AA17 - Characteristics of Sodium Oxalate Precipitates from the Bayer Precipitation Process.

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Abstract:

Sodium oxalate is an impurity in the alumina production (Bayer) process. It circulates and accumulates in process liquor and at a critical concentration, precipitates in the precipitation area of the Bayer process, with negative impacts on product quality. The morphology and some characteristics of sodium oxalate precipitated under different Chinese refinery process conditions were studied with X-ray diffraction (XRD) and scanning electron microscopy (SEM). It was found that the oxalate from all process conditions examined precipitated as roughly spherical particles, although the size and other characteristics of the precipitated sodium oxalate particles varied with the different refinery process conditions. The oxalate precipitates examined contain two significant mineral components, sodium oxalate and aluminum hydroxide, which varied depending on the process conditions. This study's findings provide a useful input into the selection of sodium oxalate removal technologies for these refineries, and others with similar sodium oxalate precipitates.

Keywords: Sodium oxalate, aluminum hydroxide, precipitation, spherical particle, surface structure characteristics.

1. Introduction

Sodium oxalate is an impurity in the alumina production (Bayer) process, and mainly comes from two sources. The primary source is from the dissolution and decomposition of organics in bauxite during the bauxite digestion process [1], where organics are broken down under the conditions of temperature and high caustic Bayer liquor to produce dissolved sodium oxalate, among other organic salts. Another pathway is the further degradation of higher-molecular organics in the recycled Bayer process liquor during redigestion [2,3,4].

With continuous oxalate input from ongoing bauxite digestion, the concentration of sodium oxalate increases in the circulating liquor inventory until it reaches a relatively balanced concentration in the liquor. The equilibrium of sodium oxalate is dynamic, responding to changes in bauxite inputs, temperature and liquor caustic concentrations and other factors in the refinery process, causing its concentration to fluctuate within a small range. After bauxite is digested, the concentration of sodium oxalate in the process liquor is increased. As the liquor flows through the production process, it will be precipitated at a certain point or multiple points in the process. This can be on the walls of precipitation tanks, on the surface of aluminum hydroxide seed [5,6], on seed filters, and during liquor evaporation, and most commonly, it can precipitate as a discreet particle mixed with aluminium hydroxide seed. Due to the precipitation of sodium oxalate in the precipitation area, the concentration of sodium oxalate in liquor is at a lower level at the end of the precipitation cycle. As the Bayer cycle continues, more oxalate is added by bauxite digestion, through the process of both extraction of new oxalate from bauxite organics and degradation of recycled organics in the liquor, increasing the oxalate in the digestion liquor to a higher level.

The precipitation of sodium oxalate has a negative effect on the Bayer process. It will lead to shorter operating cycles for precipitation tanks due to higher scaling, lower the quality of alumina products, increased caustic consumption, and affect the alumina production rate of a refinery [7, 8]. At present, there are a variety of sodium oxalate removal methods, such as red mud washing [9], aluminum hydroxide seed wash with water, lime causticisation [10], crystallization from spent liquor, Bayer liquor calcination (liquor burning), Bayer liquor wet oxidation [11, 12], etc. Due to the large difference between these methods' economics, different refineries choose different oxalate removal technologies based on their own conditions and economics.

Among the multiple sodium oxalate removal technologies, sodium oxalate precipitation during aluminum hydroxide precipitation (or 'oxalate co-precipitation') has advantages over other methods, and is often considered to be a technology with a better overall performance. Sodium oxalate precipitates in various crystal sizes and shapes during the precipitation process. Where the precipitated particle size is significantly larger than that of the aluminum hydroxide seed, a screening device can be added to separate the precipitated oxalate particles from the Bayer liquor and seed, and in doing so, remove sodium oxalate from the Bayer process. During this study of oxalate precipitates in Chinese refineries, it was found that sodium oxalate particles precipitated under different liquor conditions showed differences in particle size, chemical composition and morphology. The morphology and some structural characteristics of the particles precipitated under these different liquor conditions are reported here, and provide a reference to inform a choice of sodium oxalate removal processes and technologies.

