

Study on Dezincification Technology of Alumina Production from High Zinc Bauxite

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Abstract

In this paper, a high zinc bauxite in Guangxi region of China was studied in the process of alumina production of zinc digestion performance and dezincification technology with sodium sulfide. The dezincification test of sodium sulfide in the process of digestion shows that the dezincification rate increases gradually with the increase of sodium sulfide content and digestion temperature. When the digestion temperature is 275 °C and the sodium sulfide content is 0.7 g/L, the dezincification rate can reach 74.36 %. In the process of dilution – postdesilication, sodium sulfide is added for dezincification, and the efficiency of dezincification is greatly increased. When the sodium sulfide content is 0.5 g/L, the dezincification rate can reach 90.23 %. Based on the experimental results, the technical suggestions of dezincification in alumina production were put forward.

Keywords: High zinc bauxite, Alumina, Sodium sulfide, Digestion.

1. Introduction

With the development of aluminum industry in China, the grade of bauxite decreases rapidly, and the impurity content in the ore increases obviously, and the impurity composition becomes more and more complex. In the alumina production by Bayer process, zinc impurities are mostly brought in by bauxite, and (ZnO) in ores in some areas reaches about 0.02 % [1]. Zinc exists in bauxite in the form of sphalerite (ZnS), smithsonite (ZnCO₃), hemimorphite (Zn₄(OH)₂Si₂O₇ · H₂O), etc. [1]. During the digestion process, zinc-containing minerals react with NaOH and exist in sodium aluminate liquor in the form of sodium zincate, which is adsorbed by aluminum hydroxide in the subsequent seeded precipitation process and enters alumina products, resulting in low quality of alumina products and ultimately adversely affecting the electrolysis of alumina.

In the process of alumina production, the commonly used technologies are dithiocarbamate method, improved control filtration process, sodium sulfide method, high sulfur bauxite method and so on. Dithiocarbamate method uses the lone electron pair on the sulfur atom in the dithioammonium polar group to capture the cation, forming a stable cross-network of heavy metal ion chelates with Zn²⁺ [2], and heavy metal impurities were removed through precipitation method. This method is simple in operation and has obvious effect, but with the circulation of Bayer liquor in the production process, organic matter accumulation will be caused, which has a negative impact on production; The improved filtration process method uses Fe₂O₃ to adsorb various impurities in Bayer liquor [3,4], and uses the control filter device with tiny particle layer of Fe₂O₃ as the main part to remove zinc impurities, which has obvious dezincification effect. However, due to the periodic cleaning and replacement of the filter layer, it will increase the costs of the alumina plant. Both the sodium sulfide method and the high-sulfur bauxite method use S²⁻ to react with Zn²⁺ to generate a precipitation to achieve dezincification [5–8]. The dezincification effect needs to be further studied.

In this paper, the digestion performance of a high zinc bauxite was studied, and dezincification tests were carried out by adding sodium sulfide in the digestion process step of the Bayer process and the dilution process step of the digested slurry effluent. The influence of addition of different amounts of sodium sulfide and digestion temperature on the dezincification were analyzed, and suggestions of dezincification technology under different production conditions were put forward.

2. Test Raw Materials

2.1 Bauxite

The bauxite was obtained from an alumina plant in Guangxi, China. The main chemical composition of bauxite (%): Al₂O₃ 52.54, SiO₂ 4.92, Fe₂O₃ 23.00, TiO₂ 2.99, K₂O 0.14, Na₂O 0.07, CaO 0.49, MgO 0.18, ZnO 0.014. The main mineral composition (%): diaspore 54.6, gibbsite 3, goethite 20.8, hematite 5, illite 2, kaolinite 9, anatase 2.6, rutile 0.4, calcite 0.7, dolomite 0.3.

2.2 Liquor

The digestion liquor was obtained from an alumina plant in Guangxi, China. The chemical composition of the liquor was Na₂O_T 259.80 g/L, Al₂O₃ 130.62 g/L, Na₂O_K 243.00 g/L, Zn 5.88 mg/L, α_k 3.06.

2.3 Lime

The lime used in the experiment was obtained from an alumina plant in Guangxi, China. The CaO content in lime is 84.44 % and the effective CaO content is 80.32 %.

2.4 Sodium Sulphide

Sodium sulphide is an analytical grade reagent from Tianjin Damao Chemical Reagent Factory in China, and the content of Na₂S·9H₂O is not less than 98.0 %.

