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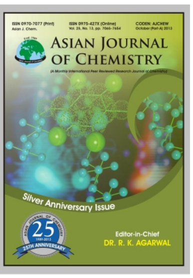

A New Process for Treatment of Waste Acid in Smelter

JIAYUAN LI[1,2], TIANZU YANG[1,*], WEIFENG LIU[1] and LIN CHEN[1]

[1]School of Metallurgical Science and Engineering, Central South University, Changsha 410083, P.R. China
[2]Department of Chemical Engineering and Life Science, Hunan University of Science and Engineering, Yongzhou City 425199, P.R. China

*Corresponding author: Tel: +86 731 88836791; E-mail: lijiayuanchen@yahoo.com.cn

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A kind of lead ash produced in the process of refining lead is used as waste acid treatment agent. The effects of experimental conditions, such as temperature, reaction time, agitation speed, catalyst dosage and velocity of waste acid flow, are investigated. The results show that agitation speed and liquid-solid ratio have little effect on removal ratio. Without catalyst, the optimum parameters are as follows: temperature, agitation speed and reaction time are 60 ºC, 400 r/min, 5 h, respectively. Under the above experimental conditions, the removal ratio of waste acid can reach above 95 %. Appropriately controlled adding speed of waste acid can greatly shorten the reaction time and lower reaction temperature when appropriate acetic acid is used as catalyst.

Key Words: Lead smelt, Waste acid, Lead ash, Comprehensive utilization.

INTRODUCTION

With the development of industry of nonferrous smelting, sulfuric acid making with smelting gas has developed rapidly in China[1,2]. In the process of acid making with smelting gas, large amounts of waste acid (waste acidic water) will generate. Sulfuric acid content is 3~10 % in the waste acid[3-5]. If the waste acid cannot meet the criterion of discharge, it will be cause to the environment pollution,

At present, there are mainly two measures about treatment of waste acid in some large smelting plants. One is the neutralization[6-12], which will produce a large number of waste gypsum residues. Another is concentration and purification to get the higher concentration sulfuric acid as the chemical raw materials[13-15], which needs sophisticated maintenance and management, high investment and high running cost.

In china, smelting factory is generally adopted to neutralize by lime. Although the method can meet the requirement of waste acid treatment, a large amount of waste gypsum residue will produce in the process of waste acid treatment. The waste gypsum residue as cement raw materials has been reported[16]. Actually, this gypsum residue cannot be reused because of high content heavy metal ions. It can only be transported to the storage yard. Furthermore, the harmful substances will cause secondary pollution to the environment if the accumulation of residue is washed by rain.

The purpose of this study is to look for a feasible and low cost treatment of waste acid. If we can use some intermediate material from the smelter instead of the traditional materials such as lime, it may become a new way for the treatment of waste acid from the non-ferrous metals. It is a valuable to protect the environment, reduce costs, make use of resources and recycle. The electrical lead ash (in the production of electrolytic lead, when we cast anode plate or starting sheet, it will generate a kind of ash containing lead oxide) is an intermediate products in lead smelter. Its major composition is an alkaline oxide, we try to use it to neutralize the waste acid from the non-ferrous metals in this paper. To our best of knowledge, the method is not yet reported.

EXPERIMENTAL

All of the reagents are analytical pure. The electrical lead ash and waste acid were purchased from a lead-zinc smelter in Hunan Province, China. The electric lead ash major composition (mass fraction) and XRD diagram are shown in Table- 1 and Fig. 1.

TABLE-1
MAIN CHEMICAL COMPOSITION OF THE ELECTRICAL LEAD ASH (%)

Pb	O	S	F	Na	Cl
76.52	12.5	1.21	3.96	2.99	1.43

In waste acid, the concentration of sulfuric acid varied from 3-10 % (mass fraction). The other pollutants include arsenic, fluorine and small amounts of heavy metal ions. Its ingredients are shown in Table-2.

