Zinc Cementation of Heavy Metals from Electric Arc Furnace Dust Recycling Process Extracted by Hydrochloric Acid Solution

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Abstract

The benefits of hydrochloric acid for selective leaching electric arc furnace (EAF) dust has been reported by many authors. Low concentration hydrochloric acid can extract zinc which presence as the majority element contained in the EAF dust while leaving the iron in the solid residue. After extraction, there are also hazardous elements that were leached into an aqueous solution such as lead and chromium. These two elements could affect the efficient currency in the electrolytic cell on the electrowinning process for zinc separation from the solution. Thus, in this study, the cementation process was investigated using zinc powder in order to cement the solute heavy metals in the zinc-rich solution prior to the further process. Then optimal conditions were found to be; Zn/Pb 3.0 molar ratio, the temperature at 60°C, and rotation speed at 500 rpm for 10 minutes. The final solution was very high purity (Pb and Cr concentration < 2 ppm) which was suitable for zinc deposition to produce metallic zinc.

Keywords: Zinc; Cementation; Electric Arc Furnace Dust; Hydrochloric Acid; Heavy Metals

1. Introduction

Steel has played an important role in world economics for ages. Many industrial sectors, such as electronic devices, transportation, mechanic, and construction, use steel as a primary material. Most of the Thai steel makers use a large amount of scrap material that is melted in an electric arc furnace at a very high temperature (>1,700^{o}C) to produce new steel alloys. The electric arc furnace (EAF) dust, a by-product is generated and typically collected by bag house filter and accounts for approximately 1-2% of feedstock [1]. It is reported that the main chemical composition of EAF dust consists of three main compounds; zinc ferrite (ZnFe2O4), zinc oxide (ZnO), and iron oxide (FexOy) [2]. X-ray fluorescence analysis reveals trace elements, in the EAF dust, of lead (Pb), chromium (Cr), cadmium (Cd), and manganese (Mn) [3,4]. The zinc and other hazardous elements in the EAF dust arise from much of the scrap having been galvanized. Therefore, the EAF dust is classified as hazardous waste, and disposal of which requires specific management. However, the EAF dust has potential as a secondary source of zinc and iron. Previous research has reported on methods to extract zinc from the EAF dust [4-9]. Pyrometallurgy has been widely studied to treat electric arc furnace dust over the past years [3]. However, high energy consumption a result of the very stable structure of ZnFe2O4, and the emission of greenhouse gases are considered as two main drawbacks of this method. Therefore, the combination of pyro-hydro-metallurgy was investigated [6,8,9]. A low concentration of acid solution was reported to extract approximately 20 wt% of zinc from the EAF dust [5]. Other researchers have focused on ZnFe2O4 decomposition using reducing agents, such as carbon [6] and iron [7], to lower the energy consumption in the process. It was reported that approximately 70 wt% of zinc ferrite was transformed into zinc oxide [6-9]. However, calcium oxide and eggshell, which was consists of calcium oxide as the main chemical composition, have been found to be an economical reducing agent [8,9]. Lime and eggshell were employed by mixing with EAF dust in order to decrease the temperature, in the pyrometallurgical process, for the decomposition of the very stable ZnFe2O4. The product of ZnFe2O4 decomposition is ZnO, which is less stable and is extractable by weak acidic solutions [10,11]. Various acidic solutions have been studied, such as sulfuric acid (H2SO4), nitric acid (HNO3), and hydrochloric acid (HCl) [5]. Low concentrations of HCl selectively leaches zinc in solution leaving iron as solid residue [8]. Furthermore, using hydrochloric acid as a leaching solution also gives a benefit in further electrowinning processes. The solution, after zinc extraction by HCl, contains ZnCl2, which could be used outright in zinc deposition for metallic zinc or zinc alloy production. After the extraction process, it was reported that trace elements such as lead (Pb), copper (Cu), and cadmium (Cd) are extracted into the solution as well [1,5]. These elements could reduce efficiency in the electrowinning process in addition to environmental issues. The cementation process has been investigated for many applications, mainly for the removal of heavy metals from solution. A well-known cementation process is the Merrill-Crowe process for removal of gold from the solution [11]. The advantage of zinc cementation not only for removing heavy metals in the solution but recovery these valuable metals back in solid-state. Zinc was found to be a potential material for cementation due to its high galvanic series. It is good at reducing electrons from other metals [10,11]. The investigation of factors affecting zinc cementation of lead and chromium in low concentration hydrochloride acid solution prior to the electrowinning process and the kinetics involved are the main objectives of this research. Operating variables of the Zn/Pb stoichiometric ratio, temperature, stirring speed and cementation time were investigated in order to maximize the removal of heavy metals from the aqueous solution. Further removal after cementation could be provided by an electrowinning process to produce metallic zinc or zinc alloy for use as a primary material for many industries.

