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A study to set-up a technological process for purification of Zinc scraps by using liquation method

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Abstract: Zinc scrap is a source of raw material for zinc oxide production. However, to qualify the requirement of raw material for zinc oxide (99.5%) production, refining this source is needed. Many methods are considered such as rectification, chemical method, etc., but difficult to apply on an industrial scale. This workfocused on the investigation of the influence of temperature and time factors for asessing the possibility of applying liquation method for the purification of impurities from scrap zinc.The experiment results show that the optimum temperature of liquation to remove Pb, Fe from zinc scrap is in the range of 440-450°C, the optimal time of the process is 8h for the pot with 8cm in height and 6cm in diameter (the quantity of raw zinc sample is about 2kg / batch), then we can obtain about 80% of zinc metal with an average Zn content of about 97,0%, both Pb and Fe content decreased to a range from 0.35 to 0.4%, and 1.0 to 1.1%, respectively, which meet the requirement of raw materials for the production of high quanlity ZnO (99,5%). Based on the parameters obtained on lab-scale, a trial on pilot scale of 250 kg / batch was conducted, The result confirms that the quality of the products meets the requirement of raw materials for production of high quality ZnO (99.5%) and a technology process for refining zinc scrap by the liquation was proposed.

Keywords: *Zinc scrap, liquation method, remove Pb.*

I. INTRODUCTION

Zinc scrap is used as a raw material for many industrial applications. One of their major uses is to produce high quality zinc oxide by oxidation evaporation. For the production of high quality zinc oxide 99.5%, the zinc metal must meet some quality standards such as: content of Zn ≥ 95%, Pb ≤ 0.5%, Fe ≤ 1.5% , etc.[1].Zinc scrap on the market ishigh in zinc (≥ 93%), but it containsa significant amount of impurities such as Pb, Fe, etc. soit does not meet the quality standards for high quality zinc oxide production.

In order to use zinc scrap as a raw material for high-quality ZnO production, a zinc refining process is required to remove impurities and improve the quality of zinc scrap before it can be loaded intoazinc oxide production line. There are some methods for separating impurities from zinc scrap like the zinc distillation and chemical methods, some good results have been achieved by using these methods, such as zinc content in the metal zinc after separation of impurities reaching over 99%, content of impurities Pb, Fe is very low. However, these methods are difficult to be appliedon an industrial scale due to the high cost of impurities separating, complicated technology and equipment [1,2].

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In order to meet the criteria of both improving the quality of zinc scrap and applicable on anindustrial scale, the liquation method of separation to remove impurities from the zinc scrap has been proposed [3,4,6]. Liquation is a metallurgical method for separation metals from an ore or an alloy. The material must be heated until one of the metal start to melt and drain away from the other and can be collected. This method is applied in zinc refining technology based on the existence of the region of immiscible liquids in the Zn–Pbsystem.. During slow cooling the melt from 550–600 to 430–450°C (near the freezing point), due to the large difference in densities of liquid Zn (6.5 g/cm^3) and Pb (10.5 g/cm^3), zinc and lead will be transfered into two separate liquid layers. This method, which is called liquation refining, is used in zinc metallurgy and makes it possible to decrease the lead concentration in zinc. This is the scientific basis for the separation of lead from zinc by liquation method. This method allows to reduce Pb content in zinc metal(containing 2–4% of lead) to less than 1.0% [3].

In addition, some impurities such as zinc oxide, aluminium and iron-containing intermetallic-compounds particles, etc., are entrained with elemental zinc and these accumulations from the surface of liquid zinc are skimmed by using ammonium chloride as a flux additive.

There are many factors that may affect the separation of impurities from the zinc scrap, this research focuses primarily on studying the effects of ammonium chloride. temperature and time of liquation on the separation of lead and other impurities from zinc scrap to evaluate the possibility of refining this zinc-containing waste source for the production of high quality zinc oxide (99.5%).

II. THE STARTING MATERIALS AND RESEARCH METHOD

A. The selection of starting materials

Zinc metal scrap is available on the market as a by-product of hot dip galvanizing plants, they are characterised by various types and chemical composition. The quality of these zinc waste depends on the technological characteristics of each hot dip galvanizing plant. Currently, the majority of zinc metal scrap in the market contains more than 93% of zinc, 1-2% of lead. In order to select the raw materials for this research, 3 typicalsamples of zinc scrap have been considered.