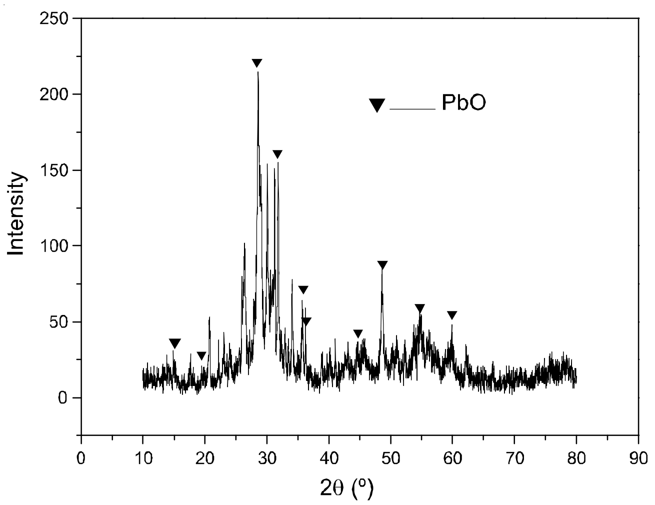

Fig. 1. XRD diagram of the electric lead ash

TABLE-2
MAJOR POLLUTANTS IN WASTE ACID FROM LEAD SMELTER (mg/L)

Zn	Hg	Cu	As	Cd	Pb	F	SS	H_2SO_4 (g/L)
0.743	1.30	0.642	910	1.757	6.01	800	1120	52

HJ-4 type magnetic stirrer, δ 320-S pH and constant temperature water bath were used as experimental instrument.

The experiment was carried out in a conical flask. First, a certain amount of electrical lead ash and waste acid are added into the conical flask. Then, adjust the temperature, stirring speed, the mass of electrical lead ash, time and dose of catalyst. After the experiments have finished, the solution and precipitation are separated by filtration. The pH value of filtrate and concentration of residual sulfate ion are detected.

RESULTS AND DISCUSSION

Relationship of the mass of electric lead ash and the removal ratio of the waste acid: Electrical lead ash of different qualities is added into a 250 mL conical flask with 135 mL waste acid. Initial concentration of waste acid is 52 g/L. Reaction temperature, reaction time and stirring speed are 80 ºC, 5 h and 50 rpm, respectively. The electric lead ash mass is gradually increased from 15 to 40 g. The results are shown in Fig. 2.

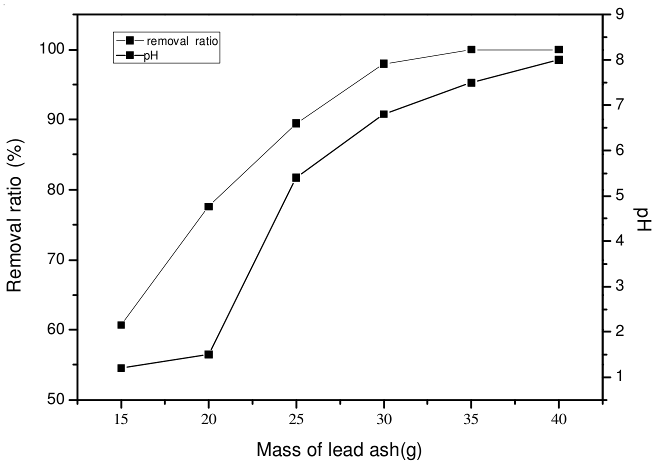

Fig. 2. Relationship of the mass of electric lead ash and acid removal

The main component of electric lead ash is lead oxide, which can neutralize acid under appropriate conditions. Fig. 2 shows that acid removal rate and pH value of the solution increase with increase of the mass of electrical lead ash. When the mass of electrical lead ash is increased to 30 g, the sulfuric acid of the acidic wastewater is removed completely. Because the electrical lead ash also contains a small amount of other soluble alkaline oxides, excessive electric lead ash can still rise slowly of the pH. In the following experiments, the electric lead ash dosage is fixed 30 g and waste acid is fixed 135 mL.

