The Effects of Washed Seed on Sodium Oxalate Precipitation and Particle Size Distribution

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Abstract

The precipitation of sodium oxalate in saturated liquor can affect the particle size distribution of the product in the precipitation process. Given this phenomenon, the behavior of sodium oxalate precipitation with washed seed was analyzed in the precipitation process. In addition, the internal theory, that the particle size of seed influenced by sodium oxalate would reduce, was also evaluated. In this paper, the results of using washed seed during three continuous precipitation cycles and the associated effect on particle size distribution is examined and discussed.

Keywords: Washed seed, Sodium oxalate, Particle size distribution, composition

1. Introduction

With China's domestic bauxite grade gradually reducing, some domestic alumina enterprises began to use overseas bauxite to produce alumina. The organic matter content was found to be higher in overseas bauxite than from the locally sourced bauxite. In the process of production, macromolecular organic matter was gradually transformed into soluble sodium oxalate under exposure to alkali and high temperature conditions [1].

When the concentration of sodium oxalate was high in the sodium aluminate solution [2], it precipitated in the process of seed precipitation and adsorbed on the surface of the alumina tri-hydrate seed. Also observed was an increase in secondary nucleation, a reduction in seed strength and a resulting reduction in the size of the product granularity [3]. The explosive precipitation of sodium oxalate significantly damaged the growth cycle of the seed and the product size was affected.

Over the past few decades, experts and scholars conducted in-depth research on the removal of organic matter in the process of alumina production. The main methods identified were bauxite and spent liquor roasting, precipitation, crystallization, ion exchange, seed washing, seawater neutralization, and wet oxidation [4].

Due to the different content and types of organic matter in the bauxite used by each aluminum oxide plant, as well as the different production processes and technical conditions, the level and types of organic matter were also different in the production systems. Therefore, studies geared towards seeking more adaptive, economically and operationally feasible methods of organic matter removal have been conducted.

In the aforementioned technologies, the seawater neutralization method required a large area and needed to be located near the sea. The solution combustion method has been used across the industry, but is cost intensive and the exhaust gases of combustion presents their own environmental problems. The wet oxidation method requires a high level of investment due to the amount of equipment and operational resources required [5]. Compared with the two-stage precipitation process used outside of China, the seed washing method is most easily adopted because of the small amount of fine seed required, and the crystallization method is relatively simple. The crystallization effect, however, is very different in different systems.

In this paper, the removal of sodium oxalate using the seed washing method was evaluated. Specifically, the precipitation behavior of sodium oxalate was studied in washed seed during the precipitation process. By managing the precipitation of sodium oxalate in the precipitation tank, the morphology of the seed was optimized, and the particle size of the product was controlled.

2. Equipment and Method

2.1 Test Equipment

The main types of equipment used for this test were:

1. Precipitation tanks with a mechanical agitators.
2. Water baths, developed by the Zhengzhou Research Institute, used to independently heat the system and maintain constant temperature
3. Analytical balances
4. Vacuum filter devices

The main equipment used for sample analysis during the test were:

1. X-ray Diffractometer (XpertProMPD) used to analyze the phase composition of the sodium oxalate impurities,
2. Ion Chromatography Analyzer (Metrohm930) for oxalate content in the solution
3. Scanning Electron Microscope (JSM6360LV) for seed morphology analysis
4. Particle Counter (Multisizer3) for seed particle size analysis
5. Chemical Titration for sodium aluminate solution composition analysis

2.2 Test Method

A sodium aluminate solution from the production process was added to the precipitation tank. After preheating to the set temperature, a specified mass of unwashed alumina tri-hydrate seed was added. The seed was initially added to the No. 1 precipitation tank, and washed seed was then added into the No. 2 precipitation tank. After the agitator was started, the system was operated under the established precipitation temperature regime. When the predetermined precipitation time was reached, separated seed from slurry. Some seed was taken for impurity composition analysis, and the rest was used as the precipitated seed for the next cycle (No. 2 precipitation tank only had one cycle of seed washing)

Three cycles of continuous precipitation tests were carried out in this time. The test conditions were as follows:

1. precipitation temperature was 52-65 ℃,
2. The initial solid content of precipitation was 600 g/L
3. The precipitation time was 45 hours
4. 25 ppm of CGM was added

The experimental conditions of seed washing:

1. the hot water temperature was 80 ℃,
2. The solid content was 600 g/L
3. The reaction time was 1 hour.