Three chosen samples of different types of zinc metal scrap, denoted as M1, M2, M3, have been analyzedby Atomic Absorption Spectrometric (AAS) method. The analytical results are summarized in Table I:

Table I. The analytical results of three typicaltypes of zinc metal scrap

Sample	Zn, %	Pb, %	Fe,%	Al,%	Note
M1	95.6	0.2	1.71	2.5	
M2	94.9	1.1	1.82	0.98	
M3	98.4	0.8			Price 15% higher.

From the above analysis, it can be seen that M1 is high in Zn content, low in Pb but very high in Al. To evaluate the effect of Al on the separation of Pb and other impurities from zinc scrap, some testing have been carried out by melting M1 and evaluating the possibility of separating aluminum . At a temperature range of 500 - 900°C, the molten specimen forms a large amount of non-liquid residue (about 20% of total mass), this will greatly reduce the performance of the impurity separation process. The cause of this residue formation can be explained by the formation of a highly durable ternary alloy Zn - Fe - Al [5,6], with a high viscosity and its boiling point is significantly higher than the boiling point of zinc metal. Resulting from the above experiments, M1 has been rejected as a starting materialfor this research.

The zinc scrap sample M3 has a high Zincand low Lead content. In terms of quality, the M3 sample can be used as a material for this research but that can not be deployed on an industrial scale due to its high cost, sothe M3 sample was not selected as astarting material for this research.

The Zinc scrap sample M2 contains higher Lead and Iron than M1 and M3, but M2 islow in Al content and reasonably low-priced so M2 was selected as a starting material for this research.

B. Research method

A process for investigating the effect of ammonium chloride on the pre-treatment of zinc scrap was conducted as follows: An exactly weighted 2000 g sample of the material was put into a testing pot, and heated to 550^{0}C, maintained for at least one hour until the sample completly melted. Ammonium chloridewas added to the molten masswith mixing, the slag was skimmedand collected (including slag powder and lump), then the content of Zn, Pb, Fe, Al in the slag was determined. This process was repeated with different amounts of ammonium chloride. Based on the weight and composition of slag in each experiment, the effect of ammonium chloride on the zinc scrap purification can be evaluated.

To study the effect of temperature on the separation of lead and other impurities fromzinc metal scrap, the experiments were conducted under the same technological conditions but at different temperature from 420 - 470°C. Zinc scrap is heatedin a pot 10 cm of height, 6 cm of diameter, the sample weight is about 2 kg (fig.1)

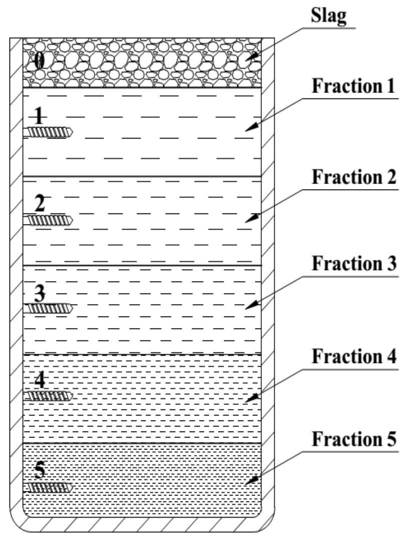

Fig. 1. Sample with points 1-5 in which the analysis was performed.

Samples were heated to desired temperature, afterremoving the floating slag on the surface of liquid zinc, the temperature of the melting mass was maintained at a desired temperature for 8 hours, then the melting mass was cooled down slowly to room temperature, while the sampling were taken by drilling at 5 different points along the heights of the pot. Fraction 1 : 0 – 2 cm from the surface, fraction 2: 2 - 4 cm from the surface, fraction 3: 4 - 6 cm from the surface, fraction 4: 6 - 8 cm from the surface and fraction 5: 8 - 10 cm from the surface. Thecontentof Zn, Pb, Fe in those fractionwill bedeterminedby ASS. From the experimental results, the effect of liquation temperature on the separation of lead and other impurities from zinc scrap will be evaluated.

The effects of liquation time on the separation of lead and other impurities from zinc scrap were conducted step by step attemperture 400^{o}C in 4-12hrs. Other technological parameters were kept as the same as when studying the effect of temperature. Theoretically, the longer liquation time, the better the efficiency of separation of lead and impurities, but carrying out the experiments is still needed tofind out the optimum time for liquation refining, while ensuring the efficiency of separation of impurities and fuel saving.

The contents of Zn, Pb, Fein the tested samples will bedetemined by Atomic Absorption Spectrometric (AAS) method.

