THEORY AND EXPERIMENT ON COOLING STRATEGY DURING SEEDED PRECIPITATION

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Abstract

The η-t curve is derived from the dynamic equation of seeded precipitation. The curve has the characteristic of a hyperbolic function and the experimental results conform to the characteristics of the curve. The η-t curve indicates that the precipitation ratio rises rapidly at the preliminary stage of precipitation, the precipitation ratio ascends slowly at middle stage of precipitation and the precipitation ratio increases more slowly at the final stage of precipitation. On the basis of this character of the η-t curve and the technology features of seeded precipitation in producing sandy alumina in Chinese alumina plants, various parameters are determined in the precipitation process as a result of intermediate lowering of temperature.

Introduction

The precipitation temperature is one of the most important factors influencing the precipitation ratio in the process of seeded precipitation. Based on the η-T curve, the precipitation ratio is highest when the temperature is somewhat lower than 40℃. In industrial production, the temperature of the pregnant precipitation liquor after leaf filtering, is higher (90~95℃), so the liquor must be cooled down and then precipitated. For cooling, the textbook and many papers have shown that we should cool down quickly at first and then slowly. There are two main cooling strategies in industrial production. One way is that the pregnant precipitation liquor is cooled to around 60℃ directly and then precipitated. In general, this route is always taken by plants producing powder alumina. But this way has also been adopted by Pechiney and Pingguo Aluminium Company producing sandy alumina.

They must add in a great deal of seed, and so the solid content in the first precipitator reaches 750~850g/l. In order to prevent the product from becoming fine, an advanced automatic monitoring system is fitted. The other approach is an intermediate lowering of temperature, that is to say, firstly the pregnant precipitation liquor was cooled down to a temperature range between 70~75℃ for agglomeration for some time, and then the intermediate lowering temperature is adopted to cool down the liquor for further precipitation. This way is used by plants producing sandy alumina with two-stage processes that is represented by the Aluminum Company of Switzerland.

Using The Strategy Of Single Stage Cooling Or Intermediate Lowering Of Temperature

In general, if the strategy of single stage cooling is adopted, the initial temperature of precipitation must be cooled to a low temperature, such as 60℃ or under, in order to make the final

temperature of precipitation very low. So the α_k (molecular ratio of Na_2O_k to Al_2O_3) of the pregnant precipitation liquor is low and the supersaturation is high. Secondary nucleation occurs and the fining of the product particle size is caused, making industrial production fluctuate. This situation is more likely to happen when the caustic concentration is high and the seed coefficient is not very high.

Some researchers have performed the experiment such that the caustic concentration of sodium aluminate liquor is 125g/l, the α_k is 1.71, the seed coefficient is 2.30, the initial temperature of precipitation is 55℃, the final temperature of precipitation is 40℃ and the liquor was precipitated for 72h. They found the product particle size didn't become fine. Given closer analysis we know that because the concentration of the pregnant precipitation liquor is lower, α_k is higher and the seed coefficient is relatively high, thus the fining of the product particle size is avoided.

Things would be different if the precipitation conditions are slightly more demanding. When the caustic concentration of sodium aluminate liquor is 150~160g/l, the α_k is 1.55. This sodium aluminate liquor was precipitated at constant temperature with a different seed coefficient. The product particle sizes with different amounts of seed are shown in Figure 1.
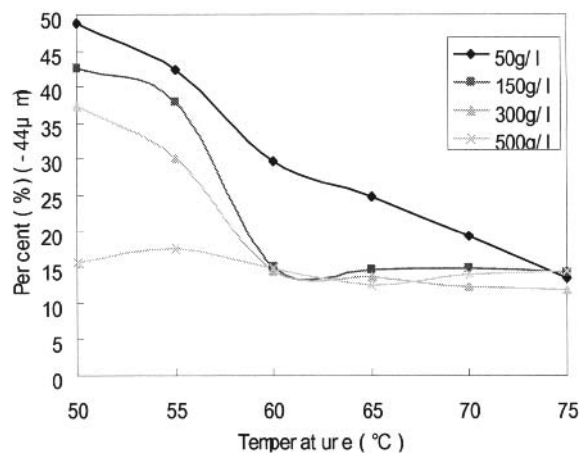

