ABSTRACT

Various surfactants were added into the sodium aluminate solution in order to investigate the influences on the precipitation of aluminum hydroxide. The results indicate that proper additives such as C, H₂, F, etc., can not only improve the precipitation rate, but also enhance the particle size as well as the intensity of the aluminum hydroxide products. The improvement effects of the surfactants in the Bayer process are ascribed to the modification of the physical-chemistry properties of the sodium aluminate solutions. Surface tension, viscosity and conductivity of sodium aluminate solution were studied in detail, and it seems that moderate decrease of surface tension as well as the decrease of the viscosity is in favor of the production of aluminum hydroxide with high yield, large particle size and high intensity. © 2005 SDU. All rights reserved.

Keywords: Surfactants; Sodium aluminate; Bayer process

1. INTRODUCTION

One of the major processes in the production of Al(OH)₃ is to add the crystal seed, Al₂O₃, into the sodium aluminate solution to precipitate another Al(OH)₃ with constant stirring under the temperature-decreasing condition. In recent years, investigations concerning Bayer process mainly focused on the factors affecting precipitation of Al(OH)₃ from Bayer solution as well as the mechanisms of the process (Pradhan et al., 2001; Bhattacharya et al., 2002; Paulaime et al., 2003). However, at present, there is still some products of Al(OH)₃ in our country can not meet the requirements of producing sandy Al₂O₃, because of the low precipitation rate (Chen, 1986). For that matter, much work has been done by researchers. Recent reports show that the precipitation process and the quality of the Al(OH)₃ can be greatly enhanced by adding certain amount of surfactants into the sodium aluminate solution (Harrey, 1990; David, 1991; Lester, 1991; Arnwald, 1995; Moody, 1995; Xue et al., 1998). When the surface active substances were added into the sodium aluminate solution, the physical-chemistry properties would be changed and this will inevitably influence the quality of Al(OH)₃ and its precipitation process.

2. EXPERIMENTAL

2.1. Major apparatus

The major apparatus used are given below: A blade-paddle mixer tank, a Model RPW-09 melting point comprehensive analyzer, a Model 1054BT electric conductivity apparatus, a Model LB-801 super constant temperature bath, and capillary viscometer.

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2.2. Methods for measuring

- The precipitation ratio $\eta$ is defined as:
  \[ \eta = \left[ 1 - \frac{a_\alpha}{a_m} \right] \times 100\% \]
  Where $a_\alpha$ denotes the molecular ratio of the primary solution and $a_m$ stands for the molecular ratio of the original solution. The measurement of Na$_2$O$_7$, Al$_2$O$_3$ and Na$_4$O$_6$ was performed with the chemical method.

- The method for measuring the particle size.
  The particle size of the Al(OH)$_3$ products was analyzed with a sifter and/or a image analyzer (Wang et al., 2002). The particle size of the products was expressed with the mass fraction of the particles that was lower than 45um in diameter.

- The method for measuring of intensity.
  The intensity was performed with a simulated ALCTA attrition index apparatus, with the pressure (N$_2$) 0.40 Mpa and the flow rate of 2.8m$^3$/h lasting 15min. The intensity of Al(OH)$_3$ products was expressed with the attrition index. The definition is as follows:
  \[ AI = \left( \frac{A-B}{A} \right) \times 100\% \]
  Where A is the mass fraction of the particles that was larger than 45um in diameter before blowing and B denotes mass fraction of the particles that was larger than 45um in diameter after the blowing.

2.3. The experimental materials

- The sodium aluminate solution was confected according to the molecular ratio and the concentration expected with the circulating mother liquor provided by the aluminium factory of Shanxi province.

- The surfactants A, G, and C were purchased abroad and the other was produced in our laboratory.

2.4. The experimental conditions

The concentration of alumina is ranging from 160 to 180g/l with the molecular ratio at 1.5, containing 570g/l of the solid seed. The precipitating time is 60h. The temperature was evenly decreased from 75 to 54℃ in the whole process.

