that 70% of zinc ferrite decomposition could be obtained at temperature as low as 600^{o}C for 2 hours and a molar ratio of zinc ferrite in EAF dust to iron powder of 1:3. The significant recovery of 80% of zinc ferrite decompositionalso could be achieved by lime and eggshell as reducing agents with the similar conditions of 800^{o}C to900^{o}Cdecomposition temperatures for 2 hours and a molar ratio of zinc ferrite in EAF dust to calcium oxide in lime or eggshell of 1:2. Iron scale and eggshell have performed the potential materials to be the reducing agentsin these innovative processes to transform zinc ferrite in EAF dust to be zinc oxide.

Keywords - Innovative Process, Zinc Oxide, Recovery, Electric Arc Furnace Dust

I. INTRODUCTION

The recycling process is an important step towards sustainability. Zinc is one of the most widely used elements due to its application in many industries especially in steel industry. As a result, zinc has been a depleted from the already limited resources of zinc ores (Zhang et al., 2011). Steel is used in many sectors of industry, such as construction, transportation, electronic devices, and machinery, and has played an essential role in the world economy for many years. In the steel making process, abyproduct called electric arc furnace (EAF) dust is generated during the melting of galvanized steel scrap at elevated temperatures. EAF dust is passed and collected in the bag house for approximately 10-20kilogramsper ton of steel production(Dutra et al., 2006). It has been reported that the dust normallycontains up to 40 wt% of zinc (Zn) (Orhan, 2005) and up to 50 wt% of iron (Fe) (Salihoglu and Pinarli, 2008). Most of zinc is found either as zinc ferrite ($ZnFe_2O_4$) or zinc oxide(ZnO). Thus, this dust has a great potential as a secondary source of material for zinc recovery andthe steel industry.

However, the dust also contains some hazardous elements such as lead (Pb), chromium (Cr), and cadmium (Cd) and is classified as a hazardous waste according to the United Stated Environmental Protection Agency (U.S. EPA.) who recommend its special management (Sofilic et al., 2004). Landfilling is the simplest ways to dispose of the dust (Donald and Pickles, 1996) but it could affectthe environment by leaching through to the groundwater. Therefore, recycling instead of disposal in to landfill should be encouraged (Hagni et al., 1991). Processes for the treatment and recycling of the zinc from EAF dust have been intensively studied for many decades.For pyrometallurgical processes, the dust is roasted at high temperatures, more than 1,200°C, to produce metallic zinc. However, high energy consumption and air pollution are the two maindisadvantage issues of these processes(Havlik et al., 2006). Hydrometallurgical processes use aqueous solutions for the recovery of metals from EAF dust. They have high operating costs and use large amounts of chemical reagents for treating liquid wastes that are in the form of acid or alkaline solutions.Inaddition, zinc ferrite inEAF dusthas a very stable structure resulting in low extraction by most solutions (Xia and Pickles, 1999).

Innovative processes by using by products from steel and food industries could be used to reduce zinc ferrite to zinc oxide. Iron scale, and eggshell are by products from steel deformation and food industriescontained rich of iron and calcium oxide (CaO) respectively.Zinc oxide is less stable than zinc ferrite and would make zinc extraction a much lower energy process.

In this research, three reducing agents were selected to use as reducing materials to transform zinc ferrite to zinc oxide. These reducing agents were iron powder,lime and eggshell. The first potential by product (waste) material was iron(iron scale), commonly found from steel deformation process. It

could be used as a reducing agent to decompose zinc ferrite to zinc oxide and iron (II) oxide (FeO) according to **equation 1**. In addition,the investigation of the effectiveness of eggshell, a food by product (waste) with large quantities disposed of in Thailand every year, as a possible reducing agent was obtained and compared to calcium oxide from lime. It was reported that the main phase at up to 94wt% found in eggshell was calcium carbonate ($CaCO_3$)(W.T. et al., 2006).Calcium carbonate is normally transformed to calcium oxide by heating. This calcium oxide could react with zinc ferriteand decomposedto zinc oxide and calcium ferrite ($Ca_2Fe_2O_5$) according to **equation 2**.