Figure 1. The product particle sizes with different amount of seed

It can be seen from the Figure 1 that when the seed addition is high (300g/l and 500g/l, for example), the product particle sizes don't become fine at a precipitation temperature 60℃, but the product particle sizes begin to become fine at precipitation temperature 55℃; when the seed addition is 150g/l, the product

particle sizes are significantly fine at precipitation temperature 55 ℃. When seed addition is low, such as 50g/l, even if the precipitation temperature is 70℃, the product particle sizes also become fine, with the fining of the product particle sizes more serious at precipitation temperature 65℃ or lower.

The major bauxite resource is diaspore ore in China. The digestion conditions of this bauxite ore are more exigent, and the concentration of the pregnant precipitation liquor is high, that is always between 140g/l and 160g/l. If the strategy of one-stage cooling is adopted to make the initial temperature of precipitation drop to 60℃ or even lower, the fining of the product particle size is difficult to avoid.

The Theory Of Intermediate Lowering Temperature

Researchers in China and abroad have carried out many studies about the dynamics of seeded precipitation in sodium aluminate liquors, and similar dynamic equations are put forward. Next, the η-t curve is derived from the dynamic equation of seeded precipitation. Take following precipitation rate equation for example to deduce the η-t curve.

$$-\frac{dA}{dt} = K_0(A - A_e)^2 \qquad (1)$$

Where A is the instant concentration (g/l) of Al_2O_3 in the sodium aluminate liquor, A_e is the equilibrium concentration (g/l) of Al_2O_3 in sodium aluminate liquor, t is the precipitation time (h), and K_0 is precipitation rate constant.

Equation (1) is transformed as follows:

$$-\frac{d(A - A_e)}{(A - A_e)^2} = K_0 dt \qquad (2)$$

Solving the differential equation (2) as follows:

$$\frac{1}{(A - A_e)} = K_0 t + C$$

When t=0, A=A_0, we can solve for C as follows:

$$C = \frac{1}{A_0 - A_e}$$

Where A_0 is the concentration (g/l) of Al_2O_3 in sodium aluminate liquor.

So we can solve for A as follows:

$$\frac{1}{A - A_e} = \frac{1}{A_0 - A_e} + K_0 t$$

$$A - A_e = \frac{A_0 - A_e}{1 + K_0 t (A_0 - A_e)}$$

$$A = A_e + \frac{A_0 - A_e}{1 + K_0 t (A_0 - A_e)} \qquad (3)$$

It then substitutes into the precipitation ratio formula, equation (3), and we can find the η as follows:

$$\eta = 1 - \frac{A}{A_0}$$

$$= 1 - \frac{A_e}{A_0} - \frac{A_0 - A_e}{A_0 + A_0 K_0 t(A_0 - A_e)}$$

$$= \frac{C_2 t}{C_1(C_1 + C_2 t)}$$

$$\eta = \frac{C_3 t}{C_2 t + C_1} \qquad (4)$$

Where:

$$C_1 = \frac{A_0}{A_0 - A_e}$$

$$C_2 = A_0 K_0$$

$$C_3 = \frac{C_2}{C_1} = K_0 (A_0 - A_e)$$

The η-t curve equation (4) is a hyperbolic function, that is to say, when the seed coefficient is fitted (if the seed coefficient is too low, the induction period will be prolonged). The characteristic of the η-t curve is that the precipitation ratio rises rapidly at the preliminary stage of precipitation, the precipitation ratio ascends slowly at the middle stage of precipitation and the precipitation ratio increases more slowly at the final stage of precipitation.

We will further explain the character of the η-t curve by the laboratory test.