3. RESULTS AND DISCUSSION

3.1. The enhanced precipitation process of sodium aluminate solution in the presence of additives

In the Bayer process of precipitation, high-intensity, large-size of Al(OH)$_3$ products can be obtained by adding proper amount of additives. In this study, three kinds of abroad products: A, G and C were employed and some kinds of surfactants were used which were produced according to the general processes. The results were shown in Table 1 and 2.

Table 1: The effects of additives on precipitation ratio, particle size as well as intensity of aluminum hydroxide (addition amount: 100mg/l)

<table>
<thead>
<tr>
<th>Additive</th>
<th>Precipitation ratio (%)</th>
<th>Number of particle (%)</th>
<th>-45μm</th>
<th>Attrition index (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>20.84</td>
<td>24.92</td>
<td>17.21</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>19.24</td>
<td>23.98</td>
<td>13.36</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>21.25</td>
<td>25.84</td>
<td>13.16</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>21.20</td>
<td>24.03</td>
<td>12.15</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>18.74</td>
<td>21.00</td>
<td>16.74</td>
<td></td>
</tr>
<tr>
<td>blank</td>
<td>21.06</td>
<td>25.81</td>
<td>17.98</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>21.68</td>
<td>28.02</td>
<td>10.04</td>
<td></td>
</tr>
<tr>
<td>H$_2$</td>
<td>22.48</td>
<td>24.94</td>
<td>14.30</td>
<td></td>
</tr>
<tr>
<td>H$_5$</td>
<td>17.84</td>
<td>26.92</td>
<td>14.00</td>
<td></td>
</tr>
<tr>
<td>H$_6$</td>
<td>16.80</td>
<td>24.32</td>
<td>17.88</td>
<td></td>
</tr>
</tbody>
</table>
Table 2
The effects of additives on precipitation ratio, particle size as well as intensity of aluminum hydroxide
(addition amount: 200mg/l)

<table>
<thead>
<tr>
<th>Additive</th>
<th>Precipitation ratio (%)</th>
<th>Number of -45μm particle (%)</th>
<th>Attrition index (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>20.96</td>
<td>25.81</td>
<td>17.85</td>
</tr>
<tr>
<td>A</td>
<td>21.56</td>
<td>24.11</td>
<td>12.64</td>
</tr>
<tr>
<td>G</td>
<td>21.04</td>
<td>24.30</td>
<td>12.68</td>
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<tr>
<td>C</td>
<td>21.88</td>
<td>24.62</td>
<td>12.86</td>
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<tr>
<td>I</td>
<td>19.32</td>
<td>28.24</td>
<td>16.90</td>
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<tr>
<td>blank</td>
<td>20.88</td>
<td>25.56</td>
<td>17.23</td>
</tr>
<tr>
<td>F</td>
<td>23.84</td>
<td>24.20</td>
<td>11.80</td>
</tr>
<tr>
<td>H2</td>
<td>23.53</td>
<td>26.60</td>
<td>17.98</td>
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<td>18.01</td>
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<tr>
<td>H5</td>
<td>18.08</td>
<td>24.94</td>
<td>18.87</td>
</tr>
</tbody>
</table>

It can be found from the above two tables that the influences of addition of the additives are differently
according to the kinds they belong to and the amount of the addition. The flowing additives: C, F and H2, can
not only improve the precipitation rate, but also can enhance the particle size and the intensity of the
products. Author had discussed the microcosmic mechanism of additives in relative paper (Zhao et al.,
2003).

The precipitation process was mainly depended on the diffusion and the surface reaction (Xie, 2000).
When the surfactants were added in this process, the physical and chemical properties of the solution such
as the viscosity, surface tension etc. would be apparently changed. Consequently, some surfactants can be
employed, in order to fasten the diffusion rate and enhance formation of the precipitation.

3.2. The influence of the additives on the surface tension of the solution

In order to explore the influence of the additives on the surface tension, various kinds of additives were
employed, keeping the concentration of Al2O3 in the solution from 160 to 180g/l with a molecular ratio of
1.52. A melt comprehensive analyzer was used to measure the surface tension at 75°C. The variations of
the surface tension of sodium aluminate solution with the concentrations of the additives were shown in
Figure 1.