2. Experimental

2.1 Materials and Chemicals

Electric arc furnace dust, collected by baghouse filter, was obtained from 13 steel recycling factories in Thailand. Calcium oxide powder was obtained from DAEJUNG Ltd., South Korea, hydrochloric acid (37% w/v) from Merck KGaA Ltd., USA and zinc powder with a purity of 99.9% and an average size of approximately 1.27 μm from AJAX Finechem Ltd., Australia. HCl, zinc powder, and CaO were of analytical grade (AR) and laboratory-grade (LR).

2.2 Analytical instruments

The phases of the solid samples were analyzed by X-ray diffraction (XRD) (Philip series X'pert). The conditions for analysis were 2θ, 20^{o} to 70^{o}, the step size was 0.02, the present time 1 second, CuKα radiation was used. Chemical composition of the EAF dust, calcium oxide, and zinc powder was analyzed by X-ray fluorescence (XRF) (Horiba XGT-5200). Each sample was measured at 3 points and the average value of wt% by elements was calculated. The conditions were; live time: 100 second, processing time: P2, XGT Dia: 1.2 mm, X-ray tube vol: 50 kV, X-ray filter: 5 Element, Cell: Nonexistence. Atomic absorption spectrophotometer (AAS) (Perkin Elmer with GBC Avanta Ver 2.01) was used to analyze the chemical concentration of the aqueous solution. Each sample was measured three times and reported by the average value with part per million (ppm).

2.3 Methods

Three steps were used to extract zinc in this study. The EAF dust was firstly calcined using CaO as a reducing agent, in order to transform the $ZnFe_2O_4$ to ZnO. The resultant EAF dust was then leached by a low concentration HCl solution. The heavy metals now leached out underwent was cementation by zinc powder.

2.3.1 Calcining

The phases present in the EAF dust samples determined by XRD. They were then mixed with CaO: $ZnFe_2O_4$ molar ratio of 1:2 and hand pressed into a disk of approximately 1 cm radius and 0.5 cm thick. The EAF dust mixed with CaO was calcined at $800^{o}C$ for 2 hours in Modultemp furnace at a $10^{o}C/min$ heating rate. The resultant material was analysed by XRD to confirm phase transformation and comparative intensities of $ZnFe_2O_4$ to ZnO peaks.

2.3.2 Leaching

The calcined EAF dust was leached by HCl solution. The leaching was carried out based on the work of previous researchers. The solution was heated on hot plate- magnetic stirrer with temperature monitored by thermometer. The optimum conditions for zinc extraction have been found to be 0.5M, HCl, a solid/liquid ratio of 1:10, a solution temperature of $60^{o}C$, stirring speed of 900 rpm, and extraction time of 20 minutes [5][8]. Atomic absorption spectrophotometer (AAS) was used to determine the concentration of lead and chromium leached into the aqueous solution prior to the cementation process. After leaching, solid residue was dried and characterized by XRD to confirm ZnO extraction.

2.3.3 Cementation

Two liters of the leachant was separated into 100 ml. aliquots for each experiment. After analysis of the leachant to determine the concentration of the lead, zinc powder was added in the molar ratios (Zn/Pb) of 1.5, 3.0, and 4.5. The solution temperatures were varied between $40^{o}C$, $50^{o}C$, and $60^{o}C$. The effect of stirring speed was investigated at 100, 500, and 900 rpm. The measurement of Pb and Cr concentrations were taken initially, then after 10 minutes and 30 minutes cementation time.

