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Kinetic Behaviour of Zinc in Fly Ash Melting Separation Process

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Secondary fly ash, resulting from melting separation processes, leads to a highly concentrated chloride solution with zinc when dissolved in water. Therefore, it is treated for the recovery of zinc as secondary resources. To better recovery of zinc, the kinetic behaviour of zinc was studied. For this purpose, iron-bath melting experiment was carried out. The correlation between the distribution of zinc in gas phase, treatment temperature and treatment time has been reviewed during melting separation processes. A kinetic model based on above has been proposed.

Keywords: Fly ash, Zinc, Melting separation process, Kinetic behaviour, Reactor model.

INTRODUCTION

Incineration of municipal solid waste has two main advantages: reducing the volume by about 90 %, reducing the chemical reactivity of hazardous organic compounds and producing energy in the form of steam, which is marketable. These incineration processes, however, generate two main environmental problems[1-3]: the solid and gas reaction products. Fly ash is one of the solid reaction products. It classified as a hazardous waste due to the high content zinc is one of reasons.

There are many methods to treat fly ash, for example cement solidification, alkali extraction, acid extraction, thermal treatment, *etc*. Anyway, thermal treatment is one of promising solutions among the various available methods though it has some drawbacks[4-6].

During the melting process, secondary fly ash was obtained which could be considered as an artificial ore because more than 90 % zinc is vapourized as $ZnCl_2$ and zinc is present in secondary fly ash at concentrations that allow an economic recovery. It is actually used as feed material to some smelters to produce zinc. It is known that if the concentration of chloride ion is high, this secondary fly ash is unacceptable for smelting processes. In such cases, acid or alkaline leaching followed by solvent extraction would be an alternative recovery process.

In order to better recovery zinc in fly ash, more attention has focused on it. Jiang *et al.*[7] investigated the effect of water-extraction process on the removal zinc in the fly ash and zinc stability in the following melting process. The results showed that water-extracted fly ash had better stability as compared to raw one, which was indicated by lower weight loss and better immobilization stability of zinc in the melting process. Jung *et al.*[8] studied the zinc behaviour in ash-melting and gasification-melting facilities. It found distribution ratio of zinc to melting fly ash was influenced by the oxidizing atmosphere in the furnace. High melting furnace fly ash generation and distribution ratio of non-volatile metals to melting furnace fly ash in gasification-melting facilities was probably caused by carry-over of fine particles to the air pollution control system due to large gas volume. Alorro *et al.*[9] proposes carrier-in-pulp method to extract and recover zinc from molten fly ash before landfilling. Shaking flask experiments were conducted under various conditions using NaCl solution, iron powder as carrier and molten fly ash. More than 99 wt % zinc was extracted from the ash. Wang *et al.*[10] investigated the effect of $FeCl_3$ on the speciation and partition of zinc in a multimetal incineration system by using a tubular furnace and $FeCl_3$ spiked simulated waste. The effectiveness of increasing the Cl/M ratio to the formation potential of metallic chlorides and on the shift of heavy metals from the bottom ash to the fly ash and/or the flue gases was found to have in increasing order as follows: Zn > Cu > Cr. Available literature on the kintec of zinc in fly ash is not extensive, though there are some recent publications on this topic.

The aim of this study was to investigate kinetic behaviour of zinc during melting process. For this purpose, iron-bath melting experiment was carried out. Treatment temperature and treatment time were focused. Furthermore, kinetic analysis of data obtained from the iron-bath melting experiment performed to identify reaction order, reaction rate and activation energy. It wishes provide a new way and help for recovery for zinc in secondary fly ash during melting process.

EXPERIMENTAL

The concentrations of the trace metals were determined by Alpha 4000 XRF (Innov-X systems Corporation. USA) X-ray tubes W anodes 10-40 KV 10-50 μA, resolving power Si PiN detector < 210 eV FWHM 5.95 keV and Z-8000 polarized Zeeman atomic absorption spectrophotometer (Hitachi, Ltd, Japan), sensitivity 10 pg Cu, wavelength 309 nm, slit width 0.4 nm, burner height 7.5 mm, filament current 7.5 mA, C_2H_2 0.16 MPa, N_2O 0.04 MPa.

This study is based on a fly ash specimen obtained from a modern waste-to-energy plant in Chngqing. This waste-to-energy plant has a capacity of 2600 ton day^{-1}. Flue gas from the plant is treated with semi dry lime adsorption and passes through a combined system of mechanical cyclones and bag filters as air pollution control system where up to 99.5 % of the dust content (fly ash) is collected. The temperature of flue gas in the SITY2000 stoke grate incinerator was > 800 ºC during the operation. Each fly ash was dried in an oven at 105 ºC until the moisture contents were determined to be about 0.4 wt % on average.

