

## AA13 - The Characteristics of Goethite in Bauxite and Synthesis of a Novel Flocculant

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### Abstract

With the extensive usage of Guinea bauxites, which have high content of goethite, there have been problems with the settling process, such as high overflow suspended solids, bad clarity and downflow with high water. In this paper, the behavior of goethite in the dissolution process of different locations were analyzed, and the influence of goethite on the red-mud slurry separation was determined. Based on these analyses, the method of polymerization modification of aqueous solutions was adopted to synthesize a suite of novel bimodal distribution flocculants. The results show that compared with the performance of some commercial flocculants in the alumina industry, the bimodal distribution flocculants exhibited a significant performance improvement in settling the very fine goethite red mud, the content of overflow suspensions was < 0.20 g/L.

**Keywords:** Goethite red mud, Flocculation, Settling, Polymerization.

### 1. Introduction

The key factors for the red mud separation process are associated with the properties of red mud slurry, specifically the mineralogy, particle size distribution and solution composition of red mud slurries. The particle size of Bayer red mud is generally fine, and the study shows that the < 325-mesh particles accounted for more than 90 %. The dissolved red mud pulp is a fine particle suspension which has many similar properties to a colloidal dispersion system. In this suspension system, the red mud particles are the dispersed phase and sodium aluminate solution is the dispersing medium. Red mud particles have an extremely diffuse surface, which shows a large residual valence force, Van der Waals force and hydrogen bonding, resulting in solvation. Under the condition of high alkalinity (Nk= 150 g/L), the surface of red mud is positively charged, and the particles of red mud are also charged and mutually repulsive. A liquid film formed on the surface due to solvation also prevents the particles from approaching each other. This makes the red mud difficult to precipitate and separate [1].

In recent years, with the reduction of domestic bauxite, greater percentages of non-domestic bauxite ores have been put into production. However, for the composition of residue generated from this bauxite and its influence on the settling process of this residue, the lack of domestic experience with this type of residue, the production sites often have problems processing these residues. These problems include, but are not limited to, high residue loads (red mud loads), poor compaction performance and high opacities of the overflow liquid during the settling process of red mud. This paper reviews the properties of diluted pulp, with particular focus on the composition of red mud mineralogy, especially the structure, occurrence state and dissolution characteristics of goethite, as well as research of adsorption principles of specific flocculants to goethitic red mud, which provides theoretical support for efficient utilization of foreign ore in China.

## 2. Mineral Composition of Red Mud

Red mud is the residue of alumina production. The phase is complex, mainly consisting of hematite, goethite, hydrated aluminum sodium silicate, dicalcium silicate, hydrated garnet, calcium titanate and a small amount of undissolved alumina hydrate. Among them, pyrite, goethite, kaolinite, opal and rutile are easy to adsorb more  $\text{Al}(\text{OH})_4^-$ ,  $\text{Na}^+$  and adsorbed water during the formation of red mud, which is not conducive to sedimentation and separation. The presence of hematite, siderite, magnetite and hydrochlorite in the red mud is conducive to settling [2–5].

Generally, flocculation sedimentation is used to separate the red mud from the solution. The flocculation process is the interaction between the functional groups of the flocculant and the surface of the red mud, trapping the red mud particles, and then flocculating and settling of the red mud particles through electrostatic forces, van der Waals forces and macromolecular bridge bonds, etc., to allow the separation process of solid and liquid phases. Therefore, the decisive factor affecting the flocculation and settling process of the red mud is the matching between the surface properties of the red mud in the ore pulp and the flocculant. Other influencing factors include solid content, temperature, time, stirring et al. [6–8].

At present, with the extensive application of bauxite with high goethite content, such as Guinea, there are some reasons for the high content of coarse liquid float in the sedimentation process of red mud, opacity and poor compaction performance. It has been pointed out that if goethite can be completely transformed into hydrophobic hematite during dissolution, the sedimentation rate of red mud can be significantly increased.

The different occurrence states of goethite in bauxite and their behaviors in the dissolution process will result in different settling performances.

## 3. Goethite in Bauxite

### 3.1 Occurrence

Goethite is a common iron-bearing mineral in bauxite. The arrangement of oxygen and hydroxide ions in goethite is hexagonal most tightly packed, belonging to the rhombic bipyramidal crystal class, orthogonal crystal fine, the crystal parallel C-axis is needle-like, columnar or parallel B-axis is thin plate or scale. Cell parameters  $a = 0.464 \text{ nm}$ ,  $b = 1 \text{ nm}$ ,  $c = 0.303 \text{ nm}$  [11]. The chemical composition of goethite is  $\text{FeO}(\text{OH})$ , which belongs to the  $\alpha$ -phase hydroxide minerals, in which Fe can be isoreplaced by Al in bauxite to form Al-goethite, and this substitution phenomenon is more common in tri-bauxite type bauxite. Due to different degrees of substitutions, the morphologies of the formed Al-goethite are very different, and they are mainly heterogeneous and uncertain aggregates [12].