2. Material and Methods

2.1. Material

Sodium oxalate particles precipitated in a Chinese refinery using a high temperature (~265 °C) digestion to process diasporic bauxite are shown in Figure 1.

Figure 1. Sodium oxalate particles precipitated from diaspore digestion process.

Sodium oxalate particles from this high temperature process are relatively large, with a diameter of about 2-5 mm. The particles before drying are a dark red color, and after drying are an earthy yellow color. For easy reference, this oxalate from a high temperature process is referred to as 'particle 1'. The appearance of sodium oxalate particles precipitated in the process of low (~145 °C) or medium temperature (~230 °C) Bayer process where gibbsitic bauxite is the raw material was similar, as shown in Figure 2.

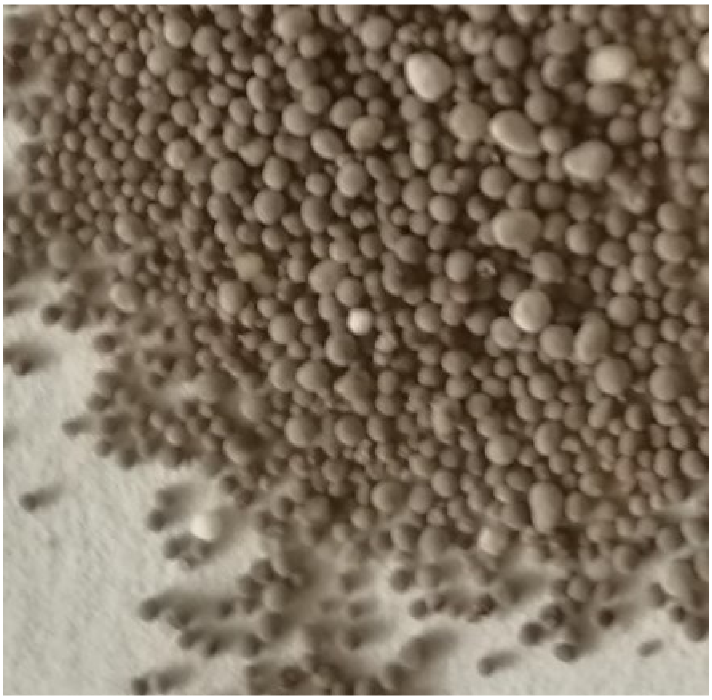

Figure 2. Sodium oxalate particles precipitated from gibbsite digestion process.

The sodium oxalate particles precipitated when gibbsitic bauxite is digested are relatively small, with a diameter of about 1-2 mm. The particle is a black color before drying and gray after. For convenience, particles precipitated in the low temperature Bayer process are called 'particle 2', and oxalate particles precipitated in a medium temperature Chinese Bayer refinery are called 'particle 3'.

2.2. Test Instruments and Methods

Scanning electron microscopy (SEM) observations of the samples were performed on a Hitachi S4800 cold field-emission scanning electron microscope equipped with an energy-dispersive X-ray spectroscopy (EDS) apparatus. The resolution ratio was 1.00 nm (15 kV), and the acceleration voltage was 0.50 to 30 kV.

A PANalytical X'Pert Pro X-ray diffractometer with a Cu target anode (Kα, λ=0.15418 nm) was used for X-ray diffraction (XRD) analysis of the samples. The voltage was 45 kV, the current was 40 mA, the scanning angle was varied from 10° to 70 °2θ, and the scanning speed was 4°2θ/min.

The oxalate content of the sodium oxalate particles was measured by mass difference after dissolution. The particles contained two major components, sodium oxalate and aluminum hydroxide (gibbsite). Sodium oxalate is soluble in water, while aluminum hydroxide is not, and this difference can be used to separate them. A sample of sodium oxalate particles were weighed and added to hot water (80 °C) to a target solid content of 10 g/L. The particles were dissolved by stirring for 60 minutes. The insoluble solids were then filtered and separated. The insoluble solids were added to the first volume of hot water and dissolved again by stirring at 80 °C for 60 minutes. The insoluble solids were filtered for a second time and once again dissolved by stirring in the same amount of hot water at 80 °C for 60 minutes. Finally, the third filter cake is considered to be aluminum hydroxide. The dried cake was weighed, and the mass divided by that of the initial sodium oxalate sample to calculate the proportion of aluminum hydroxide present. The sodium oxalate content in the oxalate sample is calculated by difference.