$ZnFe_2O_4 + Fe \longrightarrow ZnO + 3FeO$ **eq.1**

$\Delta G° = 28{,}576 – 42T$ J/mol

$ZnFe_2O_4 + 2CaO \longrightarrow ZnO + Ca_2Fe_2O_5$ **eq.2**

$\Delta G° = -32{,}114+11.329T+4.201x10^{-3}T^2-5.46x10^5/T - 3.373TlnT$ J/mol

The concept of "waste treats waste" was thus employed in this research. The focus, for thispaper, being the decomposition of zinc ferrite to zinc oxide at relatively low temperatures compared to the other pyrometallurgical processes in a heating or calcination process using a reducing agent which is, itself, a secondary product; iron scale or eggshell. In addition, the effectiveness of iron power and eggshell as reducing agents for the decomposition of zinc ferrite was also investigated.

II. MATERIALS AND EXPERIMENTAL METHODS

2.1 Experimental materials

The EAF dust employed in this work was provided by G Steel Public Company Limited, Rayong, Thailand. Iron powder was of two sizes of 10 µm and 200 µm. It was the analytically reagents from ACROS ORGANICS Company. Calcium oxide was also analytical reagent grade obtained from DAEJUNG Company. Eggshell was taken from food industries, then cleaned and manually ground with particle size of less than 220 µm.

Chemical composition and phases present in the EAF dust were investigated by X-Ray Fluorescent (XRF) at 30 kV and 1mA, Horiba XGT-5200 and X-Ray Diffractometer (XRD) with Cu Kα, Philip series X' pert over a 2θ range of 20°to 70°. Morphology was characterized by Scanning Electron Microscope (SEM) with 13.0 kV accelerated voltage, Phillips XL30.

2.2 Experimental Setup and Procedures

Three reducing agents were used in this study; iron powder, lime, and eggshell. Each of the reducing agents was mixed with the EAF dust and XRD performed on the mixes. This was so a direct comparison could be made to the mixes after heat treatment. The EAF dust and reducing agents were combined at three different mole ratios of zinc ferrite in EAF dust to the reducing agents of 1:1, 1:2, 1:3. The different mixes were then pressed at approximately 40 MPa, to form pellets with 15 mm. of diameter and 5 mm. of height and then subjected to heat in a furnace. The Gibbs free energy of equation 1 and 2 indicates thermodynamic potential that is minimized when a system reaches chemical equilibrium at constant pressure. Consequently, reaction temperatures in this research for each of the reducing agents could be obtained. The pellet mixed with iron powder was then heated inside the furnace, under argon atmosphere to prevent oxidation of iron powder, at different temperatures between 400°C and 600°C for periods of time from 0.5 hours to 2 hours. In case of the pellets mixed with lime and eggshell heating was done in air at temperatures ranging from 800°C to 1,100°C for periods of time from 2 hours to 6 hours. The resultant materials were then subjected to XRD to determine phase development and thus the effectiveness of the variables on the development of zinc oxide. Percentage reduction was calculated using the relative intensities of zinc ferrite from the XRD patterns.**Figure 1**shows the flowchart of the experiment.

III. RESULTS AND DISCUSSION

3.1 Morphology

Scanning electron microscope (SEM) showed that the morphology of the EAF dust was generally spherical. **Figure 2** shows that the dust is not thoroughly homogenous. The average particle size was approximately 0.5 µm. The particles appear porous.