The cement used as received was ordinary Portland cement 32.5 R and the iron powder was collected from Chongqing Iron & Steel Co.. Then, the samples were grinded and sieved through a 200 mesh sieve.

With the characteristics of porous, fine particle, high mass, therefore, conversion of fly ash into pellet can reduce volatilization and decrease weight loss by about 50 % during the melting procedure and would be a good option for the feed preparation before melting.

The whole experiments process had been described in previous study[11]. Little change occurred. The only different was the zinc only concern of this paper. In the iron-bath melting experiment, fly ash, water and binder were first made into pellets. Then iron powder was melted and pellets fed into the furnace. The iron phase and slag phase will separate due to gravity. This process was called iron-bath melting.

RESULTS AND DISCUSSION

Effect of treatment time: Fig. 1 depicts the distribution of zinc in iron phase, slag phase and gas phase with different melting time. Melting time has little influence on the distribution of zinc because reaction keeps a dynamic balance before 15 min. Moreover, the boiling point of Zn, $ZnCl_2$ and ZnO is 420, 600 and 1020 ºC, respectively. Treatment temperature was 1350 ºC that is higher. So the majority of zinc vapourized and transferred to gas phase which was helpful for recovery zinc in the secondary fly ash.

Effect of treatment temperature: Fig. 2 displays the distribution of zinc in iron phase, slag phase and gas phase with different melting temperature. Zinc vapourized immediately during the melting process. The collection rate of zinc in slag phase and iron phase was various, while the residual fraction of zinc in flue gas increased slightly with a rise in temperature and falls with a decrease in temperature.

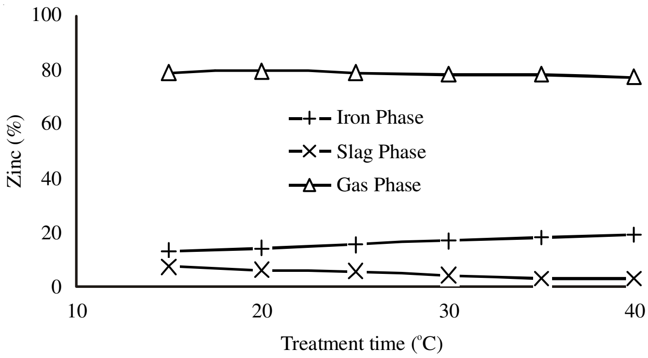

Fig. 1. Effect of treatment time on the distribution of zinc

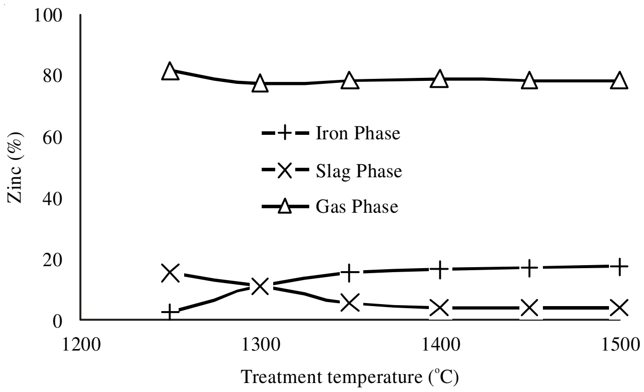

Fig. 2. Effect of treatment temperature on the distribution of zinc

Kinetic modeling

Rate model: The reaction happened between zinc oxide in fly ash and carbon in liquid iron. It belongs to interfacial reaction between molten slag-liquid iron which can be described two reaction processes.

$$ZnO + CO = Zn + CO_2$$

$$C + CO_2 = 2CO$$

Reduction reaction consists of three steps: gas transfer (mass-transfer between CO and CO_2 encapsulated with film), liquid transfer (mass-transfer between ZnO in molten slag and carbon in liquid iron) and liquid-iron interfacial reaction. The key reaction process is not the process of cell nucleation because the reaction condition is high temperature and heterogeneous nucleation but interfacial reaction process.

So the reaction rate is following:

$$r = k \cdot C_{ZnO} \cdot C_{CO} \quad (1)$$

According to eqn. 1, it is first order reaction for Zn^{2+}.

Reactor model: The distribution of low boiling point zinc in gas phase:

$$ZnO + 2Cl^- \longrightarrow ZnCl_2 + 0.5O^- \quad (2)$$

The model proposed is based on the mass balance of the gas phase, iron phase and slag phase representing the distribution of zinc during melting process. The following equation represents in the gas phase,

$$dC_{Zn} / dt = kC_{Zn} \quad (3)$$

where C_{Zn} is the concentration of zinc in gas phase; t is time; k means reaction rate.