3. Results and Discussion

The surface of the initial sodium oxalate particles precipitated in the precipitation process is covered with liquor and fine aluminum hydroxide seed, which need to be removed before sample testing. The samples were therefore screened on a standard sized screen to remove the associated aluminum hydroxide seed, before quickly washing the samples with cold water to remove the particle's surface liquor, leaving relatively clean sodium oxalate particles. After drying, the samples were sent for testing.

3.1 Sodium Oxalate Particles Precipitated from a Diaspore High Temperature Process

The sodium oxalate particles (particle 1) separated from diaspore digestion process were analysed by XRD. The results are shown in Figure 3.

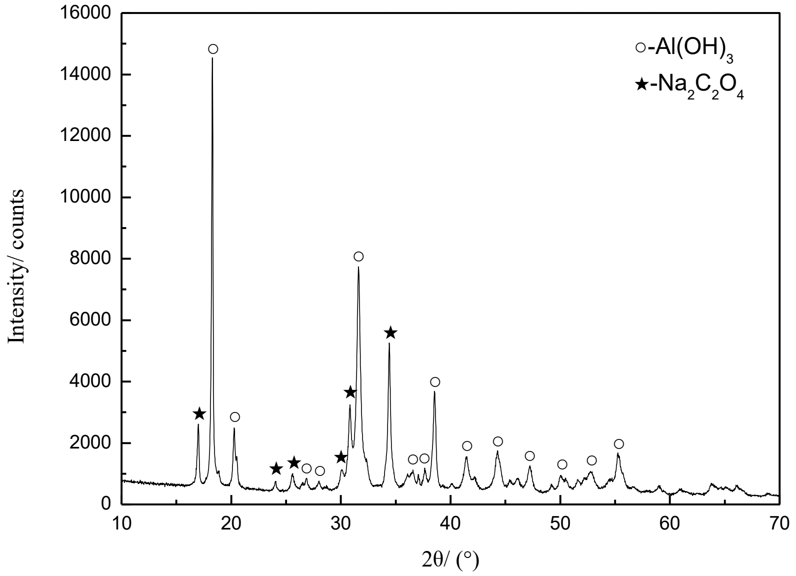

Figure 3. XRD patterns of sodium oxalate particle 1.

Figure 3 shows particle 1 contains two main components: aluminum hydroxide and sodium oxalate, with the main diffraction peaks of aluminum hydroxide being generally the larger.

