

Preparation of Grinding Aid Using Waste Acid Residue from Plasticizer Plant

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Abstract. The grinding aid for granulated blast-furnace slag were prepared from waste acid residue from plasticizer plant through neutralization, de-methanol and granulation process. In this process, sulfuric acid was transformed into gypsum which has much contribution for grinding effect by combined use with the glycerol and poly glycerin in the waste. Fly ash was used for granulation for the composite grinding aid. Methanol can be recycled in the process. The result showed that the suitable addition of grinding aid is 0.03 % of granulated blast-furnace slag (mass). In this case, the specific surface area is 14% higher than that of the blank. Compared with the common grinding aids, it has excellent performance and low cost.

1. Introduction

With the rapid development of economy, the demand of building materials is increasing. In recent years, with the cement industry reducing excess production capacity to save energy and reduce carbon dioxide emission, the demand for concrete mineral admixture will increase year by year. Commonly used mineral admixtures are silica fume, fine grinding slag, fly ash, blast furnace slag and so on. In order to improve the activity of these materials, they are necessary to be ground to certain fineness. The addition of grinding aids is of great significance to improve the activity of raw materials and reduce energy consumption.

Grinding aids have found widely use in cement and concrete industry [1-3]. The research of grinding aids is mainly focused on the development of high efficiency grinding aids and composite grinding aids recently. As early as the beginning of twentieth century, many scholars used alcohol, alcohol amine, inorganic salts and polymers for slag grinding. The grinding mechanism was investigated, which mainly includes: strength weakening theory by X.J.Gao [4], film theory by Wu Xiusheng [5] and particle dispersion theory by A.T.Albayrak [6]. The development of composite grinding aids mainly adopts the mix design methods. Jiao Xiaofei et al [7] tested four kinds of common grinding aids (including glycerin, triethanolamine, sodium stearate, sodium lignosulfonate). The results showed that the grinding effect of glycerol is the best, sodium stearate gives optimal particle size distribution. Lin Hui et al [8] studied the influences of molecular size and functional groups of esters on the grinding effect. It turned out that the esters of large molecules and more polar possesses better grinding effect, and effect only when the powder fineness reaches certain fineness. At the same time, esters can improve the material density, increase the later strength. Lin Maosong et al [9] used polyol and sodium stearate to prepare composite grinding aids for steel slag and granulated blast-furnace slag. In this case, the grinding time is reduced by 20% with the target fineness of 425 m²/kg compared with



the blank.

Considering the industrial waste residue contains glycerol, which is a commonly used grinding aid for cement, we utilized this material, through pre-treatment, to prepare grinding aid in order to improve the performance of the products and reduce cost. In the same time, we try to find a rational path of using waste acid residue from plasticizer plant.

2. Experimental

2.1. Materials

The waste acid residue which is highly corrosive and difficult to dispose is from fatty acid methyl ester plasticizer plant with the compositions: methanol 6~8 %, glycerin poly-glycerol 42~46 %, sulfuric acid 36~40 %, water 10~12 %. Lime (with the calcium oxide content of 90%), fly ash and granulated blast-furnace slag were from Hebei Jingye Group. Triethanolamine, thri-isopropanolamine and sodium stearate with CP grade are commercially available.

2.2. Methods

First of all, the concentrated sulfuric acid in the waste acid residue is neutralized by lime, the product with grinding effect, calcium sulfate, is obtained. Neutralization heat and a small amount of external heat were used to steam out harmful methanol. Then, add some fly ash in the mixture, which mainly includes calcium sulfate, glycerol and polyglycerol, mixed. The mixture is granulated to obtain grinding aid. See figure 1.

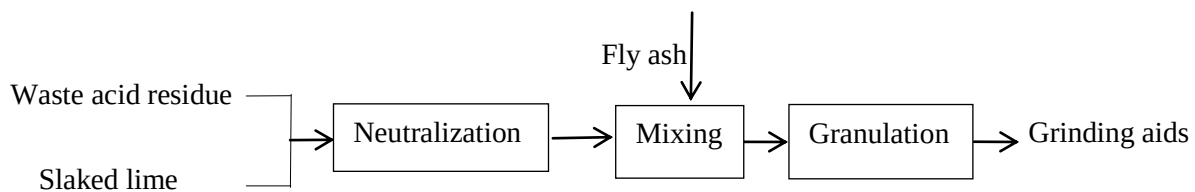


Figure 1. Waste acid residue treatment process.