After the reaction, the precipitation residue was analyzed by using X-ray diffraction.The result is shown in Fig. 3. It can be seen that a large number of lead sulfate produced after waste acid was neutralized by the electric lead ash.

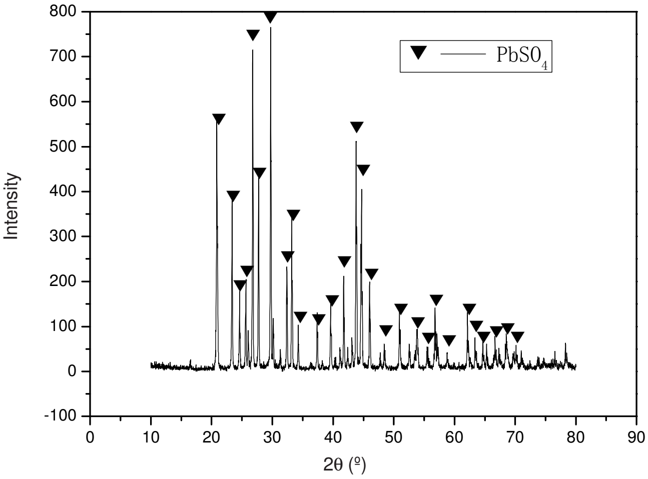

Fig. 3. XRD pattern of neutralization sludge

Effect of reaction temperature: In this experiment, initial concentration of waste acid is 52 g/L. The reaction is performed for 5 h at 20~80 ºC under stirring speed of 500 rpm. The results of removal acid are shown in Fig. 4.

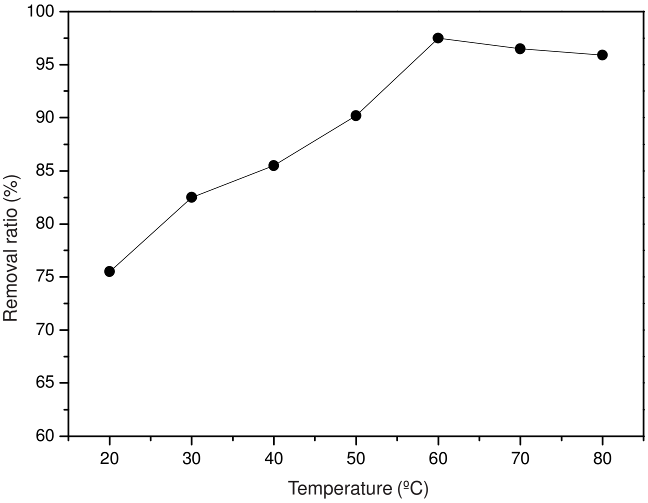

Fig. 4. Effect of temperature on removal rate of waste acid

It is obvious, the removal rate of acid increases with the reaction temperature rising in the temperature of 20~60 ºC. The removal rate almost does not change when the temperature increases from 60 to 80 ºC. Lead oxide is covered with passivating surface film in waste acid, which is unfavourable for the reaction. The passive film can be damaged in the temperature over 60 ºC. The kinetic experiment shows that the reaction is controlled by the inner diffusion. Solubility of lead sulfate increases with increasing of temperature from a thermodynamic viewpoint, which is disadvantageous to removal of SO_4^{2-}. When the reaction temperature is 60 ºC, waste acid removal rate can reach more than 95 %.

Effect of reaction time: The experiments are carried as follows. The initial concentration of the waste acid was 52 g/L, temperature is 60 ºC and the stirring speed is 500 rpm. The reaction time is 1~7 h. Effect of time on removal rate of the waste acid is shown in Fig. 5. As shown in Fig. 5, the waste acid removal rate is less than 60 % when the reaction time is below 1 h. The removal rate gradually increases with the increase of the reaction time. The removal rate of waste acid exceeds 95 % after 5 h and remains stable afterwards. The main reason is that the rate-controlling step is possibly internal diffusion. So, the reaction time of 5 h is chosen for waste acid neutralization process.