3. Test Methods

3.1 Bauxite Digestion Test

The bauxite digestion tests were carried out in a steel bomb digester heated by fused salt. The volume of the steel bomb digester is 130 mL According to the requirements of the ingredients, a portion of bauxite, digestion liquor, lime and sodium sulphide were added into the steel bomb, installed in the rotating steel bomb rack, at a predetermined temperature and immediately stirred. When the predetermined reaction time is reached, the reaction mix is cooled to a temperature of 80 °C in 15 to 30 minutes, the liquor is separated from the treated solid phase, and the chemical composition of the liquor is analysed. After washing and drying, the solid phase was analysed for chemical composition.

The digestion efficiency of total alumina (η_A) is calculated with A/S (the weight ratio of Al₂O₃ and SiO₂) in the bauxite and in the red mud according to the following formula:

$$\eta_A = \frac{(A/S)_B - (A/S)_R}{(A/S)_B} \times 100\% \quad (1)$$

where:

(A/S)_B - The weight ratio of Al₂O₃ and SiO₂ in the bauxite

$(A/S)_R$ - The weight ratio of Al_2O_3 and SiO_2 in the bauxite residue.

The digestion rate of zinc (η_{Zn}) is calculated with Zn/S (the weight ratio of ZnO and SiO_2) in the bauxite and in the red mud according to the following formula:

$$\eta_{Zn} = \frac{(Zn/S)_B - (Zn/S)_R}{(Zn/S)_B} \times 100\% \quad (2)$$

where:

$(Zn/S)_B$ - The weight ratio of ZnO and SiO_2 in the bauxite

$(Zn/S)_R$ - The weight ratio of ZnO and SiO_2 in the bauxite residue.

The removal rate of zinc (η) in the test process is calculated according to the change of zinc concentration in sodium aluminate liquor before and after dezincification, and the calculation formula is as follows:

$$\eta = \frac{C_{Zn-Blank} - C_{Zn-Liquor}}{C_{Zn-Blank}} \times 100\% \quad (3)$$

where:

$C_{Zn-Blank}$ - The concentration of Zn in the liquor of the blank test, mg/L

$C_{Zn-Liquor}$ - The concentration of Zn in the liquor after dezincification, mg/L.

3.2 Dezincification Test in Dilution Desilication Process

The digested slurry was prepared by high pressure digestion, adjusted to the set concentration and solid content of the diluted slurry, and different amounts of sodium sulfide were added to the diluted slurry to study of dezincification during the dilution process. $Na_2S \cdot 9H_2O$ is added in the test and the added amount is measured as Na_2S .

3.3 Analytical Methods

PANalytical PW2403 X-ray fluorescence spectrometer was used to analyze the contents of Al_2O_3 , SiO_2 , Fe_2O_3 , TiO_2 , K_2O , Na_2O , CaO , MgO and ZnO in bauxite. The contents of Na_2O_T , Al_2O_3 and Na_2O_k in sodium aluminate liquor were analyzed by chemical titration. The mineral composition of the solid phase was analyzed by Nalytical X, Pert Pro MPD X-ray diffraction analyzer. The content of CaO in lime was determined by X-ray fluorescence spectrometry. The effective CaO content in lime was determined by titration method. The concentration of Zn ions in the liquor was analyzed by ICAP7000 inductively coupled plasma emission spectrometer. All graphs generated for the various test results were acquired using Origin software.

4. Test Results

4.1 Experimental Study on Digestion Property of Bauxite and rReaction Behavior of Zinc

4.1.1 Effect of Lime Addition on Digestion Performance of Bauxite and Digestion Rate of Zinc

The effect of different lime additions (C/S : 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, and C/S is the weight ratio of CaO and SiO_2) on the digestion rate of zinc was studied under the following conditions: Na_2O_k concentration in Test Tank (digestion) liquor of 243 g/L, digestion temperature of 265 °C and digestion time of 60 min. The effect of lime addition on A/S and N/S in the bauxite residue is shown in Figure 1, and the effect of lime addition on the digestion rate of zinc is shown in Figure 2.