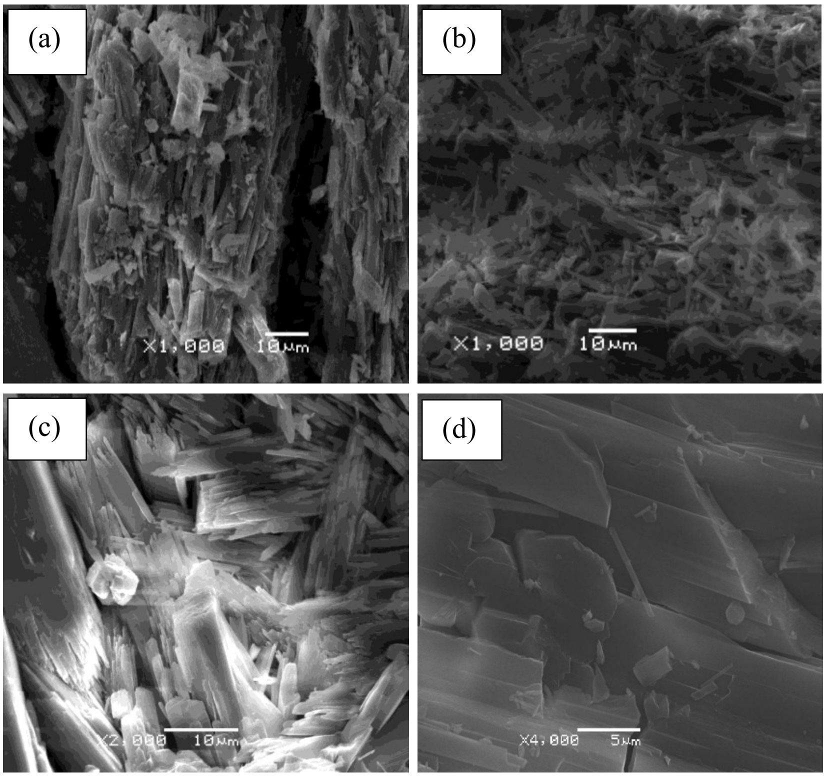

Figure 4. SEM images of sodium oxalate particle 1.
(a) fibrous crystal bundles; (b) crystal section; (c) crossed crystal growth; (d) internal structure of the crystal.

Particle 1 was digested in hot water and the aluminum hydroxide content of the particles determined in duplicate using the dissolution method. The aluminum hydroxide content of particle 1 was found to be about 60 %. Since this particle contains only two major components, the content of sodium oxalate is about 40 % by difference.

SEM imaging was conducted after particle 1 was treated, and the results in Figure 4 show that the internal structure of the particles precipitated from diaspore digestion are fibrous looking crystals. Other structural characteristics of fibrous crystals are not obvious, and the direction of crystal axes are disordered in some areas inside the particles. However, the growth of the oxalate fibers inside the spheres is dense, as shown as Figure 4 (d).

3.2 Sodium Oxalate Particles Precipitated from Low Temperature Gibbsite Digestion

Samples were taken from two process conditions which utilise gibbsitic bauxite as raw material. One used a low temperature Bayer process (particle 2), while the other used a medium temperature Bayer process (particle 3). Both processes precipitated spherical sodium oxalate particles.

3.2.1 Sodium Oxalate (Particle 2) Precipitated from Low Temperature Bayer Process

The XRD test results of particle 2 are shown in Figure 5.

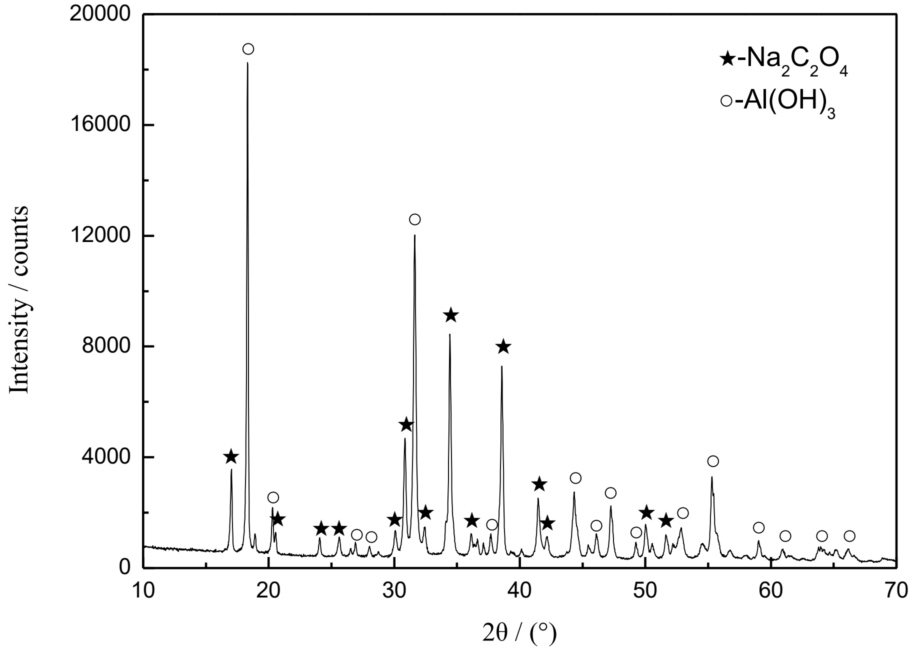

Figure 5. XRD patterns of sodium oxalate particle 2.