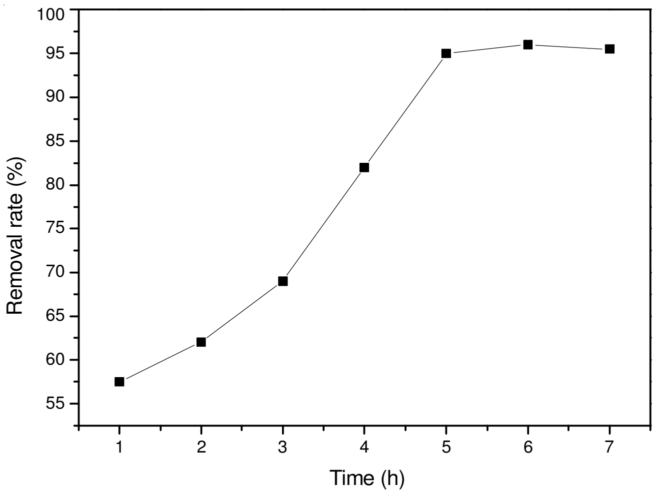

Fig. 5. Effect of time on removal rate of waste acid

Effect of stirring speed: The other conditions remain unchanged. The stirring speed is 100, 200, 300 and 400 rpm, respectively. Effect of stirring speed on removal rate is shown in Fig. 6.

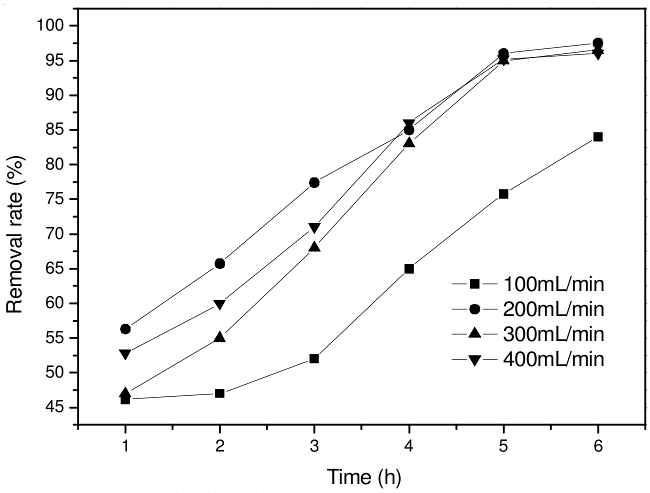

Fig. 6. Effect of stirring speed on removal rate

Fig. 6 shows that under different stirring speed, acid removal rates increase with increase of the stirring speed. At the same time, the faster stirring speed, the higher acid removal rate. When the stirring speed is 100 rpm, the electrical lead ash is likely deposition partly. As a result, the acid removal rate is lower. The increasing range of the acid removal rate is less than 10 % when stirring speed increases from 200 to 400 rpm. This suggests that the stirring speeds have little influence on acid removal rate.

Effect of acetic acid (catalyst)

Effect of different adding methods of the waste acid and acetic acid: The volume ratio of acetic acid to the waste acid is 1:400 ([AcOH]≈2.5 g/L). The reaction temperature is 60 ºC and stirring speed is 300 rpm. There are two methods for adding waste acid. One is the simultaneous addition of waste acid, electrical lead ash and acetic acid. Another is that a certain amount of acetic acid and electric lead ash are first mixed and then the waste acid is added by a rate 1 mL/min. Fig. 7 displays effect of different adding methods of the waste acid on removal rate.