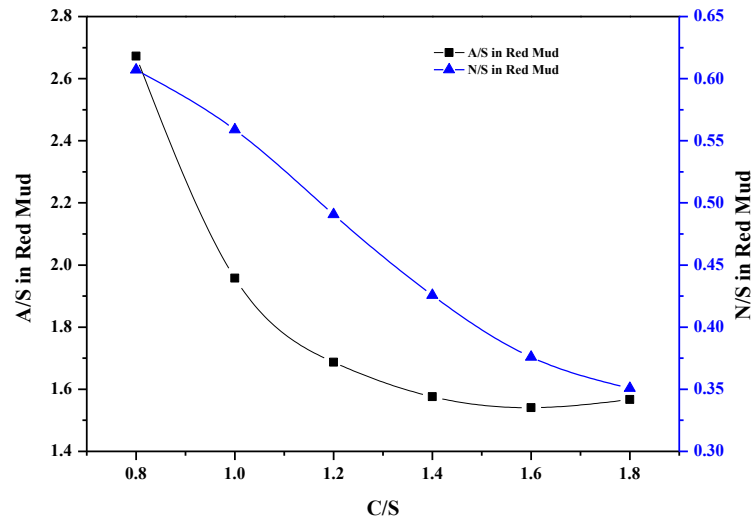


Figure 1. Effect of lime addition on A/S and N/S in the bauxite residue.

Figure 1 shows that under the above test conditions, with the C/S increasing from 0.8 to 1.8, the A/S in the red mud decreased first and then increased slightly. When the C/S was 1.6, the A/S in the red mud was the smallest (1.54), and the bauxite digestion effect was the best, and the alumina digestion rate reached 85.44 %. With the increase of lime content, the N/S in the bauxite residue decreased from 0.61 to 0.35.

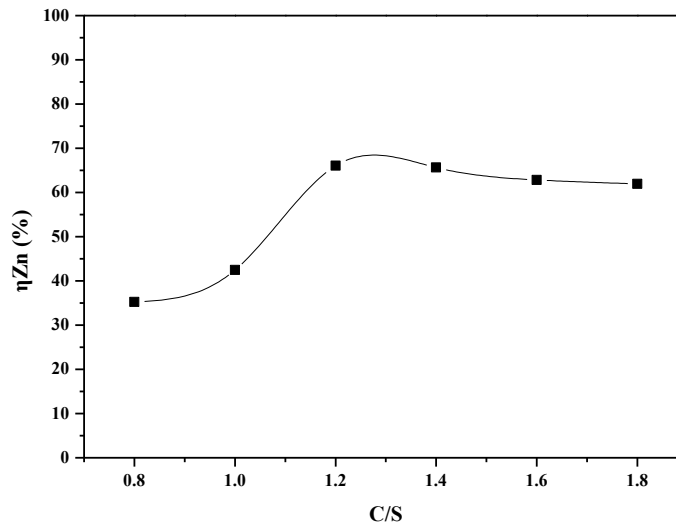


Figure 2. Effect of lime addition on digestion rate of zinc.

Figure 2 shows that under the above test conditions, with C/S increasing from 0.8 to 1.8, the digestion rate of zinc increased first and then slightly decreased. When C/S was 1.2, the digestion rate of zinc was the highest (66.06 %).

4.1.2 Effect of Temperature on Digestion Performance of Bauxite and Digestion Rate of Zinc

The effect of digestion temperature (260 °C , 265 °C , 270 °C , 275 °C) on the digestion rate of zinc was studied under the following conditions: Na₂O_k concentration in Test Tank (digestion) liquor of 243 g/L, digestion time of 60 min and the C/S of 1.2. The effect of temperature on A/S in the bauxite residue is shown in Figure 3, the effect of temperature on N/S in the bauxite residue

is shown in Figure 4, and the effect of temperature on the digestion rate of zinc is shown in Figure 5.

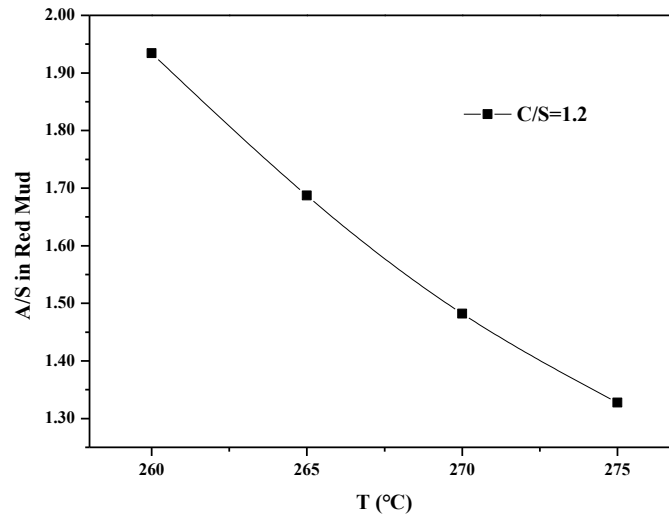


Figure 3. Effect of digestion temperature on A/S in the bauxite residue.