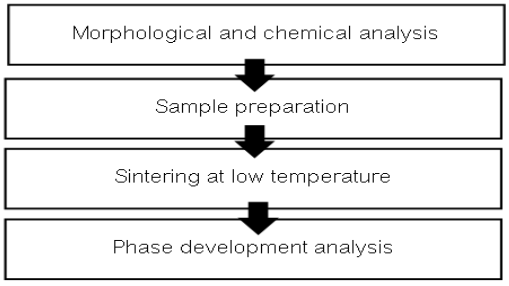


Fig. 1. Diagram of experiment

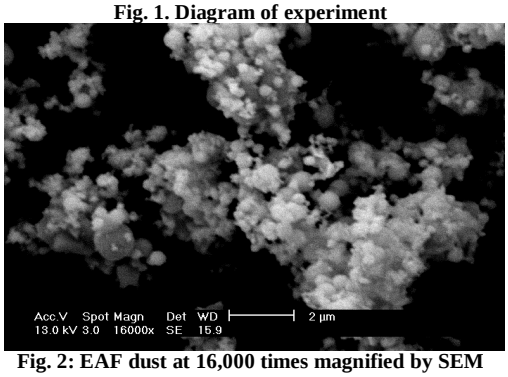


Fig. 2: EAF dust at 16,000 times magnified by SEM

3.2 Chemical composition and characterization of electric arc furnace dust

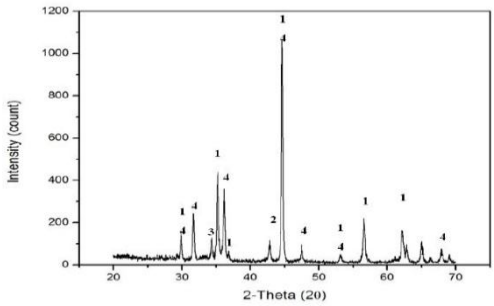
The chemical composition of the EAF dust was investigated by X-ray fluorescence (XRF). It was found that zinc and iron were the two major elements with 36.164 wt% and 25.561 wt% respectively as shown in the **Table 1**.X-ray diffraction determined these elements in the form ofzinc ferrite ($ZnFe_2O_4$) and zinc oxide (ZnO). For the eggshell, XRF indicated that calcium and oxygen were the two main elements at 69.290 wt.% and 28.989wt.% respectively. X-ray diffraction determined these elements were in the form of calcium carbonate ($CaCO_3$).

3.3Characterizationof electric arc furnace dust treated with iron powder

Figure 3 shows the phases present in the EAF dust – Fe powder mix, as determined by XRD. It could be seen that the main compound of the EAF dust was zinc ferrite ($ZnFe_2O_4$). **Figure 4**shows the results of EAF dustafter heat treatment withiron powderat a temperature of 600°C, an iron particle size of 10 µm, and a molar ratio of zinc ferrite in EAF dust to iron powder of 1:3. These parameters gave the optimum reduction conditions. It was found that the amount of zinc ferrite remaining tends to increase with increased temperature. However, after 2 hours at temperatures of 500°C and 600°C the efficiency of the reduction remained constant and giving more zinc peroxide (ZnO_2) formation than at 400°C due to the limitation of the reduction of zinc ferrite in EAF dust. The smaller iron particles increased the efficiency of the reaction. In the same way, when increasing the amount of iron powder to a 1:3 mole ratio of zinc ferrite in EAF dustto iron powder at 600°C gave the maximum on zinc ferrite decomposition at up to 70%.

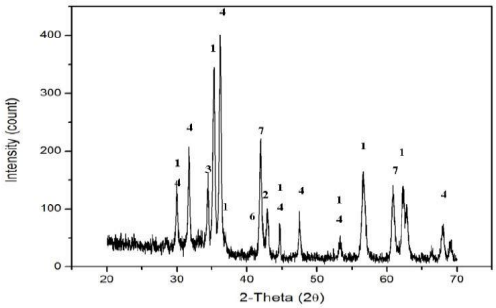
3.4Characterizationof electric arc furnace dust treated with lime

Figure 5 shows the phases present in the EAF dust – lime powder mix, as determined by XRD. It could be seen that the highest peak was calcium carbonate which is the chemical composition of lime and the main compound of the EAF dust was $ZnFe_2O_4$. **Figure 6**shows the diffractogram for the optimum conditions for this mix,800°C for 2 hours and a 1:2 mole ratio of zinc ferrite in EAF dusttolime giving approximately 80% zinc ferrite decomposed. Increasing temperature, roasting time, and quantity of time gave no real change in a conversion.



1-$ZnFe_2O_4$, 2-Fe, 3-Ca_3SiO_5, 4-ZnO_2, 5-Fe_3O_4, 6-ZnO, 7-FeO

Fig.3. Phase present, by XRD, for the EAFD mixed with Fe



1-$ZnFe_2O_4$, 2-Fe, 3-Ca_3SiO_5, 4-ZnO_2, 5-Fe_3O_4, 6-ZnO, 7-FeO

Fig.4. Phase development, by XRD, for the EAFD heat treated with Fe

Elements wt.%	Si	K	Ca	Cr	Mn	Fe	Cu	Zn	Pb	O
EAF dust	2.100	1.307	5.746	0.219	1.270	25.561	0.169	36.164	1.665	25.801
Eggshell	0.012	0.025	69.290	0.045	0.035	0.041	0.003	0.007	-	28.989