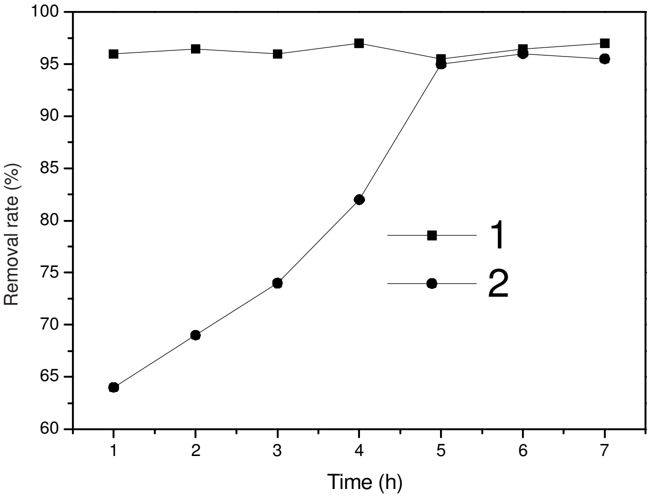

Fig. 7. Effect of different adding methods of the waste acid on removal rate; Curve 1: the waste acid is added by a rate 1mL/min; Curve 2: the simultaneous addition of waste acid, electrical lead ash and acetic acid

The acetic acid shows little catalysis with simultaneous addition of waste acid, electrical lead ash and acetic acid. The removal rate of waste acid was less than 70 % when the reaction proceeds for 3 h. The reason is that the waste acid acts directly on the surface of solid lead oxide forming a layer of passive film. If the waste acid is added into the mixture of acetic acid and electric lead ash by an appropriate rate, high removal rate of waste acid is achieved in a short time. The reason may be that the acetic acid can dissolve lead oxide to produce lead ions in solution. Sulfate ions can be precipitated with lead ions when the waste acid is added by an appropriate rate. Therefore, the surface of lead oxide doesn't form passive film and the neutralization reaction proceeds rapidly. The removal rate of waste acid exceeds 95 % within 1 h.

Effect of the waste acid adding speed: The reaction time is 1 h. With other conditions unchanged, waste acid is added with different speeds. Effect of the waste acid adding speed on removal rate is shown in Fig. 8. It shows that the removal rate of acid is related to the speed of the waste acid influx. The higher the speed of waste acid, the lower the acid removal rate. The removal rate of acid is more than 95 % at the speed of the waste acid influx below 5 mL/min. In order to get a high acid removal rate in the finite time, the waste acid flow rate should be maintained not more than 5 mL/min in this experimental.

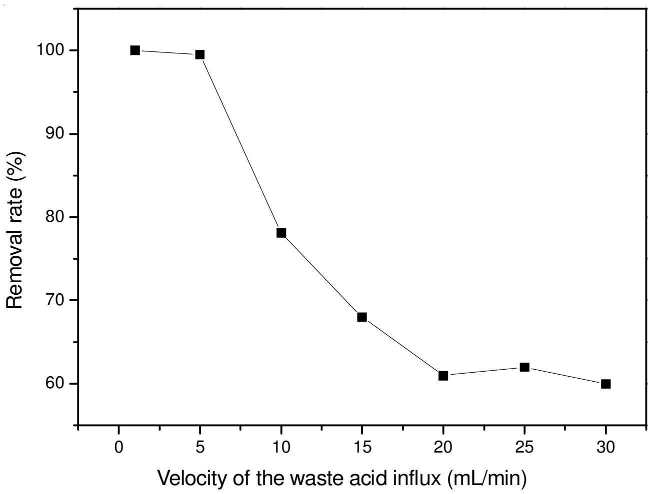

Fig. 8. Effect of the waste acid adding speed on removal rate

Effect of acetic acid dosage: Waste acid initial concentration is 52 g/L. The reaction is performed for 1 h at 60 ºC under stirring speed of 400 rpm. The concentration of acetic acid and the velocity of the waste acid influx are changed. Effect of acetic acid dosage on removal rate is shown in Fig. 9.