![Figure 1. Effect of amount of additives on the surface tension](image)

From Figure 1, it can be seen that all of additives used are enable to make the surface tension of the
solution decease greatly, appear a lowest value and then go to a stable state. Of course, different additives
have their own break point of concentration and the decreasing amplitudes are also different. Moreover, it
is not easy to say exactly the relation between the decrease of the surface tension and the enhancement of
the precipitation. Although the lower of the surface tension is favorable to the formation of crystal nucleus,
over decreasing can lead to the high forming rate of crystalline particles, making too much branching
crystals on its surface, resulting the intensity decrease. The experiments showed that when the surface tension of the sodium aluminate solution was controlled in the range from 0.015 to 0.02N/m, the Al(OH)₃ products precipitated bear good both intensity and particle size.

3.3. Effect of additives on the viscosity of the sodium aluminate solution

A capillary viscometer was used to measure the viscosity of the solution in order to investigate the influence of the additives on the viscosity of the solutions. The operating conditions are given below: the concentration of Al(OH)₃ is 160-170g/l; molecular ratio 1.52 and temperature at 75°C. The whole process was performed with stirring well.

Figure 2 shows that the viscosity of the sodium aluminate solution can be remarkably changed when the surfactants were added. Generally, the additives play an important part in the intensity and particle size of Al(OH)₃ because of decreasing the viscosity of sodium aluminate decrease. At the beginning of precipitation, the viscosity was always below the blank value, making the diffusion speed, which is in agreement with the precipitation mechanism of the sodium aluminate solution.

2.4. Effect of additives on the conductivity of solution

In this part, a 1056BT model conductivity apparatus was used to measure the solution conductivity for studying the effect of the additives on the conductivity of solutions. The original solution was made by 160-170g/l of aluminium oxide (molecular ratio 1.52) with various additives at 75°C. The results were shown in Figure 3.
The experiments indicated that the five additives: F, H₂, H₅, H₆, and A have little effect on the conductivity, while G or C can make a little, and only additive I can make it decrease significantly. This can be understood by the facts that the additive I is a kind of anion surfactant, and when the amount of the addition is over the CMC (critical micelle concentration), the conductivity became unchanged. While the degree of ionization of surfactants decreases with the increases of its concentration, as a result, the conduction of the solution decreases with the increasing of the surfactant concentration (Shen et al., 1997). For the nonionic surface-active agents such as model F, the addition concentration has little effect on the solutions conductivity (Zhao, 1996). There seems no relationship between the concentration and the solution conductivity for the other additives due to the complexity of the system.

4. CONCLUSIONS

Proper surfactants such as C, H₂, F, etc., added into sodium aluminate solution can not only improve the precipitation rate, but also enhance the particle size as well as the intensity of the aluminum hydroxide product.

The improvement of the precipitation process of aluminum hydroxide can be ascribed to the variations of the physical-chemistry properties of the sodium aluminate solutions after addition of the surfactants. Moderate decrease of surface tension of the solution is in favor of the production of aluminum hydroxide with a better quality. The additives which can lead to the decrease of the viscosity of the solution can enhance the intensity and particle size of the product. Although there seems no obvious relationship between the conductivity of the solution and the quality of the product, it can be implied that the best additives exert their influences by adjusting the crystal growing rate as well as ion diffusion rate in the solution to optimal values.

ACKNOWLEDGEMENT

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REFERENCES

Arnwald, W., The produce of sand-alumina using improved technology of ADS. Light Metals, 1995, 171-175.


Xie, Y.L., Researches on enhancing precipitation of sodium aluminate liquors and coarsening the particle size of aluminum hydroxide product. Ph.D. Thesis of Northeastern University, 2000, 1-123.


Zhao, S., Bi, S.W., Yang, Y.H., Xie, Y.L., Effect of Additives on particle Size and Intensity of Aluminum Hydroxide Produced by Decomposition After Seed Crystal Being Added. Journal of Northeastern University(natural Science), 2003, 10, 984-986.