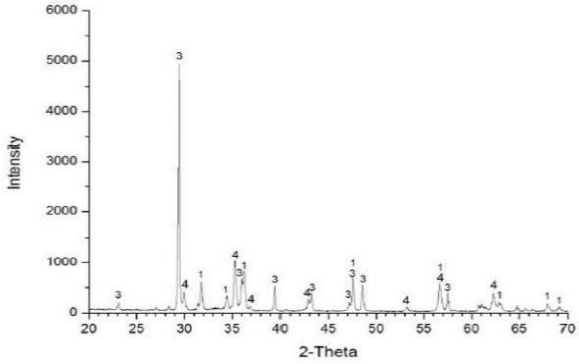
Table 1: Chemical composition of EAF dust by X-ray fluorescence

3.5Characterization of electric arc furnace dust treated with eggshell

The results of zinc ferrite decomposition in EAF dust by using eggshell as a reducing agent are depicted in **Figure 7 and Figure 8**.Zinc ferrite was decomposed to zinc oxide by approximately 80% under the optimum condition of 900°C, a roasting time at 2 hours, and a 1:2 mole ratio of zinc ferrite in EAF dust to eggshell. More details could be followed with Polsilapa et al., 2017.

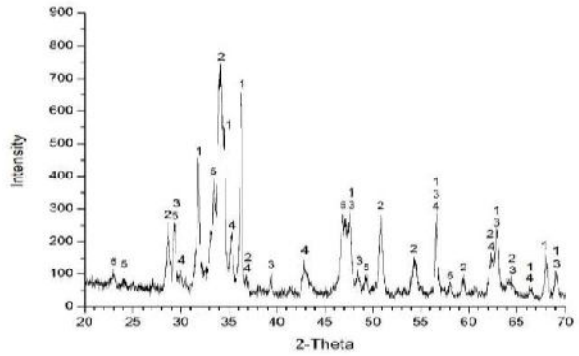
3.6 Summary

Zinc ferrite in EAF dust could be transformed by reducing agents mixed to zinc oxide at relative low temperatures compared to the other pyrometallurgical processes. It was found that significant recovery of zinc could be achieved at 600°C for 2 hours and a molar ratio of zinc ferrite in EAF dust to iron powder of 1:3, and 800°C by lime reducing agent and 900°C by eggshell reducing agent for 2 hours and a molar ratio of zinc ferrite in EAF dust to calcium oxide of 1:2. The decreasing of zinc ferrite intensity patterns obtained from XRD in **Figure 4, 6, and 8** confirmed the decomposition of zinc ferrite to zinc oxide.



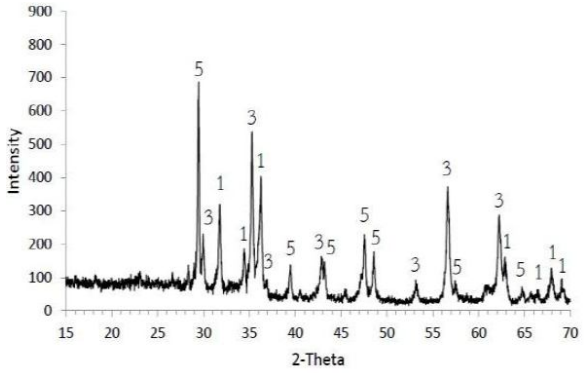
1-ZnO, 2-$Ca(OH)_2$, 3-$CaCO_3$, 4-$ZnFe_2O_4$, 5-$Ca_2Fe_2O_5$

Fig.5.Phase present, by XRD,for the EAFD mixed with lime



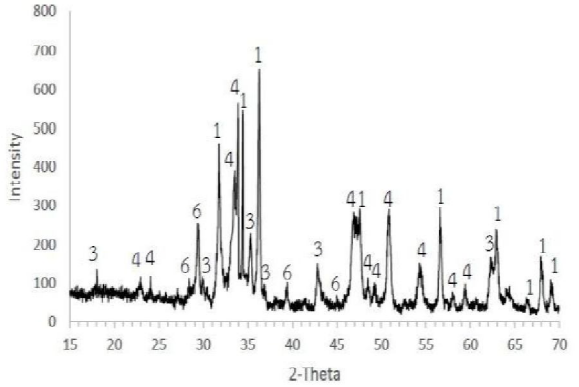
1-ZnO, 2-$Ca(OH)_2$, 3-$CaCO_3$, 4-$ZnFe_2O_4$, 5-$Ca_2Fe_2O_5$