III. EXPERIMENTALS

A. The effect of amonium chloride

The experiments were carried out by using ammonium chloride 0.05%, 0.1%, 0.2% and 0.3% to the weight of zinc scrap sample. The weight and the composition of the collected slag were determined which allows to calcualte the percentage of slag to the starting material after each experiment. The effect of ammoinium chloride on the produced slag volume also can be shown in the Table II and Fig.2.

Table II. The effect of ammonium chloride on the volume of produced slag

NH_4Cl,%	Lumped slag,grs	Powder slag, grs	Total slag, grs	Slag colle-cted, %
0	80.6	0	80.6	8.06
0.05	64.4	3.5	67.9	6.79
0.1	55.6	7.2	62.8	6.28
0.2	52.1	5.0	57.1	5.71
0.3	51.8	5.2	57.0	5.70

The chemical composition of the slag were shown in the table III.

The separation efficiency of the impurities such asPb, Al, Fe after the pre-treatment by using ammonium chloride is calculated based on the weight and chemical composition of the slag,

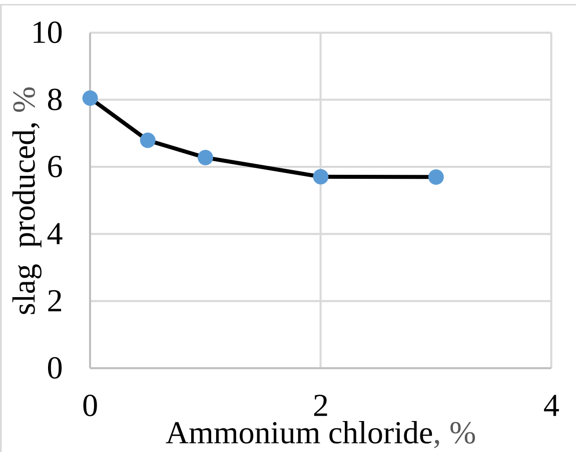

Fig. 2. The effect of ammoni-chloride on the volume of produced slag

Table III. Composition of slag collected

Slag type	% slag volume	% Zn	% Pb	%Fe	% Al
Slag powder	0.5	78.8	1.3	8.0	3.7
Lumped slag produced without NH_4Cl	8.1	91.5	1.1	3.5	2.2
Lumped slag produced with NH_4Cl	5.2	90.6	1.0	3.8	4.6

B. The effect of liquation temperature

The liquation process for zinc scrap was investigated at temperatures of 420°C, 430°C, 440°C, 450°C, 460°C and 470°C for 8 hours. Then the samples collected at 1, 2, 3, 4, 5 areas (as described in Fig.1) were determined for Zn, Pb, Fe content. From the results of the analysis, the average content of Zn, Pb, Fe can be calculated from fractionno.1 to fractionno.4 (equivalent to 80% of mass) of thezincscrap sample after the liquation process at different temperatures. Data obtained were presented in Fig.3.

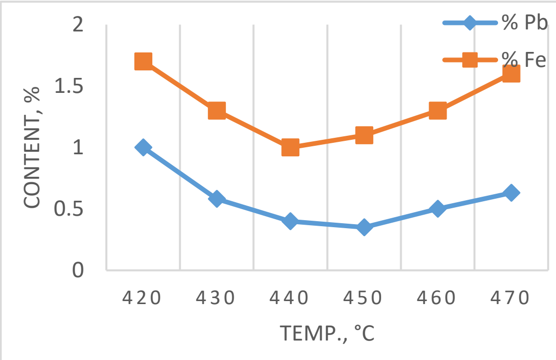

Fig. 3. The Effect of liquation temperature on the separation of Pb, Fe (Liquation time 8hrs)

C. The Effect of liquation time on the separation of Pb, Fe

Based on the compositions offraction No.1, 2, 3, 4 and 5 of the tested samples after liquation process at 440°C for a diffrent time intervals, the average content of Zn, Pb, Fein each fraction from 1 to 4 (equivalent to 80% mass) will be calculated. The experiment data obtained are shown in Fig.4.