After the reaction, a solid-liquid separation was carried out with a suction filter bottle, and the washed seed was added to the No.2 precipitation tank for the precipitation test.

The method of analysis for oxalate in seed included the rinsing and drying of the seed with alcohol. Then 50 g of dried washed seed was added to 100 mL of ultrapure water and stirred at 80 ℃ for 20 minutes. Vacuum filtration was carried out after full dissolution. Then 200 mL of filtrate were removed and the volume was fixed to 250 mL in a volumetric flask. The oxalate was analyzed and converted into oxalate content of seed in the solution.

3. Result and Discussion

3.1 Experimental Phenomenon

After three cycles of precipitation the macroscopic morphology of the seed was assessed. These results are shown in Figure 1 below.

Figure 1. Comparison of sodium oxalate precipitation from seed after three precipitation cycles

No impurities were seen in the seed after washing once (right), while the original seed still had dark red impurities in the precipitation cycle (left). By washing the seed, the separate crystallization of sodium oxalate was inhibited in the sodium aluminate solution.

The dark red impurities were removed and their morphology was observed after agglomeration, as shown in Figure 2.

Figure 2. Macroscopic morphology of impurities

Phase analysis was performed on the material, and the main impurities were determined to be sodium oxalate and aluminum hydroxide. The results are shown in Figure 3.

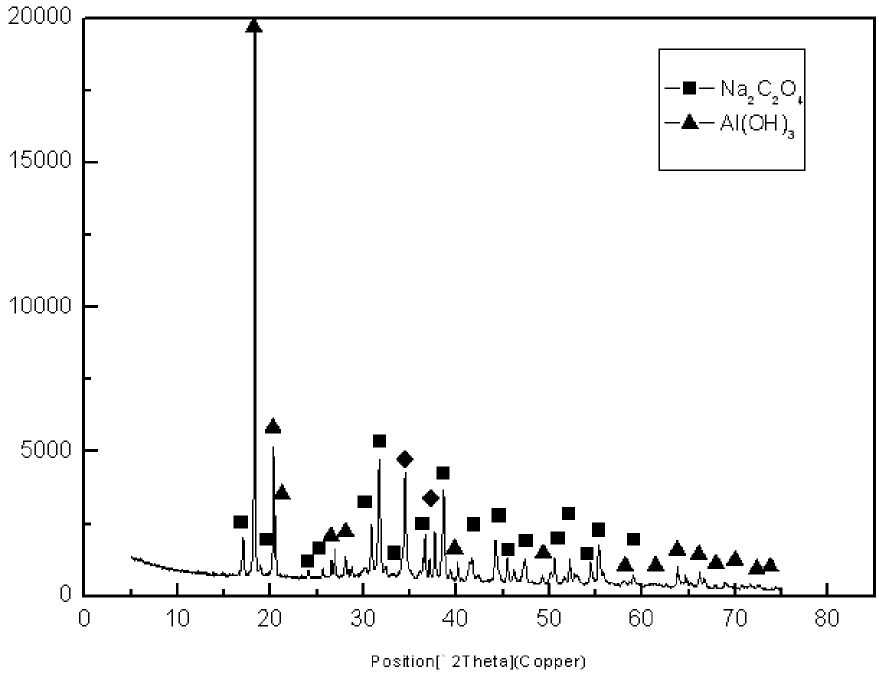

Figure 3. Impurity phase diagram

3.2 Analysis of Experimental Chemical Components

Table 1, Table 2 and Figure 4 show the precipitation test results of three cycles of washed seed.

Table1. Liquid phase results of three cyclic precipitation tests, g/L

Sample name	N_2O_T	Al_2O_3	N_2O_K	$C_2O_4^{2-}$
green liquor-1	186.8	176.3	158	1.78
spent liquor with unwashed seed-1	197.8	105.7	166	1.44
spent liquor with washed seed-1	191.0	179.4	156	1.82
green liquor -2	191.0	179.4	160	1.57
spent liquor with unwashed seed-2	196.7	102.4	170	1.21
spent liquor with washed seed-2	196.7	101.8	168	1.59
green liquor -3	192.3	178.4	162	1.50
spent liquor with unwashed seed-3	199.9	107.1	170	1.20
spent liquor with washed seed-3	198.1	106.7	170	1.50

Table2. Weight percentage of oxalate on the surface of seed in three cycles, %

Sample name	Oxalate Content of Seed
original seed	0.22
unwashed seed-1	0.21
washed seed -1	0.07
unwashed seed-2	0.18
washed seed -2	0.04
unwashed seed-3	0.19
washed seed -3	0.05