The crystalline characteristics of goethite results in the polymers generally having concentric layers and radial fiber structure like that of a spherical, stalactite mass, mostly in the form of fine acicular microcrystalline clusters and acicular radial aggregates, as shown in Figure 1.

**Problem 1:** Because of the physical form of goethite, it easily generates fine particles in the process of alumina production from bauxite due to the influence of crushing, grinding and the dissolution process, resulting in high surface activity and significant solvation.

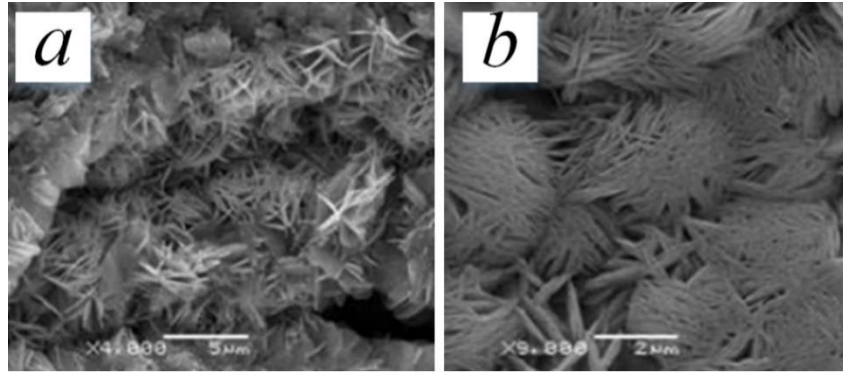
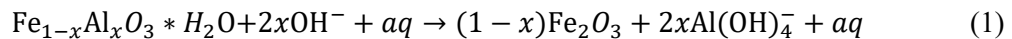


Figure 1. Crystal structure and microstructure of goethite in a bauxite [12].

### 3.2 Goethite in Dissolution Process

Pure goethite is transformed into hematite and magnetite under the condition of 143 °C and no additives and is transformed into magnetite after long-term heat treatment. The (aluminum) goethite in bauxite is changed into hematite under the conditions of lime addition at 250 °C. The  $\text{Al}_2\text{O}_3$  in the (aluminum) goethite is dissolved at the same time, the reaction is as follows [13].



According to the different compositions of goethite in bauxite, that is, the differences of in-phase substitution rates, there will be different rates of conversion. Literature shows that goethite does not transform when the dissolution temperature is 110–240 °C and goethite can be converted into hematite in large quantities only when the temperature is above 260 °C and the dissolution time is as long as 1h. Goethite does not convert into hematite in large quantities below 240 °C [14-15].

Lime can reduce the temperature at which the goethite phase becomes hematite, as part of  $\text{Fe}^{3+}$  is replaced by  $\text{Al}^{3+}$  at the goethite lattice junction, forming the aluminum-oxygen bond, and adding lime accelerates the destruction of the aluminum-oxygen bond.

**Problem 2:** Whether goethite can be effectively transformed into hematite with hydrophobic properties under certain dissolution conditions.

### 3.3 Influence on Settling

The leaching process of goethite was simulated. No phase transition occurred at low temperature, and the sedimentation performance of goethite was better. This is inconsistent with many research literature papers and production practices.

It is noteworthy that if goethite can be completely transformed into hydrophobic hematite during dissolution, the sedimentation rate of red mud can be significantly increased [9]. For example, the Guangxi Pingguo bauxite contains more goethite. Under the conditions of more lime addition, high dissolution temperatures and alkali concentrations, the red mud after high pressure dissolution still has good settling performance [7]. However, when the content of anatase is low, the settling performance of red mud is not improved even if the goethite is completely transformed into hematite during the high-pressure dissolution process. Indonesia Bintan bauxite contains more goethite, but the content of anatase is low. In the process of high-pressure dissolution, although goethite has been transformed into hematite, the settling performance of red mud is still low. If anatase is added before dissolution, the settling performance of red mud will be greatly improved [10].

**Problem 3:** Why does goethite which has undergone the dissolution process exhibit different sedimentation characteristics?