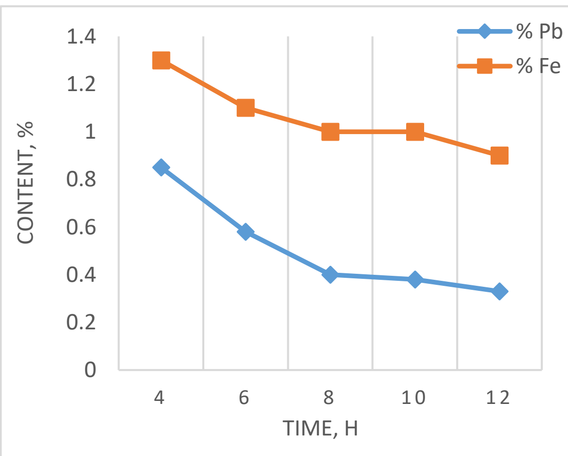

Fig. 4. The effect of liquation time on the separation of Pb and Fe from zinc metal scrap (at 440°C).

IV. DISCUSSION

The Fig. 2 shows that when the ammonium chloride content increases, the amount of slag is reduced. However, when increasing the ammonium chloride content to more than 0.2%, the separation efficiency did not increase significantly, so the choice is of 0.2% of ammonium chloride on the weight of zinc scrap in the liquation pot. With 0.2% of ammonium chloride ofthe total amount of ingredients in the pot the amount of slag residue can be reduced from 8.05% to 5.7%.

On the other hand, the results in Table III show that the use of ammonium chloride not only reduces the amount of slag but also has a good effect on the separation of impurities such as Al, Fe from the zinc scrap and reduces the amount of zinc lost by slag.

The experimental results can be explained based on the phase diagram [3] of the Zn-Pb system (Fig. 5).

From the experimental results shown in Table 2 and Figures 3 and 4, it can be seen that when carrying out the liquation refining at 420°C, the impurities such as Pband Fe are almost not separated. This is explained by the fact that at the temperature of 420°C, the Zn-Pb system is just near the melting temperature, the viscosity of this molten metal is high, so the deposition process of lead metal droplets is poor and the separation of Pb from Zn is almost negligible. When increasing the temperature to about 430-450°C, the separation of lead and iron from the molten metal zinc increases significantly, especially at temperatures between 440 and 450°C. Approximately 80% of zinc in the zinc scraps was recovered with Zn content is about 97.0% , Pband Fe content is 0.35-0,4% and 1.0-1.1% respectively. At a higher temperature of the liquation, the separation of Pb and Fe decreases, which is theoretically consistent with the phase diagram of Zn-Pb system shown in Figure 5 that when increasing the temperature, the mutual solubility of the Zn - Pb and Zn - Fe metals will increase accordingly. Thus the optimum temperature for the separation of the Pb and Fe from zinc scrap by liquation refining is in the range of 440-450 ° C.

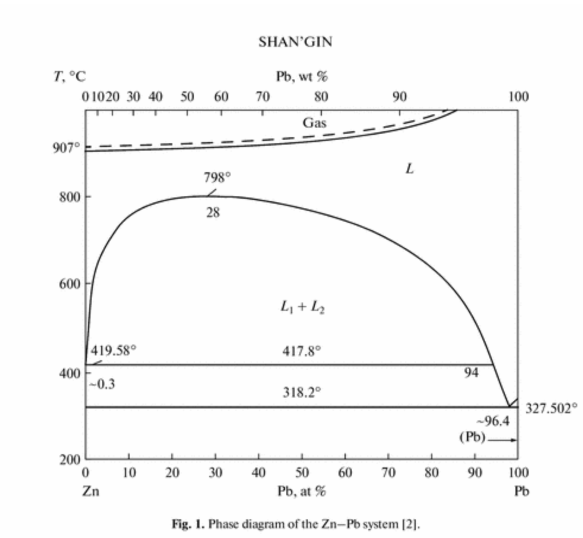

Fig. 5. Phase diagram of Zn-Pb system [3]

From the experimental results shown in Table III and Figures 3 and 4, we can see that when increasing the time of liquation, the separation of lead and iron from zinc metal scrap also increased. However, when the time of liquation exceeds 8 hours, the separation efficiency increase but not much. With the goal of zinc metal composition Zn ≥ 95%, Pb≤ 0.5% and Fe ≤ 2% after the refining, combined with the reducing fuel consumption, so the optimumtime for liquation is 8 hrs when using a liquation pot 10 cm of heigh, 6 cm of diameter.