The Character Of The η-t Curve In Laboratory Tests

We have done the precipitation testing in the laboratory to simulate plant conditions. The caustic concentration of the sodium aluminate liquor is 155g/l, the α_k is 1.55. This sodium aluminate liquor was precipitated at constant temperature with different seed coefficients. The seed additions are 300g/l and 500g/l respectively with the seed obtained from the Henan Branch China Aluminium. The η-t curves are shown in Figures 2 and 3 respectively.
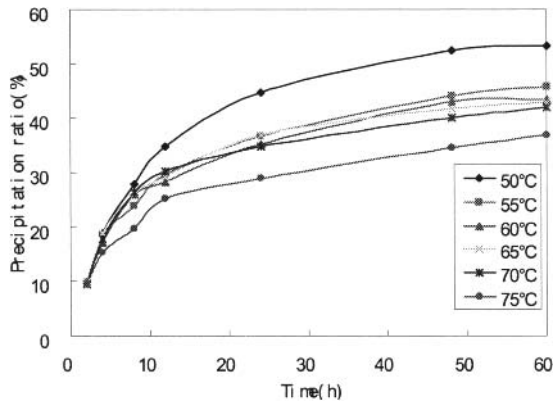
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Figure 2. The η-t curve with 300g/l seed addition

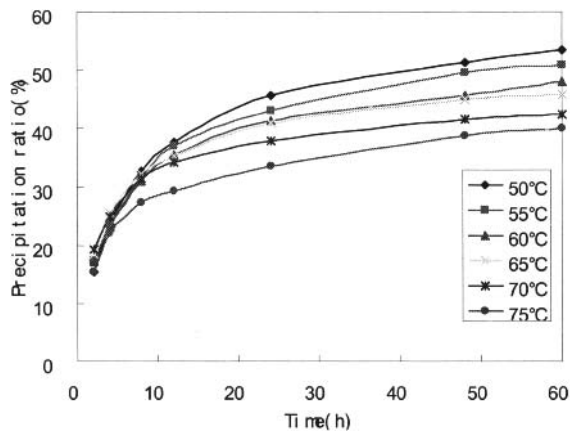

Figure 3. The η-t curve with 500g/l seed addition

The η-t curves in Figures 2 and 3 are completely in conformity with the change rules of the above-mentioned η-t curve derived from the dynamic equation. The precipitation ratio rises rapidly at the preliminary stage of precipitation. It can be seen from Figures 2 and 3 that in the temperature range of 50~70°C, the precipitation ratios reach about 30% for the first 12 hours which is the 65 per cent of the total precipitation ratios for 60 hours when the seed addition is 300g/l; the precipitation ratios reach about 35% for the first 12 hours, which is 70 per cent of the total precipitation ratio for 60 hours when the seed addition is 500g/l. But the precipitation ratio ascends slowly over the middle stage of precipitation and the precipitation ratio increases slower and slower at final stage of precipitation. The precipitation ratios are about same at different times for the first 8 hours in the temperature range of 50~70°C; the precipitation ratios are also about same for the first 12 hours in the temperature range of 55~70 °C ; the precipitation ratios are different at different temperatures after precipitation for 24 hours, the gap increases with longer time of precipitation, and the precipitation ratios are higher with decreasing temperature.

If the precipitation temperature is too high (75°C), the precipitation ratios are much lower than that in the temperature range of 50~70°C at the preliminary, middle and final stage of precipitation; if the precipitation temperature is too low (50°C),

the precipitation ratio is about as high as that in the temperature range of 55~70 °C when the seed addition is 500g/l, the precipitation ratio is much higher than that in the temperature range of 55~70 °C after precipitating 12 hours when the seed addition is 300g/l.

The Determination Of Various Parameters Of Intermediate Lowering Temperature By Using The Change Rules Of The η-t Curve

The Determination Of The Initial Temperature Of Precipitation

Because the precipitation ratios are about the same for the first 12 hours in the temperature range of 55~70 °C , it is proper to determine the initial temperature of precipitation in the temperature range of 65~70°C which is a bit higher within the temperature range of 55~70°C. By doing this, the precipitation ratios are not affected and the fine particles of aluminium trihydroxide can be agglomerated very well.

The Determination Of The Time Of Intermediate Lowering Temperature

Because the precipitation ratios are about same in the above-mentioned temperature ranges, and the gaps become too big for different temperatures with the longer times of precipitation, we should cool down after precipitation for 12~14 hours. In this way the liquor can be precipitated at a low temperature in time, and the precipitation ratio is improved. If the time of intermediate lowering of temperature is too late, the liquor is still precipitated at high temperature, so the precipitation ratio is influenced. The later it is cooled down, the greater the precipitation ratio is influenced. It is not appropriate to cool down too early, for example after precipitating 7~8 hours, if so, the product particle size may become fine and scale is readily produced on the interstage cooling equipment.