3. Results and discussion

3.1. Determination of lime consumption

Waste acid residue contains much sulfuric acid, which can be neutralized with alkaline. Among the alkali materials, lime is relative cheap and available. More important, the neutralization product is gypsum which is an essential component in cementing materials. Less of lime will lead to excess in the waste acid residue. And it will lead to corrosion of equipment when used as grinding aid. As lime is add to the waste acid residue, it will react quickly with sulfuric acid to form dense calcium sulfate on the surface particle of the slake lime, resulting in incomplete of reaction in the core of the lime particle, and thus reducing the reaction rate. Therefore, appropriate addition of excessive amount of lime on theoretical basis is needed.

It can be seen from Table 1 that the theoretical dosage of lime is 100 %, which cannot ensured the system to be neutral after a week. Only part of the slaked lime participates in the reaction because of the formation of dense calcium sulfate. The proper dosage of lime should be 106 % of the theoretical amount to guarantee the pH value of the system to be 7 after a week.

Table 1. pH value of waste acid residue with various lime dosage

No	Lime dosage /% (Relative to theoretical value)	pH value after a week
1	100	4
2	101	4
3	102	5
4	103	5
5	104	5
6	105	6
7	106	7
8	107	8

3.2. Neutralization temperature control

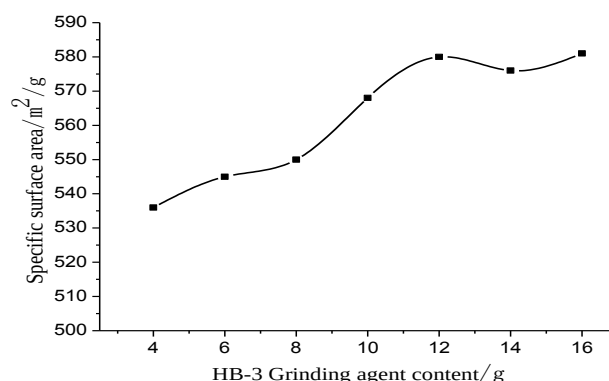
On the one hand, we must control the temperature through the neutralization heat and external heating to guarantee the methanol completely removed. On the other hand, we should prevent the neutralization process from huge boiling or bubble entrainment. The temperature of removing methanol was determined to be 63~66°C. Keep the temperature until no liquid can be distilled off.

3.3. Grinding aids

The main component of the waste acid residue after neutralization and distillation are calcium sulfate, glycerin, polyglycerol and water, which can be used as grinding aids directly. However, it is hard for transport and storage. Therefore, fly ash is used to be solidifying material. The material proportioning of the final composition of the grinding aid (HB-3): waste acid residue 15 %, slaked lime 6 %, fly ash 75 % and water 4 %.

4. Application of HB-3 grinding aid

Granulated blast-furnace slag (4 kg) was mixed with the grinding aids, and then added into mill (SM Φ 500mm $\times$ 500mm), grinding for 70 min. The specific surface area of the power was determined. The results are shown in figure 2.

**Figure 2.** Grinding effect of different dosage of HB-3.

As is shown in the figure 2, the specific surface area is increased with the addition of HB-3. When the dosage of HB-3 is 12 g, the specific surface area of the slag powder tends to be smooth. That is to say, the optimum dosage of HB-3 is 0.3 % of slag.

Table 2 gives the grinding effect of different grinding aids, HB-3 and commercially available grinding aids.

Table 2. Comparison of different grinding aids in application.

Grinding aids	Grinding aid addition /%	Specific surface area of powder (m ² /kg)
Blank	0	514
HB-3	0.03	586
Tri-ethanolamine	0.012	572
Tri-isopropanolamine	0.012	590
Sodium stearate	0.012	600
Glycerol	0.012	596

As can be seen from Table 2, the effect of HB-3 grinding aid is obvious when used for slag grinding, and the specific surface area increased by 14% compared to the blank. HB-3 rivals commercial grinding aids in performance. However, the cost of HB-3 is much lower than the others.

5. Summary

HB-3 grinding aid with good performance was prepared using waste acid residue discharged from the plasticizer plant through neutralization, methanol removal and modification with fly ash. The grinding aid was applied to slag grinding, the specific surface area is 14 % higher than that of the blank, and the cost is much lower than commercial grinding aids.

This process provides a practical resource utilization method for waste acid residue from production of plasticizer. At the same time, a low cost grinding aid was obtained, which has much contribution for the energy saving and carbon emission in the production of granulated blast-furnace slag powder.

6. References

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