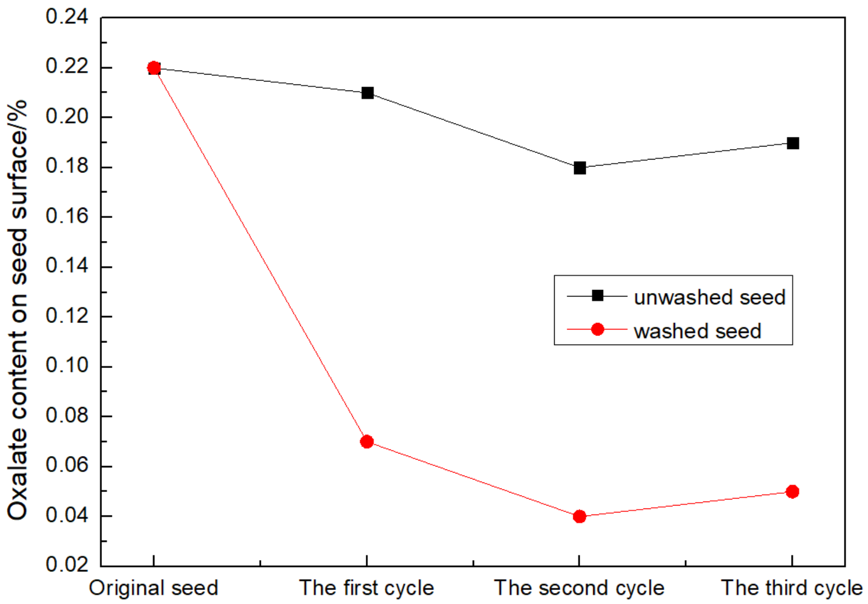

Figure 4. Weight percentage of oxalate on seed surface of three cycles

There was statistically no difference of sodium oxalate between spent liquor and green liquor after seed washing, while the difference of sodium oxalate was about 0.3g/L between unwashed spent liquor and green liquor.

After three precipitation cycles, the sodium oxalate content was reduced to less than 0.1% on the surface of the washed seed, while the sodium oxalate content was maintained at 0.2% on the surface of the unwashed seed.

After the seed was washed, sodium oxalate no longer precipitated on the surface of the aluminum hydroxide, and the content of sodium oxalate increased in the spent liquor. This condition was more conducive to the removal of sodium oxalate in the subsequent spent liquor. After seed washing, sodium oxalate content could be reduced for a long time in the seed.

3.3 SEM Morphology of Seed

The original seed morphology, the unwashed seed morphology, and the washed seed morphology are shown in Figures 5-7 below.