3. Results and discussion

3.1 Chemical composition and phase analysis

X-ray fluorescence was used to analyze the chemical composition of the EAF dust, EAF dust mixed with CaO, zinc particle, and CaO powder. Table 1 shows a high concentration of zinc in the EAF dust at 32.163 wt%. As to be expected, there was a high level of iron available at 31.681 wt%. The concentration of the hazardous elements, lead and chromium, were found to be 2.602 wt% and 0.200 wt% respectively.

The phases present in the EAF dust before and after calcining were determined by XRD and the resultant diffractographs are shown in Figure 1 and Figure 2. Prior to calcination the major phase present is $ZnFe_2O_4$, the only other phase present being ZnO. After calcination, the major phase present is now ZnO. The $ZnFe_2O_4$ phase is still present but at a much reduced level. Indicating decom position of $ZnFe_2O_4$ to ZnO has taken place.

After HCl leaching to extract the zinc, the solid residue was analysed by XRD. Comparison of Figure 3 with Figure 2 shows the intensity of the ZnO peaks decreasing significantly, suggesting the leaching process is successful. Figure 3 shows the major peak to be that belonging to Fe_3O_4. Atomic absorption spectrophotometry gives the initial concentrations of Pb and Cr in the aqueous solution as 40.48 ppm and 0.12 ppm respectively.

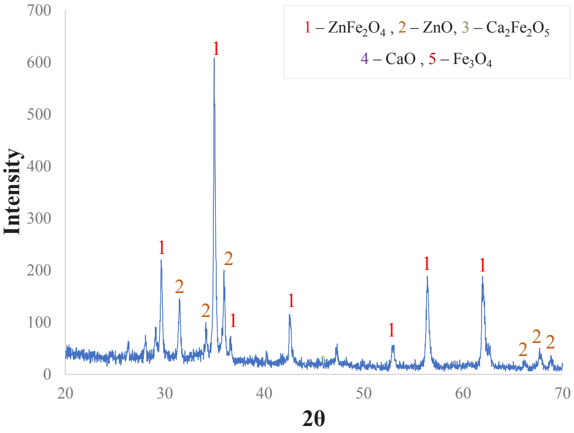

Figure 1 XRD pattern of EAF dust sample from factories

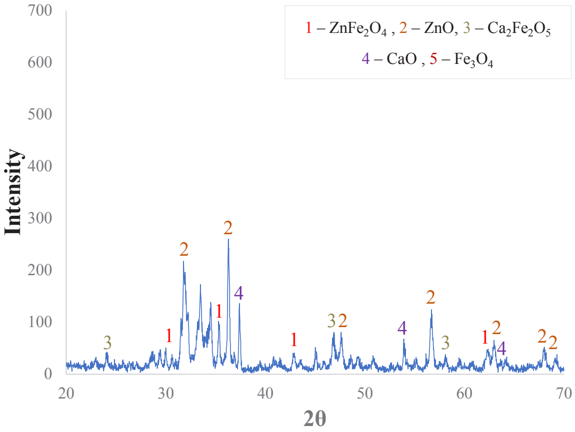

Figure 2 XRD pattern of EAF dust after treatment by CaO

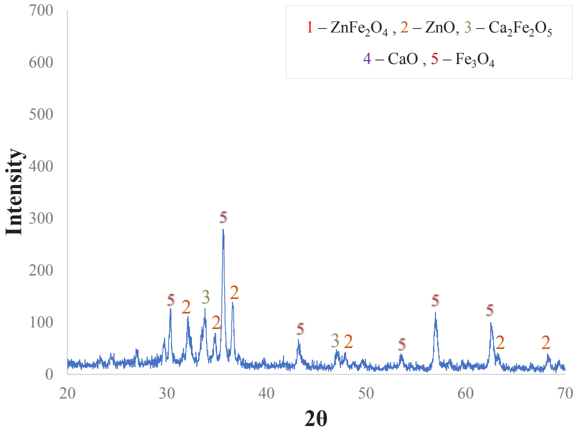

Figure 3 XRD pattern of EAF dust after leaching by HCl

Table 1 Chemical composition of EAF dust, Zinc powder, CaO by X-ray fluorescence

Elements wt.%	K	Ca	Cr	Mn	Fe	Cu	Zn	Pb	O
EAF dust	1.540	4.991	0.200	1.570	31.681	0.202	32.163	2.602	25.052
Zinc powder	0	0	0	0	0.030	0	99.970	0	0
CaO powder	0	71.469	0	0	0	0	0	0	28.581