Figure 3 shows that under the above test conditions, with the digestion temperature increasing from 260 °C to 275 °C , the A/S in the bauxite residue decreased from 1.93 to 1.33, and the alumina digestion rate increased from 81.72 % to 87.45 %.

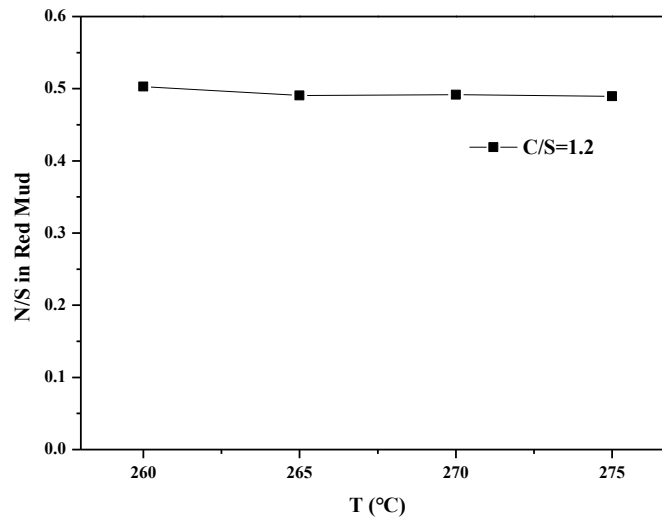


Figure 4. Effect of digestion temperature on N/S in the bauxite residue.

Figure 4 shows that under the above test conditions, with the digestion temperature increasing from 260 °C to 275 °C , the N/S in the bauxite residue did not change significantly, ranging from 0.49 to 0.50.

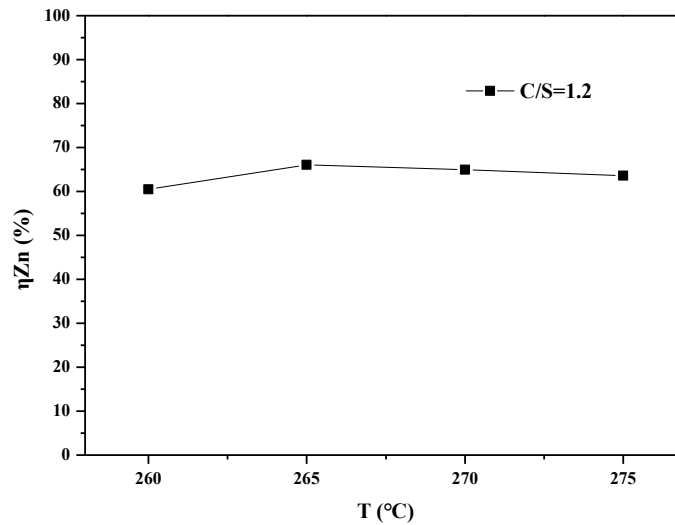


Figure 5. Effect of digestion temperature on digestion rate of zinc.

Figure 5 shows that under the above test conditions, with the digestion temperature increasing from 260 °C to 275 °C, the digestion rate of zinc increased from 60.46 % to 66.06 %, and then as the temperature was increased to 275 °C, the digestion rate of zinc did not change significantly.

4.1.3 Effect of Reaction Time on Digestion Performance of Bauxite and Digestion Rate of Zinc

The effect of reaction time (45 min and 60 min) on the digestion rate of zinc was studied under the following conditions: Na_2O_k concentration in Test Tank (digestion) liquor of 243 g/L, digestion temperature of 265 °C and the C/S between 0.8 and 1.8. The effect of time on A/S in the bauxite residue is shown in Figure 6, the effect of time on N/S in the bauxite residue is shown in Figure 7, and the effect of time on the digestion rate of zinc is shown in Figure 8.