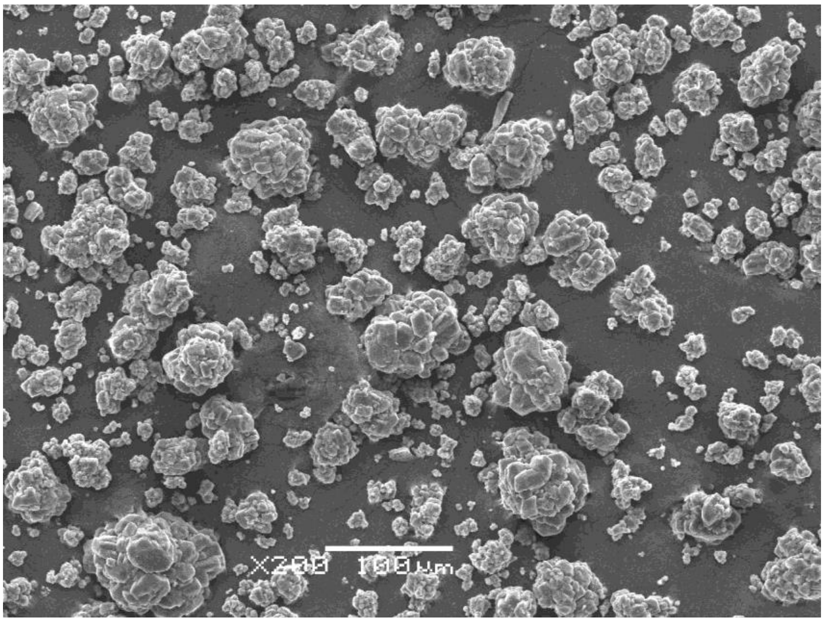

Figure 5. Original seed morphology

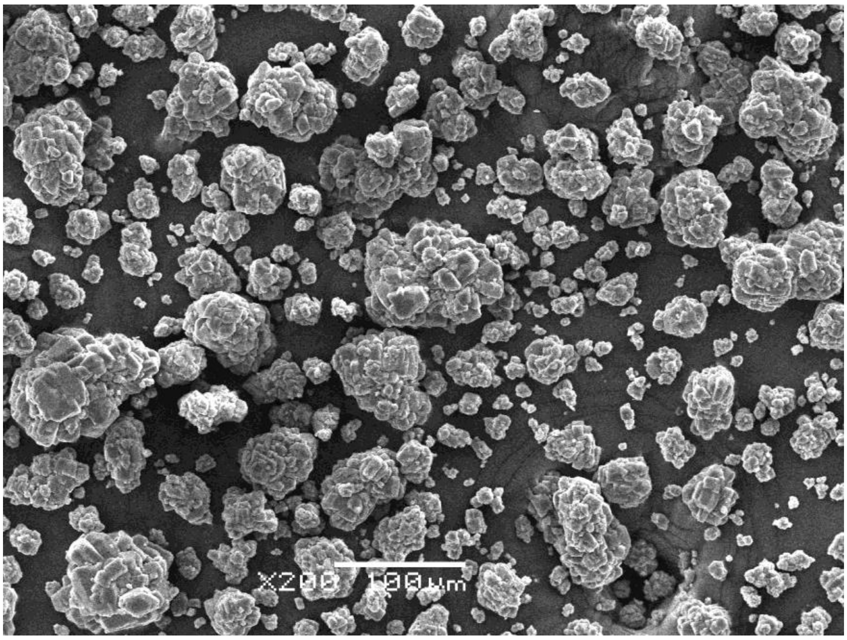

Figure 6. Unwashed seed morphology

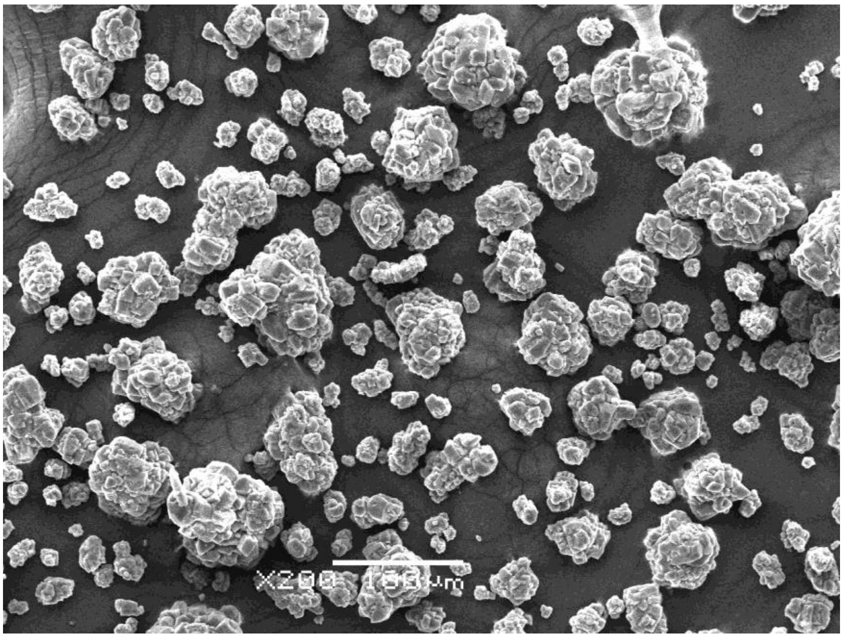

Figure 7. Washed seed morphology

The increase of sodium oxalate adsorbed on the surface of the seed hindered the agglomeration of alumina tri-hydrate, thus increasing the nucleation frequency of the seed and is expected to result in the reduction of product particle size.

After washing, the number of fine particles was significantly reduced in the seed, the particle size coarsened after agglomeration, the crystal type improved, and the strength of the seed increased.

At present, the alumina enterprises use the particle counter to analyze the nucleation frequency and particle size distribution of the seed. The device is sensitive to particle size nucleation and can detect coarsening or fining trends very early. ,Based on the change to the finest fraction of the grain seed, timely adjustments may be made.

The results of the seed size distribution during the test are shown in Table 3 and Figure 8.