For upgrading the liquation process to a pilot scale of 250 kg /batch the optimum technological parameters identifiedat lab scale have to be maintained such as ammonium chloride (0.2%, liquation temperature 420 - 450ºC. However, in order to reach a homogeneous liquid state before starting the liquation process, the zinc scrap was heated to 720-750°C for melting all its metals completely. To simplify the design of the liquation pot and bypass aheat exchanger, the molten mass was kept for cooling naturally from 720ºC to the liquation temperature (420ºC). For discharging the zinc product, the zinc liquid was heated up to 500ºC for lowering the viscosity of liquid zinc metal

Based on the obtained experimental data and the above arguments, the process of refining zinc scrap at a pilot scale of 250 kg / batch was conducted and the procedure was as follows:

- Zinc scrap was loaded into liquation pot and heated to 720ºC

- Ammonium chloride as an additives was added to liquation pot at 500ºC, then zinc slag will be skimmed

The time for heating zinc scrapto 720°C is approximately 3.5 hours for the first batch; subsequent batches are made when the oven is hot at 250°C, so the heating time is reduced to 2.5 hours.

The time for cooling the liquid zinc mass from 720ºC to 420ºC is 26 hours, while the temperature drops from 500°C to 420°C for 18 hours.

To collect product, the pot was heated to 500ºC for lowering the viscosity of molten zinc before discharging the purified zinc scrap.

Test data and product quality evaluation are presented in Tables IV and V.

Table IV. The Trial Product quantity

Starting materials		Product	By-product	
Zinc scrap	Gas	Purified zinc	Zinc slag	Bottom dross
2000 kg	95	1620 kg (81%)	88 (4.4%)	284 kg (14.2%)

Table V. The trial Product quality

Product Type	Zn (%)	Pb (%)	Fe (%)	Al (%)
Starting material	95.6	1.4	1.8	0.6
Zinc purified	97.4	0.5	1.2	0.5
Zinc slag	79.5	1.6	8.5	2.9
Zinc bottom dross	90.3	6.5	3.0	0.4

The experiments results show that the obtained zinc product satisfied the material requirement for the high quality ZnO 99.5% production,the recovery efficiency is up to 80%, the fuel consumption is 0.06 kg/ kg of zinc product. Based on the research results, a technology has been proposed. in Fig.5.

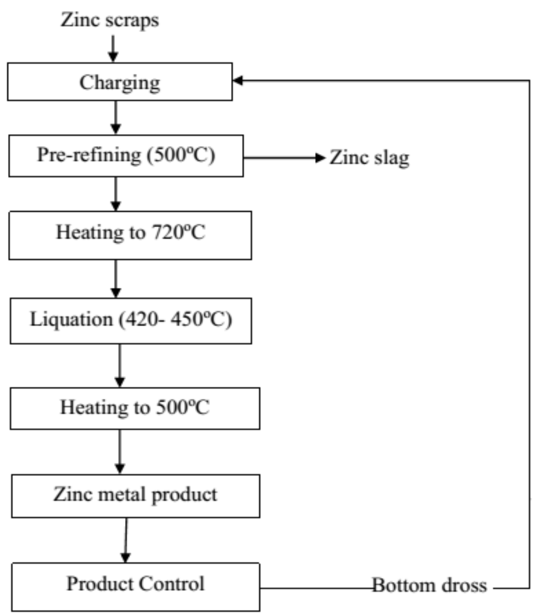

Fig. 6. A proposed technology process for refining zinc scrap by the liquation

V. CONCLUSIONS

The liquation method allows the refining of zinc metal scrap to meet the material requirements for the production of high-quality ZnO. The temperature and time of the liquation process have a great influence on the efficiency of separating the impurities from the zinc metal scrap by liquation method.

The suitable amount of ammonium chloride for refining is 0.2% to the weight of zinc scrap. The optimum temperature for separating impurities such as Pb, Fe from zinc metal scrap is in the range of 440-450°C, the optimum time is 8 hours for the pot 10cm of height and 6 cm of diameter (quantity of zinc sample is about 2kg/batch), then we can obtain about 80% of metal zinc with average content of about 97.0% of zinc, Pb, Fecontent decreased to about 0.35 - 0.4% respectively,, satisfying the material requirements for production of high quality ZnO 99.5%.

A trial on a pilot scale of 250 kgs/batch with 0.2% of ammonium chloride as an additive, melting temperature 720°C, time for naturally cooling 26 hrs, temperature for zinc product discharging 500ºC has been tested. The results show that the zinc product satisfied the material requirements for production of high quality ZnO 99.5%., recovery efficiency is up to 80%, fuel consumption is 0.06 kg/ kg of zinc product.Based on the research results, a process for refining zinc metal scrap technology by the liquation has been proposed.

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