As shown in Figure 5, sodium oxalate and aluminum hydroxide are the major components of the particle. The diffraction peaks of aluminum hydroxide are more intense relative to the oxalate peaks.

Particle 2 was digested in hot water and the content of aluminum hydroxide in the particle was calculated by the dissolution method. Duplicate analysis gave the content of aluminum hydroxide in the particle as about 10 %. Since this particle also contains two main components, the content of sodium oxalate can be calculated by difference to be about 90 %. SEM imaging was conducted on particle 2 and is shown in Figures 6 and 7.

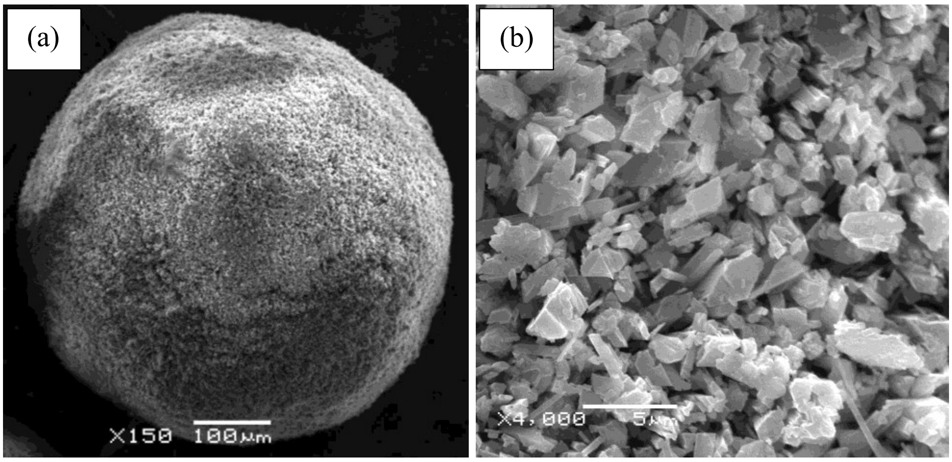

Figure 6. SEM images of sodium oxalate particle 2.
(a) complete appearance of the spherical particle; (b) surface of the spherical particle

Figure 6 (a) shows the spherical shape of particle 2 at the microscopic level. Figure 6 (b) shows that the surface of the particle is not smooth. Combined with Figure 6, it can be inferred that the surface of the sphere is the longitudinal growth face of the sodium oxalate crystal. Due to the pits in the surface, aluminum hydroxide may be integrated in the growth process of the spherical particle.

Figure 7 shows the internal crystal structure of the spherical particle 2. As shown in figure 7, the fibrous crystal structure of particle 2 spreads radially from the center of the sphere. It can be speculated that the growth of such particles is dominated by growth along these radial directions, similar to a dandelion structure, shown as figure 8. It can be seen from Figure 7 (d) that the fibrous crystal structure inside is densely intergrown.