The Modes Of The Precipitator Before The Intermediate Lowering Of Temperature

Seeded precipitation is performed in batch operation or continuous operation. Currently, continuous operation is adopted in most plants. The disadvantage of continuous operation is that the pregnant precipitation liquor with the lower a_k flows continuously into the precipitator to rapidly mix with the precipitated liquor (a_k is higher) in this precipitator, so the a_k is increased immediately and the precipitation ratio is decreased. Of course, the precipitation ratio of the liquor flowing from this precipitator is also decreased.

From the characteristics of the above-mentioned η-t curve, we know that the precipitation ratios for the first ten hours or more, are 65~70 per cent of the total precipitation ratios for the full precipitation time. So it is at the initial stage of precipitation (more specially, it is at the first precipitator) that the seeded precipitation performed in continuous operation influences the precipitation ratio remarkably. But there are no obvious influences on the middle and final stages of precipitation. To a certain extent, the disadvantage of continuous operation can be overcome by adopting the strategy of intermediate lowering of temperature. That is to say, the pregnant precipitation liquor flows into the precipitator from the top which is stirred interlayer, so the a_k of the pregnant precipitation liquor is not significantly increased,

then the precipitated slurry flows out from the bottom of the precipitator and was pumped into interstage cooling equipment.

The Technical Projects On The Intermediate Lowering Of Temperature

Cooling The Pregnant Precipitation Liquor By Plate Heat Exchangers

The pregnant precipitation liquor was cooled down to the temperature ranges between 65~70℃ from the temperature 95℃ by using plate heat exchangers. It is calculated that it will be possible to save 200,000 tons of steam every year, generating 10 million yuan every year in economic returns, if the spent seed precipitation liquor was preheated by the way of cooling down the pregnant precipitation liquor.

The Location Of Interstage Cooling Equipments In The Series Of Precipitators

It has been mentioned above that it is appropriate to cool down the liquor after precipitating 12~14 hours. So the location of interstage cooling equipment will depend on the retention time of the liquor in each precipitator. If the retention time of the liquor in each precipitator is range of 10~12h, we should begin to cool down the liquor after it flows out from the first precipitator. Of course, we should begin to cool down the liquor after it flows out from the second precipitator, if the retention time of the liquor in each precipitator is in the range of 5~8h.

The Tube Heat Exchangers As The Interstage Cooling Equipment

Because there are a lot of Al(OH)$_3$ solids in the liquor, the plate heat exchangers are easily blocked, so the plate heat exchangers are not suitable for this application. Tube heat exchangers and vacuum heat exchangers are preferred equipment. The tube heat exchanger is simple and practical, which was developed in Hungary and used successfully in industrial production.

The temperature of the slurry is 65~70℃ as mentioned above, and it needs to be cooled to around 50℃, thus the cooling requirement is considerable. So if it is not enough to cool down by using one-stage cooling equipment, we can adopt a multi-stage series to cool down the liquor to the set temperature.
To conclude, the temperature of the pregnant precipitation liquor after leaf filtering is 90 ~ 95 ℃. It was cooled down to temperature ranges between 65 ~ 70 ℃ by the plate heat exchangers and flows into the first precipitator from the top, then the precipitated slurry flows out from the bottom of the precipitator and was pumped into multi-stage tube heat exchangers to cool down to temperature ranges between 50~55 ℃ and then was feed into follow-up precipitator series to continue precipitation. The temperature of the precipitated slurry in the last precipitator is 40~45℃.

Conclusion

The characters of the η-t curve are studied by the way of the basic theory of precipitation, combined with experiments. This characteristic curve elucidates the rationale for adopting the strategy of intermediate lowering of temperature in the process of seeded precipitation and the technical parameters are determined.

These include the time of intermediate lowering of temperature, the initial temperature of precipitation and the cooling extent of intermediate lowering of temperature and so on. This has certain direct significance to the determination of the temperature decreasing strategy in the process of seeded precipitation.

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