3.2 Effects of operating factors to cementation rate

3.2.1 Zn/Pb mole ratio

To investigate the effect of the Zn/Pb ratio, temperature and stirring speed were maintained at 60°C and 900 rpm. Figure 4 and Figure 5 show the effect of molar ratio as a function of time. Increasing the Zn/Pb introduces more zinc ions into solution could increase the cementation rate. High zinc particle in the solution meaning that increasing the chemical surface area of reaction between zinc and heavy metals.

Increasing the Zn/Pb ratio, a high amount of zinc powder added into solution also increases the chance of molecules collision together affecting the chemical reaction between Zn0 in the solution and heavy metals. The cementation reaction proceeds rapidly up to 10 minutes. The concentration of heavy metals, detected by atomic absorption spectrophotometry are shown in Table 2. The cementation rate consistently proceeds after 10 minutes until the concentration of lead and chromium 1.54 ppm and 0.007 ppm respectively. Therefore, Zn/Pb molar ratio 3.0 resulted in the optimal condition for zinc cementation.

Table 2 The concentration of Pb and Cr in the leachant before and after cementation which was performed under the optimal condition

Elements	Concentration (ppm)	
	Before cementation	After cementation for 10 minutes
Pb	40.48	1.54
Cr	0.12	0.007

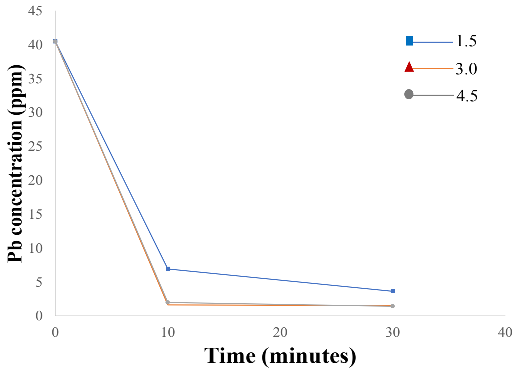

Figure 4 Residual Pb concentration as a function of time for various Zn/Pb ratios

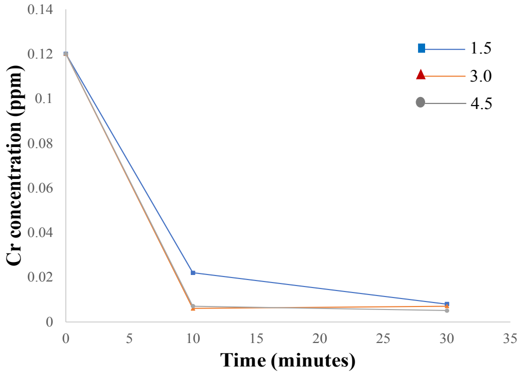

Figure 5 Residual Cr concentration as a function of time for various Zn/Pb ratios

3.2.2 Temperature

The experiment was performed at a Zn/Pb ratio 3.0 and stirring speed 900 rpm. The concentration of the heavy metals, Pb and Cr, in the solution decreased below 2 ppm as seen by Figure 6 and Figure 7 in the first 10 minutes of zinc cementation. The higher temperatures show a faster cementation for both of Pb and Cr. The results show that 60°C for Pb and Cr cementation are the optimal temperatures for their cementation. The increase in temperature providing an increase in cementation rate can simply be explained by the increase in kinetics due to the molecules moving faster, increasing collision frequency and collision more energy.