According to eqn. 3, integral equation is obtained.

$$\ln C_{Zn} = \ln C_0 + kt \qquad (4)$$

So the kinetic model of zinc is following during iron-bath melting separation process:

$$C_{ZnO} = C_g(1 - e^{-k_{ZnO}t/d}) \qquad (5)$$

where C_g is saturation in gas phase of $ZnCl_2$ and d means crucible thickness.

Model effectiveness

Orders of reaction: The method for determining orders is indirect and unlikely to be asked on a test. Because the integrated rate law solutions for zero, first and second order expressions are different functions but all can be written in the form of a straight line. This means that if the concentration was plotted as a function of time for each expression below, the correct order should yield a straight line function. For examining it for the data in a first order reaction, but apply the functions for all three equations. According to the iron-bath melting experiment data, a straight line function Y = 4.78410-3.5269t will be yielded by Matlab if it is first order. So the iron-bath melting experiment for zinc can be described using first order, which match with the rate model.

Activation energy: The Arrhenius equation is a simple, but remarkably accurate, formula for the temperature dependence of reaction rates. The equation may be expressed as

$$k = k_0 e^{-E_a/(RT)} \qquad (6)$$

where E_a, k_0, R and T means activation energy, pre-exponential, gas constant and absolute temperature respectively.

Taking the natural logarithm of the Arrhenius equation yields:

$$\ln k = -E_a/(RT) + k'_0 \qquad (7)$$

When a reaction has a rate constant that obeys the Arrhenius equation, a plot of ln (k) *versus* T^{-1} gives a straight line, whose gradient and intercept can be used to determine E_a and k. This procedure has become so common in experimental chemical kinetics that practitioners have taken to using it to define the activation energy for a reaction. That is the activation energy is defined to be (-R) times the slope of a plot of ln (k) *vs.* (1/T):

$$E_a \equiv -R\left(\frac{\partial \ln k}{\partial(1/T)}\right)_P \qquad (8)$$

The activation energy of Zn^{2+} in fly ash was $E_{(Zn)}$ = 121 kJ mol^{-1} according to the iron-bath melting experiment data about treatment temperature and treatment time. The lower activation energy showed the reaction was easier reacted.

Model verification: The validity of the proposed mathematical model was verified by comparing with experimental data. The simulated data is represented by the solid lines as shown in Fig. 3. It is evident that the mathematical model prediction lies very close to the experimental data. It indicated excellent agreement between the experimental and predicted data and confirmed the model's ability to interpolate the multidimensional initial conditions of the melting process with satisfactory accuracy. Although the mathematical model possesses excellent interpolation properties, some error also exist. Because the composition of the fly ash is complex and some hypothesizes were proposed before building model and so on. Anyway, this mathematical model for zinc is excellent.

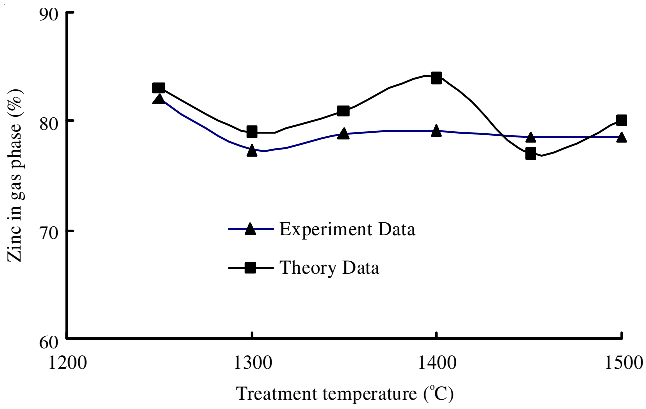

Fig. 3. Effect of treatment temperature on the distribution of zinc

Conclusions

In this work, a specimen of municipal incinerator fly iron ash from a modern waste-to-energy plant was used for studying its extractability of zinc by iron-bath melting experiment. Based on the experimental results obtained, the following conclusions can be drawn.

(1) The majority of zinc vapourized as $ZnCl_2$ which is helpful for recovery zinc in secondary fly ash.

(2) Kinetic model of zinc is $C_{ZnO} = C_g(1 - e^{-k_{ZnO}t/d})$ during iron-bath melting separation process. It is excellent.

(3) The iron-bath melting experiment for zinc can be described using first order and the activation energy was 121 kJ mol^{-1}.

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