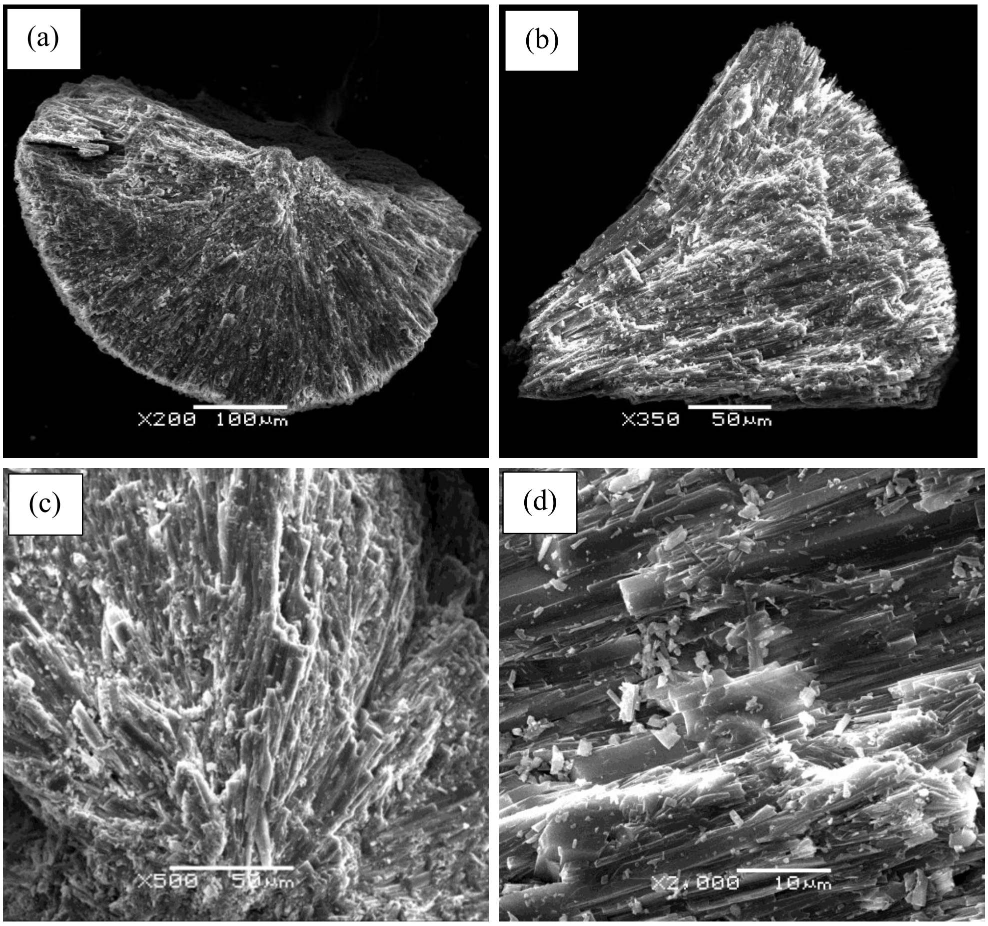

Figure 7. Inside SEM images of sodium oxalate particle 2.
(a) fragment of spherical particle; (b) particle fragment showing radial growth; (c) radial crystal growth; (d) detailed crystal growth.

Figure 8. Dandelion structure.

3.2.2 Sodium Oxalate Particles Precipitated from Medium Temperature Bayer Process (Particle 3).

The XRD test results from particle 3 are shown in figure 9.

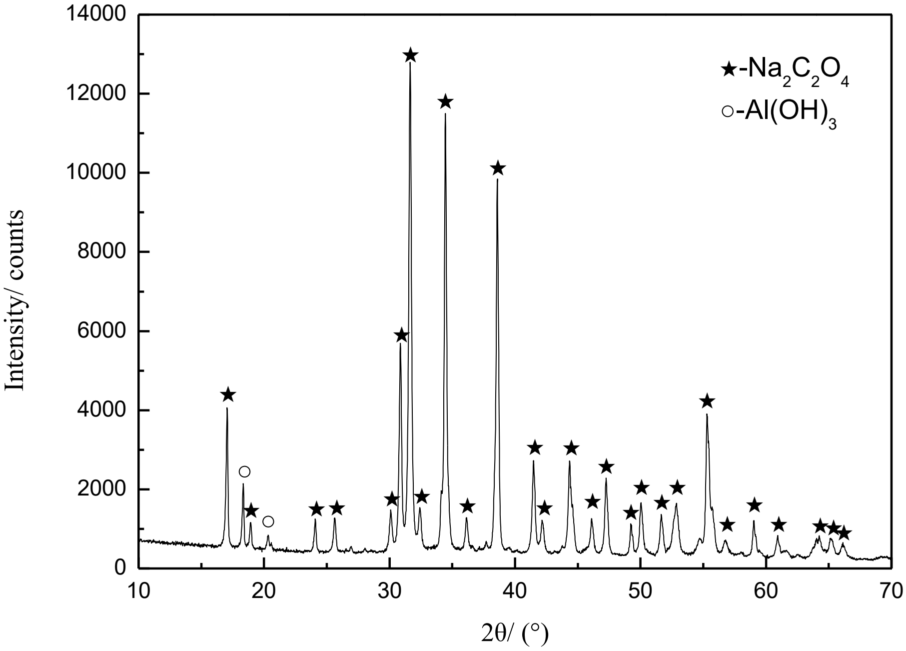

Figure 9. XRD pattern from sodium oxalate particle 3.