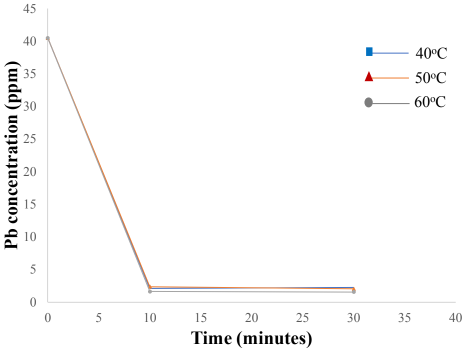

Figure 6 Residual Pb concentration as a function of time for various temperatur

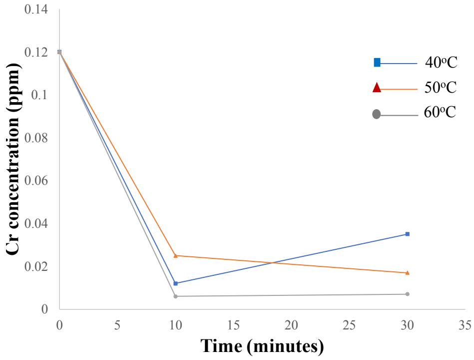

Figure 7 Residual Cr concentration as a function of time for various temperature

3.2.3 Stirring Speed

To investigate the effect of stirring speed, a Zn/Pb ratio of 3.0 was employed and a temperature at 60°C. The stirring speed has little effect on the cementation kinetics for the Pb, but an increasing in speed increases the rate of removal of the Cr. Theoretically, increasing stirring speed from 100 rpm to 900 rpm should increase the cementation rate because of at higher speed there would be an increase in molecule collisions. As seen in Figure 8 and Figure 9, the concentration of Pb and Cr could be closely reduced below 2 ppm. Figure 8 and Figure 9 show at 500 rpm give the best result of Pb and Cr cementation. The results were compared to other investigations [12,13]. Theory states that when stirrer was rotated at very high speed it could increase the dissolution of the oxygen gas into the solution. The side reaction between metals and oxygen forming metal oxide especially lead oxide could impede the chemical reaction with zinc particles which is occurred here as well. The cementation efficiency at very high rotation speed could be lower than low rotation speed.

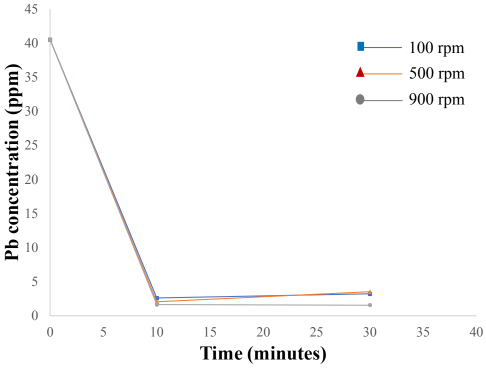

Figure 8 Residual Pb concentration as a function of time for various stirring speed

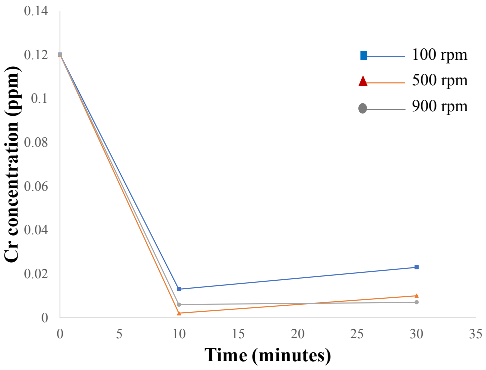

Figure 9 Residual Cr concentration as a function of time for various stirring speed

3.3 Cementation kinetics

The rate of reaction between heavy metals and more noble metals has been investigated in various studies [12-14]. However, side reaction with the presence of oxygen in the solution was not considered for this study. Thus, in this work, the following heterogeneous first-order rate equation was applied to calculate the rate constant.

$$\ln [A] - \ln [A0] = -kt \quad (1)$$

Where A is the concentration of lead and chromium at time *t*.

The rate constant (k) of the reaction was determined by the slope of the graph between the relationship of ln[concentration] and time. From the Figure 10 and Figure 11, the results show the cementation rate constant (k) of Pb and Cr. At t_1, temperature 40°C (313.15K), the rate constant (k_1) of lead and chromium were found to be 0.0825 min^{-1} and 0.0276 min^{-1} respectively. At t_2, temperature 50°C (323.15K), the rate constant (k_2) were found to be 0.0869 min^{-1} and 0.0586 min^{-1} respectively. For the t_3, temperature 60°C (333.15K), the rate constant (k_3) of lead and chromium were found to be 0.0937 min^{-1} and 0.0801 min^{-1} respectively. From Table 3, it was clearly seen that rate constant increasing when increase temperature because at high temperature the activation energy (E_a) is declined. However, the authors suggested additional batch experiments of cementation between 1 to 10 minutes for accuracy cementation kinetic and mechanism.