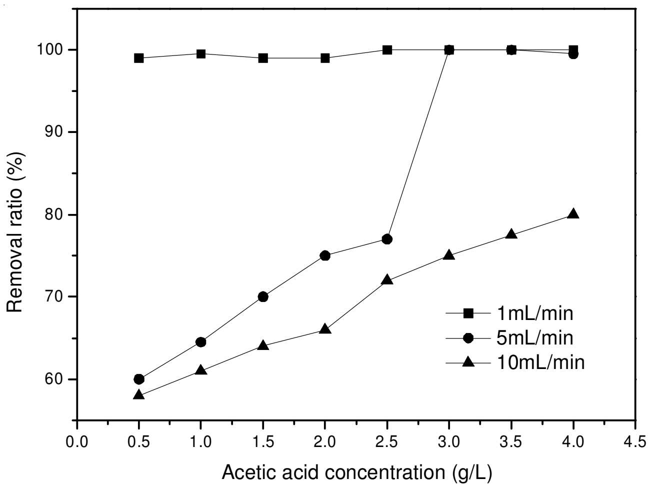

Fig. 9. Effect of acetic acid dosage on removal rate

As shown in Fig. 9, increasing the amount of the catalyst and decreasing the velocity of the waste acid are of benefit to remove of waste acid. Under the former conditions, the removal efficiency of waste acid is best at the velocity of the waste acid of 5 mL/min and concentration of acetic acid of 3.0 g/L. However, we generally need as possible as to increase the flow rate of the waste acid and reduce the dosage of the catalyst in order to decrease the production cost. Hence, we must handle correctly the relations between them in practical production.

Effect of reaction temperature: Waste acid initial concentration, acetic acid concentration, the velocity of the waste acid, stirring speed and the reaction time are 52 g/L, 3.0 g/L, 5 mL/min, 400 rpm and 1 h, respectively. Fig. 10 depicts effect of reaction temperature after adding in the catalyst on removal rate.

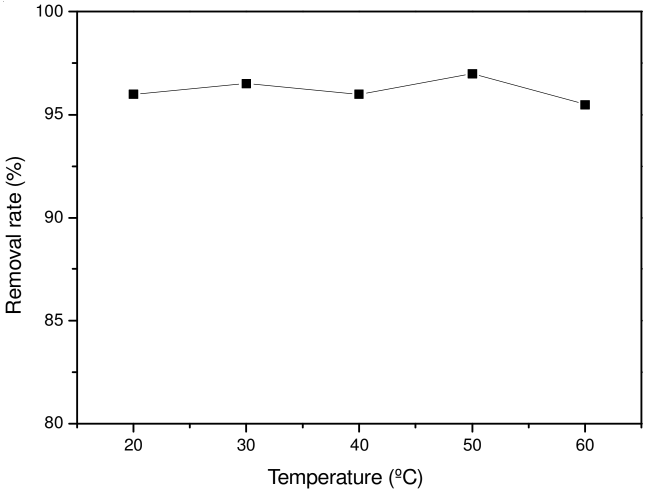

Fig. 10. Effect of reaction temperature after adding in the catalyst on removal rate

The result shows that the reaction is quick at room temperature when the proper amount of acetic acid is added. Increase of temperature has little influence on removal rate. The main reason is that the acetic acid can react with lead oxide to form soluble lead acetate and then the waste acid can be removed rapidly by neutralization precipitation. This method avoids lead sulfate passive film formation, which is favourable for reaction.

Conclusion

- Using electric lead ash instead of lime and other materials to treat waste acid is feasible. On one hand, we can use the smelter intermediate product as raw material in order to reduce cost. On the other hand, precipitation slag of lead sulfate and other valuable metals can be returned the pyrometallurgical process. It can avoid gypsum slag accumulation and environmental pollution owe to absence of the gypsum slag containing heavy metals.
- Many factors can affect the treatment efficiency of waste acid without catalyst. The principal ones are reaction time and temperature. The results show that the treatment efficiency is better at longer time and higher temperature without catalyst.
- The reaction temperature becomes lowered and reaction time becomes shorter with addition of acetic acid catalyst. Removal rate of acid can reach more than 95 % at 20 ºC for 1 h.

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