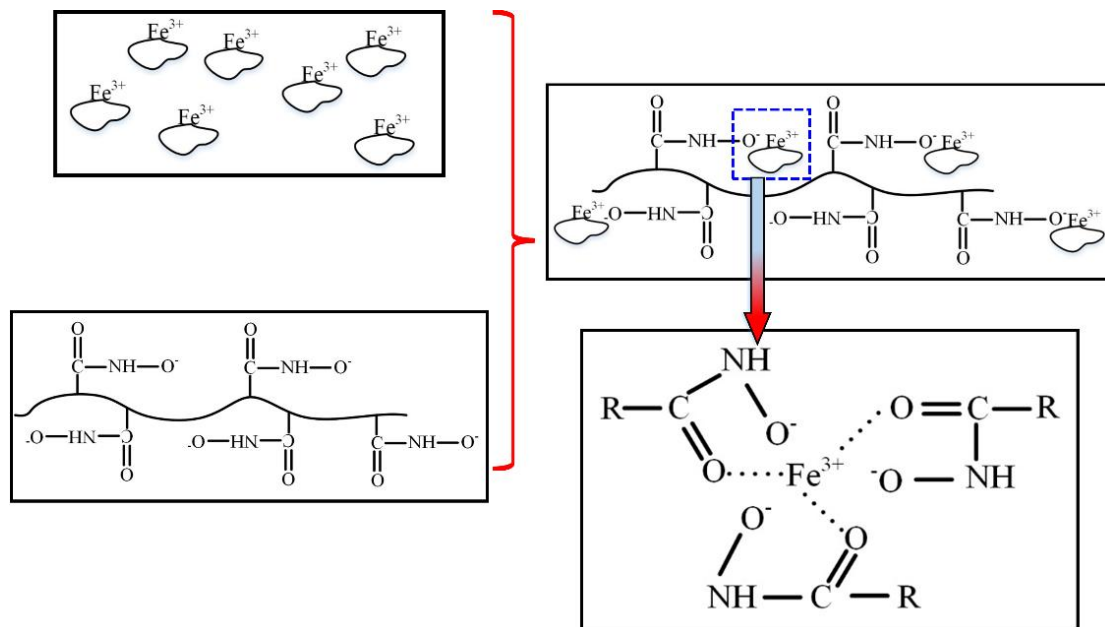
#### 4. Principle Analysis

The sedimentation performance of red mud is closely related to its surface properties, such as surface charge (how to produce: lattice fragmentation, ion adsorption in solution, etc.), surface free energy and other essential factors. A basic conclusion is that if the particle size is finer, the surface free energy is higher, the solvation trend of particles in solution is significant, and the sedimentation performance is worsened. At the same time, there are external controls on the sedimentation process.

Considering the three problems above, the essential reason is the different physical occurrence of goethite. In the dissolution process, the first step of crushing and grinding will cause the selective dissociation of goethite, which may cause the uneven distribution of goethite particles, causing different degrees of solvation. These differences will result in varied settling performances. Some of these very fine particles, even if transformed into hematite, will still be difficult to settle. The main reason is that the very fine particles are too difficult to dissolve and will also be difficult to flocculate.

The core problem: How to regulate the interface properties of red mud, enhance the interaction between flocculants and red mud particles, and effectively improve the settling of extremely fine red mud.

The oxamic acid flocculant mentioned in the literature can effectively flocculate goethite, and its mechanism is shown in Figure 2.



**Figure 2. Schematic diagram of the action of hydroxamic acid flocculant on goethite.**

Therefore, through theoretical and empirical analysis, small molecular flocculants can be used as strengthening agents in the sedimentation process to help capture extremely fine particles, granulate first, and then settle them through the flocculation effect of large molecular flocculants, so as to regulate the sedimentation process.

## 5. Synthesis of a novel flocculant

With different molecular weights of polyacrylamide as raw materials, through the nucleophilic substitution reaction of high molecular weight polyacrylic acid, flocculants with different molecular weights ( $> 5\,000\,000$ ) distribution were synthesized. Then, through an acrylamide monomer polymerization-modification method, molecule boosters (molecular weight  $< 1\,000\,000$ ) were synthesized. By mixing these two flocculants in a pre-specified ratio, the high efficiency flocculants for the sedimentation of goethite red mud were obtained. The sedimentation experiments of red mud were as follows.

Red mud pulp properties: solid content 60 g/L, Nk 140 g/L. The types of flocculants were respectively, flocculants used in the production site, named ZL and self-made flocculants S1 and S2. The results were shown in Table 1. Due to the properties of the pulp, the sedimentation rate caused by each flocculant in this experiment was high, and the difference was mainly reflected in the level of suspended solids. ZL flocculant had the worst effect, and when the added amount was 133 g/t, the suspended solids were 0.864 g/L, as shown in Figure 3. The comparison of the settling effect between ZL and S2 showed that when the ZL flocculant was used, the crude slurry was very turbid, there were more fine particles and the compaction was worse. When the added amount was 85 g/t, for S1 flocculant, the content of suspended solids was 0.268 g/L and for S2 flocculant the content of floating matter is 0.200 g/L, which was markedly lower than that of the ZL flocculant. The custom-made high efficiency flocculant was found to have better settling properties.



Figure 3. Settling process comparison diagram.

Table 1. Red mud settling test results table.

Flocculant	Dosage, g/t	Settling velocity, m/h	Content of suspended solids, g/L	Settling volume, mL
ZL	133	28.31	0.86	50
	200	35.08		50
S1	85	22.81	0.268	54
	170	75.60		50
S2	85	24.08	0.20	54
	170	75.60		55

## 6. Conclusion

With the extensive application of bauxite with high goethite content such as Guinea, problems of high slurry turbidity, overflow opacity and poor compaction performance during the sedimentation of red mud have been observed. The behavior of different occurrences of goethite in the dissolution process was reviewed and analyzed, and the influence of goethite on the settling process of red mud was determined. Then, with different molecular weights of polyacrylamide as raw materials, through the nucleophilic substitution reaction of high molecular weight polyacrylic acid, efficient flocculants were synthesized. For the very fine goethite red mud, the custom-made flocculants had better settling properties than the standard flocculants, and the content of suspended solids was  $< 0.200$  g/L.

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