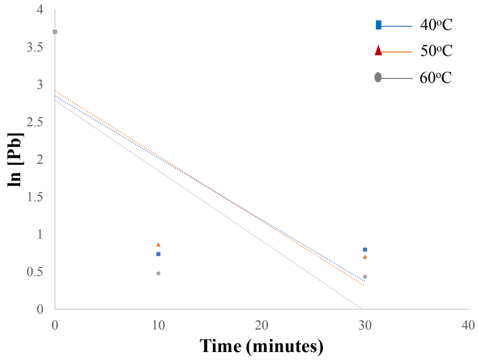

Figure 10 The relationship between ln[Pb] and time

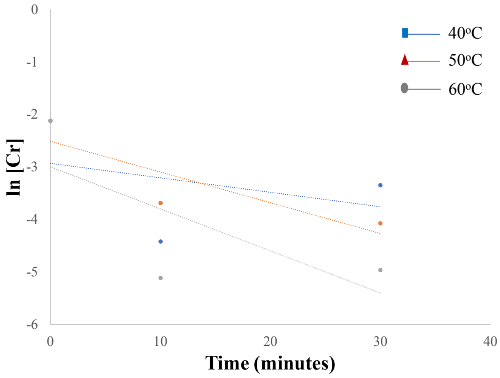

Figure 11 The relationship between ln[Cr] and time

Table 3 Cementation rate constant, k, as a function of temperature

Elements	Rate Constant, k, min^{-1}		
	40°C 313.15K	50°C 323.15K	60°C 333.15K
Pb	0.0825	0.0869	0.0937
Cr	0.0276	0.0586	0.0801

4. Conclusion

The steel recycling factories in Thailand generate a by-product called electric arc furnace dust (EAF dust). It is mainly $ZnFe_2O_4$ and ZnO. X-ray fluorescence analysis confirmed the chemical composition of EAF dust of 32.16 wt% zinc and 31.68 wt% iron. The EAF dust could be recycled instead of the direct disposal into landfill. However, $ZnFe_2O_4$ the main chemical source of zinc in the EAF dust, is difficult to transform into ZnO because of its stability complex compound. A reducing agent was employed to decrease the energy consumption in the calcining process. Calcium oxide (CaO) was combined with EAF dust at a 1:2 molar ratio and then sintered at 700°C for 2 hours.

The calcined EAF dust, with a high level of ZnO, was then leached by HCl. The optimum conditions were found to be; 0.5M HCl, the S/L ratio of 1/10, temperature at 60°C, and stirring speed of 900 rpm for 20 minutes. The solid residue after extraction was found to be a potential source of iron. The concentration of lead and chromium after leaching at optimum conditions was 40.48 ppm and 0.12 ppm respectively. Zinc cementation was applied to reduce the impurities in the aqueous solution prior to the electrowinning process. The optimum conditions for cementation of the acidic leaching solutions were found to be; Zn/Pb stoichiometric ratio of 3.0, temperature at 60°C, and 500 rpm stirring rate for 10 minutes operation. The leachant performed under the optimal conditions was sufficient for reducing lead and chromium to be 1.54 ppm and 0.007 ppm respectively. Approximately 95% of lead and chromium were removed from the aqueous solution. The zinc-rich solution after zinc cementation is expected to be suitable for further refining to produce metallic zinc for the next process.

5. Acknowledgments

The authors would like to thanks the Faculty of Engineering, Kasetsart University for the financial supported throughout this research. Thanks to several steel-making companies in Thailand for providing the electric arc furnace dust sample in the research. Thanks, is also extended to Dr.Greg Heness for the valuable comments. Lastly, thank you the Department of Materials Engineering and Scientific Equipment and Research Division, Kasetsart University for laboratory and equipment supported.

6. References

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