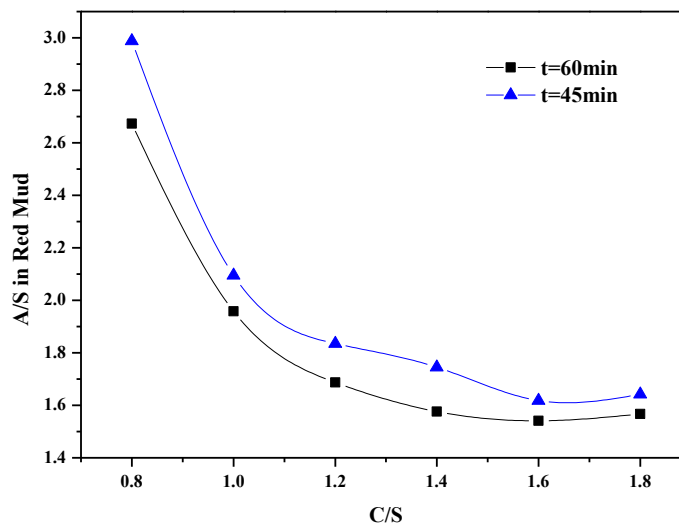


Figure 6. Effect of reaction time and lime addition on A/S in the bauxite residue.

Figure 6 shows that under the above test conditions, the A/S in the bauxite residue when the digestion time is 60 min is lower than that of 45 min, and the digestion rate of alumina when the digestion time is 60 min is higher than that of 45 min.

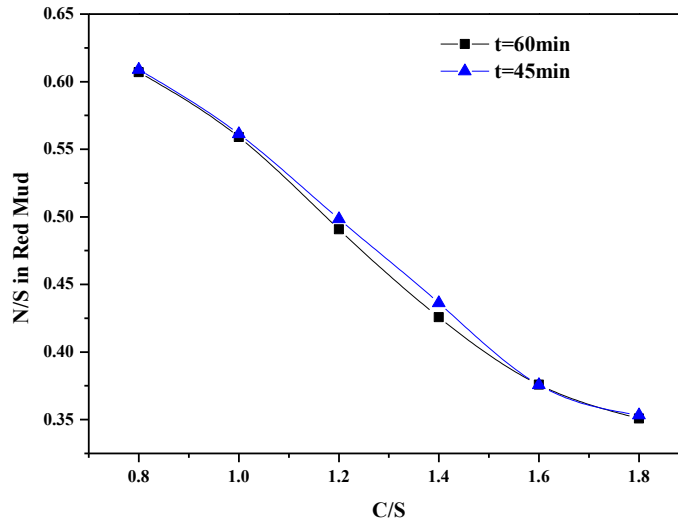


Figure 7. Effect of reaction time and lime addition on N/S in the red mud.

Figure 7 shows that under the above test conditions, the digestion time of 60 min and 45 min had no significant effect on N/S in the bauxite residue.

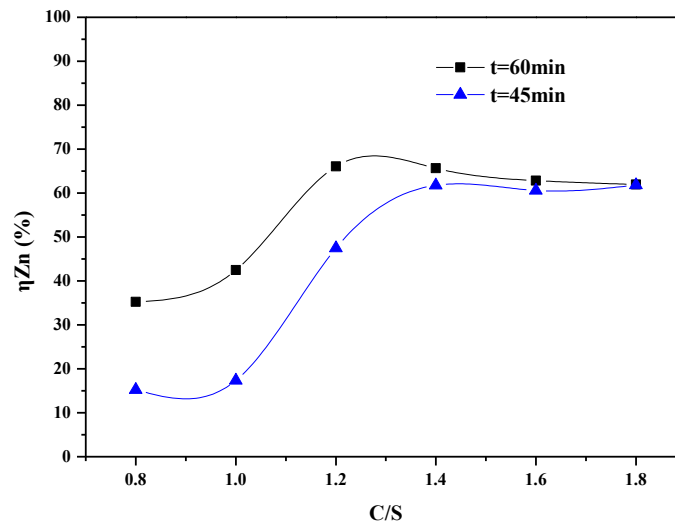


Figure 8. Effect of reaction time and lime addition on digestion rate of zinc.

Figure 8 shows that under the above test conditions, the digestion rate of zinc under the condition of digestion time of 60min is higher than that of 45min in general. When the C/S is 0.8~1.2, the digestion rate of zinc is significantly different, and the difference is 18.60~19.98%. With the increase of lime addition, the difference between zinc digestion rates decreases gradually. When the C/S is 1.4~1.6, the difference of zinc digestion rate is 2.25~3.86%, and when the C/S is 1.8, the zinc digestion rate is similar.