Fig.6. Phase development, by XRD,for the EAFD heat-treated with lime



1-ZnO, 2-$CaSO_4$, 3-$ZnFe_2O_4$, 4-$Ca_2Fe_2O_5$, 5-$CaCO_3$, 6-CaO

Fig.7.Phase present, by XRD,for the EAFD mixed with eggshell



1-ZnO, 2-$CaSO_4$, 3-$ZnFe_2O_4$, 4-$Ca_2Fe_2O_5$, 5-$CaCO_3$, 6-CaO

Fig.8.Phase development, by XRD,for the EAFD heat-treated with eggshell

CONCLUSION

Iron powder as a reducing agent shows the efficiency in the zinc ferrite treatment with approximately 70% reduction led to using iron scale from the steel deformation industry as one of the secondary sources for waste treating reagent. Eggshell, also a waste material, was used in this innovative “waste treats waste” process approach to treat zinc ferrite in EAF dust. The level of zinc ferritein EAF dust, as high as 80% could be decomposed by using either lime or eggshell as one of the reducing agents, in addition similar optimum reduction conditions were achieved. Zinc oxide, the main product afterlow heat-treated process, was obtained. Zinc oxidealsocould be recovered byfurther processes to employ metallic zinc which is a very valuable metal for many industries. Iron scale, lime, and eggshell could all be found as the secondary materials from the steel and food industries and their using for treating the other waste materials to recover the valuable metals has been encourage.

ACKNOWLEDGEMENTS

The authors would like to express our thank to Piyakarnt Khamsriraphap, Nakarin Sriyowong, and Peerawit Kongmuang for their assistant in sampling preparation and experiments. Thanks also to G Steel public company limited for supporting the electric arc furnace dust and Department of Materials Engineering, Faculty of Engineering, Kasetsart University for supporting the equipment employed in this research. The authors are thankful to Faculty of Engineering, Kasetsart University for the funding support and the valuable comments from Dr. Greg Heness.

REFERENCES

[1] A.J.B.Dutra, P.R.P.Paiva and L.M.Tavares, “Alkaline leaching of zinc from electric arc furnace steel dust”, Minerals Engineering, vol.19, no.5, pp.478-485, April 2006.

[2] A.M. Hagni,R.D.Hagni and C. Demars, “Mineralogical characteristics of electric arc furnace dusts”, JOM, vol.43, no.4, pp.28–30, April 1991.

[3] D.K. Xia, C.A. Pickles, “Kinetics of zinc ferrite leaching in caustic media in the deceleratory period” MineralsEngineering, vol.12, no.6, pp. 693-700, June 1999.

[4] G. Orhan, “Leaching and cementation of heavy metals from electric arc furnac dust in alkaline medium”, Hydrometallurgy,vol.78, no.3-4, pp.236-245, August 2005.

[5] G. Salihoglu, V. Pinarly, “Steel foundry electric arc furnace dust management stabilization by using lime and Portland cement”, Journal of Hazardous Materials, vol.153, no.3, pp.1110-1116, 30 May2008.

[6] J.R.Donald, C.A.Pickles, “Reduction of electric arc furnace dust with solid iron powder”, Canadian Metallurgical Quarterly, vol.35, no.3, pp.255-267, 18 July 2013.

[7] S.Polsilapa, P.Jaithakul, , and T.Gulrueang , “Zinc Recovery from Electric Arc Furnace Dust Using Eggshell”

International Journal of Advances in Science Engineering and Technology. vol.5 iss.4 SpI Issue Part 3, pp 1-4, 2017.

[8] T. Havlik, M. Turzakova, S.Stopic and B. Friedrich, "Atmospheric leaching of EAF dust with diluted sulphuric acid", Hydrometallurgy, vol.77, no.1-2, pp.41-50,April 2005.

[9] T. Sofilić, A. Rastovčan-Mioč, Š. Cerjan-Stefanović, V. Novosel-Radović and M. Jenko, "Characterization of steel mill electric-arc furnace dust", Journal of Hazardous Materials, vol.109, no.1-3 pp. 59-70,18 June 2004.

[10] W.T. Tsai, J.M. Yang, C.W. Lai, Y.H. Cheng, C.C. Lin and C.W. Yeh, "Characterization and adsorption properties of eggshells and eggshell membrane" Technology Bioresource, vol.97, no.3, pp.488-493,February 2006.

[11] Y.Zhang, X. Yu and X. Li, "Zinc recovery from franklinitebysulphationroasting", Hydrometallurgy, vol.109, pp.211-214, October 2011.

★★★