As shown in Figure 9, particle 3 contains only two major components, sodium oxalate and aluminum hydroxide. Sodium oxalate seems to be the dominant phase, as indicated by the more intense diffraction peaks of sodium compared to those of aluminum hydroxide.

Particle 3 was digested in hot water, and the aluminum hydroxide content was measured in duplicate by the dissolution method used on other samples at about 2.5 %. Based on this result, the sodium oxalate content (by difference) is about 97.5 %.

Particle 3 and particle 2 appear to have similar spherical particle morphology, similar appearance and similar color. SEM imaging was carried out after particle 3 was treated, and the results are shown in Figure 10.

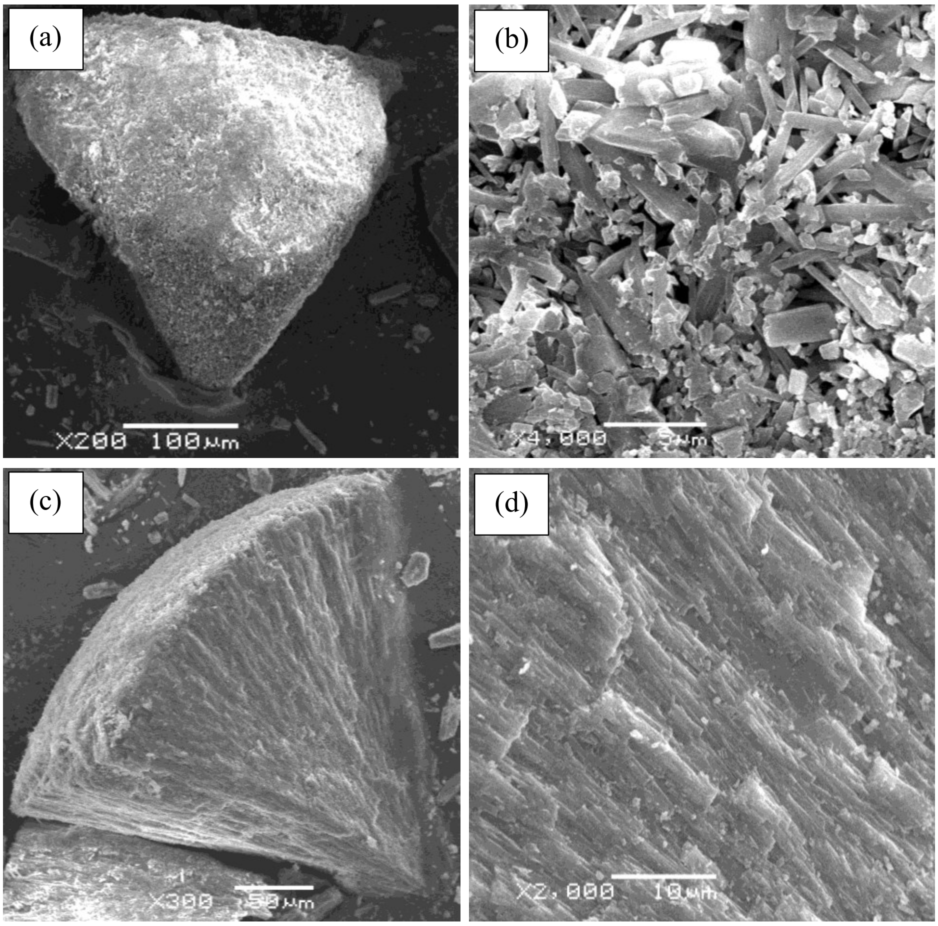

Figure 10. SEM images of sodium oxalate particle 3. (a) particle surface; (b) microstructure of the particle surface; (c) fan-shaped radial crystal growth; (d) internal structure of the particle.