4.2 Experimental Study on Dezincification by Adding Sodium Sulfide in Digestion Process

4.2.1 Effect of Sodium Sulfide Addition on Dezincification Effect

The effect of different sodium sulfide additions (0, 0.1, 0.3, 0.5, 0.7, 0.9 g/L) on the dezincification effect was studied under the following conditions: Na_2O_k concentration in Test Tank (digestion)

liquor of 243g/L, digestion temperature of 265 °C, digestion time of 60 min and the C/S is 1.2. The effect of sodium sulfide addition on the dezincification rate is shown in Figure 9.

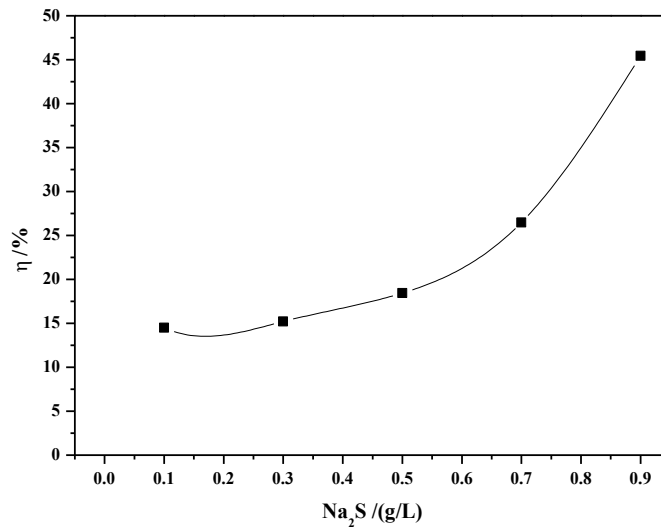


Figure 9. Effect of sodium sulfide addition on the dezincification rate.

It can be seen from Figure 9 that under the above test conditions, with the addition of sodium sulfide increasing from 0.1 g/L to 0.9 g/L, the dezincification rate increased from 14.49 % to 45.44 %. When the added amount of sodium sulfide reaches 0.9 g/L, the amount of sodium sulfide is excessive, and long-term operation will lead to excessive sulfide input into the production system, resulting in equipment corrosion and increased Fe content in the product.

4.2.2 Effect of temperature on dezincification effect

The effect of different digestion temperatures (260 °C, 265 °C, 270 °C, 275 °C) on the dezincification effect was studied under the following conditions: Na₂O_k concentration in Test Tank (digestion) liquor of 243g/L, digestion time of 60 min, the C/S is 1.2 and amount of sodium sulfide is 0.7 g/L. The effect of temperature on the dezincification rate is shown in Figure 10.

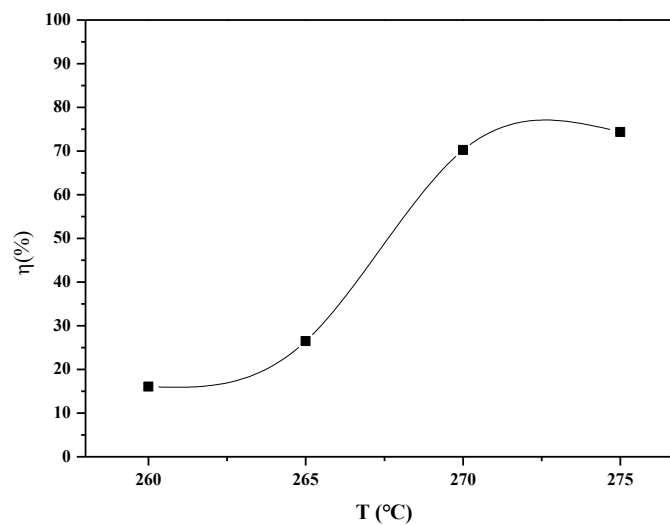


Figure 10. Effect of digestion temperature on the dezincification rate.

It can be seen from Figure 10 that under the above test conditions, with the digestion temperature increasing from 260 °C to 275 °C, the dezincification rate increased from 16.08 % to 74.36 %. The results show that increasing the digestion temperature can accelerate the reaction of S^{2-} with Zn^{2+} to form ZnS and improve the efficiency of dezincification. Therefore, in the initial operation of the digestion unit, the dezincification efficiency can be improved by maintaining a high temperature, and the addition of Na_2S can be appropriately reduced to avoid the adverse effects of excessive sulfide entering the process. Higher digestion temperature makes possible to reduce the retention time of digestion and dissolve more diaspore than at lower digestion temperature.