Table 3. Results of particle size analysis

Sample name	Nucleation frequency (*10^5)				Weight percentage (%)		
	f1.92 (µm)	**f2.62 (µm)**	**f3.55 (µm)**	**f5.34 (µm)**	**-9 (µm)**	**-14 (µm)**	**-45 (µm)**
original seed	11.58	4.68	1.95	0.68	0.12	1.42	28.66
unwashed seed-1	11.27	4.72	2.15	0.61	0.12	1.45	29.54
washed seed -1	12.20	4.27	1.51	0.67	0.13	1.53	28.97
unwashed seed-2	11.24	4.77	2.01	0.67	0.10	1.31	28.17
washed seed -2	11.97	4.23	1.33	0.45	0.08	1.37	28.18
unwashed seed-3	12.95	4.58	1.76	0.72	0.10	1.55	26.87
washed seed -3	11.10	3.52	1.27	0.23	0.05	0.97	25.81

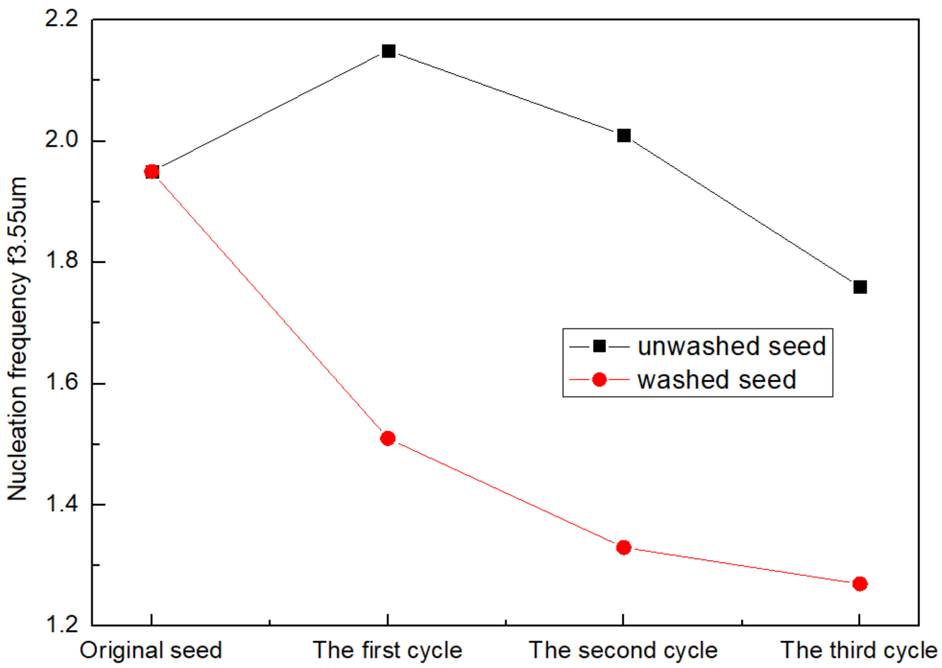

Figure 8. Analysis of seed nucleation frequency

The results of the particle size analysis showed that, after seed washing, the nucleation frequency f3.55µm decreased from 1.95 to 1.27, close to the control target value of 1.20, and the agglomeration ability of the seed increased significantly. Meanwhile, the number of -9µm and -14µm fine particles decreased. The content of -45µm required thirty days growth period and didn't change much. There was a noticeable improvement in the seed size.

4. Conclusion

The increase of the oxalate content of the green liquor resulted in an increase of the oxalate content of the seed. The oxalate content of the seed affected the nucleation frequency and morphology. It suggests that the oxalate content of the seed should be less than 0.1% during production.

The inhibition effect of washed seed on sodium oxalate was manifested in two aspects

1. No sodium oxalate crystals appeared in the precipitation tank; the adsorption capacity of sodium oxalate was weakened on the seed's surface, and the content of sodium oxalate was reduced from 0.2% to 0.1% on the seed's surface
2. After three precipitation cycles, the morphology of washed seed was visibly optimized. The nucleation frequency of f3.55µm decreased from 2.0 to 1.3, and the seed size began to coarsen

In the alumina production process, when sodium oxalate is precipitated in the precipitation tank, the sodium oxalate content would increase on the seed's surface, resulting in a grain size reduction. After washing the seed, the sodium oxalate content of the seed on the surface would be reduce, and the influence of sodium oxalate on precipitation would be suppressed in the longer term, as well as prevent product grain size reduction.

5. References

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