As shown in Figure 10, the surface of particle 3 is like that of particle 2. Its surface is considered to be the longitudinal growth face of the fibrous crystal, and there are many pits on the surface. During the growth of the particle, fine alumina hydroxide crystals are easily included in the growing particle. The fibrous crystals inside particle 3 still radiate from the center of the sphere, and the fibrous crystals are densely intergrown. Comparing Figure 7 and Figure 10, the microstructure of particles 2 and 3 are basically the same.

3.3 Difference Between Types of Particles

Based on the particle images, the average diameter of particle 1 is relatively large, with most particles larger than 3 mm. Examples of particle 1 are not completely spherical, and often appear as a more flattened shape. The wet particle is a dark red color, and after drying it is earthy yellow. The inside of the spherical particle is densely intergrown radial fibrous sodium oxalate crystals.

Particle 2 and particle 3 are similar in appearance. The diameter of the particles is usually 1-2 mm. From a macro view, the surface of the particle is smooth and more consistently spherical. The wet particle is dark and shiny, while after drying, is a gray color. The inner particle structure is again the radial fibrous sodium oxalate crystal growth seen in particle 1, similar to the structure of a dandelion. From the microscopic point of view, the surface of the particle appears to be the longitudinal growth face of the fibrous crystal, with many pits on the surface.

All particles contain two identified components, sodium oxalate and aluminum hydroxide. The content of sodium oxalate in particle 1 is about 40 %, in particle 2 it is about 90 %, and in particle 3 it is about 97.5 %. The results show that the sodium oxalate content was the lowest in the particles precipitated from the diaspore digestion system, while the aluminum hydroxide content was the highest, up to about 60 %. With gibbsitic bauxite as the refinery input, the content of sodium oxalate in the precipitated particles was the highest in the medium temperature digestion system, and it was lower in low temperature digestion process than that in the medium temperature digestion process. On the whole, the sodium oxalate content in the particles is higher than that of the diaspore digestion system when using gibbsite as raw material.

Particle 2 and particle 3 have smaller spherical diameters than particle 1, which could be related to their microstructure. Because the crystals studied have a radial structure, with growth from center to the sphere surface, its volume has a cubic relation with its spherical diameter, so needs a large amount of sodium oxalate precipitation for the particle growth process. The relatively low concentration (and supersaturation) of sodium oxalate in Bayer liquor makes it difficult to provide such conditions, and so promotes a larger numbers of smaller diameter particles. However, the crystal structure inside particle 1, do not show an obvious radial structure, and could be the product of the agglomeration of multiple particles. The higher proportion of aluminum hydroxide particles support this hypothesis as they are more likely to be wrapped in the particle during agglomeration process. The occurrence of particles observed in the production process of refineries is basically consistent with this analysis, with a large number of smaller particles 2 and 3 are observed to be mixed with aluminum hydroxide seed, while the number of larger diameter particle 1 mixed with aluminum hydroxide seed is relatively less.

4. **Conclusions**

The precipitated sodium oxalate particles in the alumina production process are spherical particles, which contain two main components, sodium oxalate and aluminum hydroxide. The particles formed in a diaspore high temperature digestion process are not so spherical, and the content of sodium oxalate in them is lower, accounting for about 40 %, and aluminum hydroxide accounts for about 60 %. The sodium oxalate particles precipitated from low temperature gibbsite digestion process are more spherical, and the sodium oxalate content is higher. From the low temperature gibbsitic bauxite digestion process, the content of sodium oxalate and aluminum hydroxide in the particles precipitated accounted for 90% and 10% respectively, while those from the medium temperature gibbsitic bauxite digestion process was 97.5 % and 2.5 % respectively.

Crystals of sodium oxalate in the sodium oxalate particles have a fibrous structure. In particles precipitated from diaspore digested solution system, except for the fibrous structure the other structural characteristics of sodium oxalate crystals are not obvious. Judging from the structure, such particles may be the product of agglomeration and growth, with aluminum hydroxide incorporated in the particles during the growth process. In the particles precipitated from the process based on gibbsite digestion, the crystals of sodium oxalate grow radially outward from the spherical center of the particle. The surface of the particle is the longitudinal growth direction of the fibrous crystals, with many pits, and small amounts of aluminum hydroxide particles may be included during the growth process.

5. References

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