4.3 Experimental Study on Dezincification by Adding Sodium Sulfide in Dilution-Postdesilication Process

The digestion slurry was prepared when Na_2O_k concentration in Test Tank (digestion) liquor of 243 g/L, reaction temperature of 265 °C, digestion reaction time of 60 min, the C/S is 1.2, which was adjusted to the concentration and solid content of diluted slurry. Different amounts of sodium sulfide (0, 0.1, 0.3, 0.5, 0.7, 0.9 g/L) were added to the diluted slurry to carry out the dezincification tests. The removal temperature was 95 °C, the removal time was 2 h, the Na_2O_k was about 175 g/L, and the solids content of the slurry was about 85 g/L. In the process of dilution-postdesilication, the effect of sodium sulfide addition on the dezincification rate is shown in Figure 11.

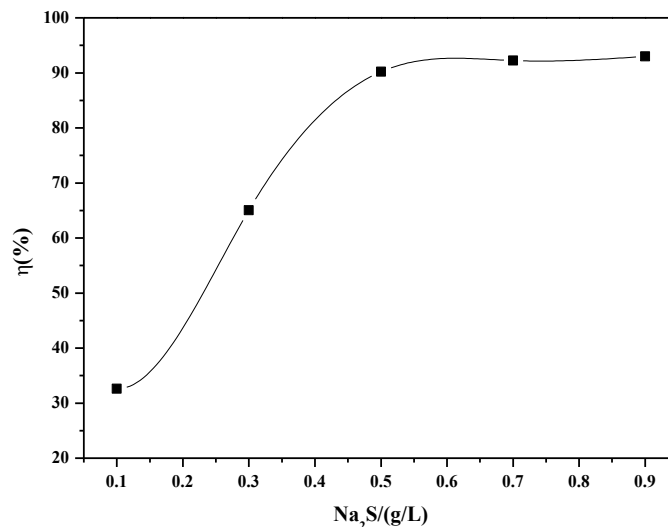


Figure 11. Effect of sodium sulfide addition on the dezincification rate.

Figure 11 shows that under the above test conditions, with the addition of sodium sulfide increasing from 0.1 g/L to 0.5 g/L, the dezincification rate increased rapidly from 32.63 % to 90.23 %. When the addition of sodium sulfide was 0.9 g/L, the dezincification rate reached 93.11 %.

Compared with Figure 9 and Figure 11, it can be seen that when sodium sulfide is added in the digestion process, with the addition of sodium sulfide increasing from 0.1 g/L to 0.9 g/L, the dezincification rate increases from 14.49 % to 45.44 %; when sodium sulfide is added in the dilution-postdesilication process, the dezincification rate increases from 32.63 % to more than 93 %. The dezincification rate when the sodium sulfide is added in the dilution-postdesilication process is higher than that of the digestion process, so if sodium sulfide is used for dezincification, it is recommended that the addition point be selected at the dilution-postdesilication process.

5. Conclusion

(1) With the increase of lime content, the digestion rate of zinc increased first and then slightly decreased. When C/S was 1.2, the digestion rate of zinc was the highest, reaching 66.06 %. The influence of digestion temperature on the digestion of zinc is not obvious.

(2) When the sodium sulfide is added during digestion process to remove zinc, with the increase of the amount of sodium sulfide and the increase of the digestion temperature, the dezincification rate gradually increases. When the digestion temperature is 275 °C and the amount of sodium sulfide is 0.7 g/L, the dezincification rate can reach 74.36 %.

(3) When the sodium sulfide is added during dilution-postdesilication process to remove zinc, with the increase of sodium sulfide content, the dezincification rate gradually increases. When the sodium sulfide content is 0.5 g/L, the dezincification rate can reach 90.23 %, and the dezincification efficiency is significantly higher than that of the digestion process.

(4) For the case of high zinc content in alumina production system, sodium sulfide dezincification method can be used, but because sulfide has a great impact on alumina production, the amount of dezincification taken by adding sodium sulfide should not be excessive, and the addition point should be selected at the dilution-postdesilication process.

6. Reference

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