# The Hydrochemical Series Process for Low Grade Diasporic Bauxite

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**Abstract**

The principles of a hydrochemical path for processing low grade diasporic bauxite, laboratory digestion results from processing three low-grade diasporic bauxites, along with industrial test results are presented in this article. The reactions of Si-minerals during hydrochemical treatment of Bayer red mud is studied using XRD, SEM and energy-dispersive XRF. The transformation of cancrinite in the Bayer red mud into Fe-hydrogarnet results in very low A/S ($Al_2O_3$:$SiO_2$) and N/S ($Na_2O$:$SiO_2$) in the treated residue. It is beneficial to use high iron bauxite for the best results, which included A/S = 0.54 N/S = 0.02, $Na_2O$ = 0.28 % achieved in the treated residue. The 'Hydrochemical Series Process' has lower energy consumption, higher recovery of alumina and lower caustic consumption, making it suitable to deal with low grade diasporic bauxite, and recovery of soda from high iron Bayer red mud.

**Keywords:** Hydrochemical Series Process, Bayer residue, Desilication Product, Fe-Hydrogarnet, High $\alpha_K$ caustic solution

## 1. Introduction

China is the world's largest alumina producer, accounting for around 55% of global production in 2019. It is also a bauxite resource-poor country, with bauxite imports reaching 100 million tonnes in 2019. There is however, more lower grade bauxite in China. With the shortage of bauxite resources and the lower grade of bauxite produced in China, a new alumina production process is being studied and developed to deal with the available lower grade diasporic ores, to achieve a higher alumina recovery and lower energy and caustic consumptions [1]. It has become an important problem to be solved in China's alumina industry.

At present, the treatment of low-grade bauxite has two main directions. One approach is to improve the ore grade, where options include silica reduction by flotation, and chemical dressing roasting pre-desilication [2,3]. After improving the ore grade, the bauxite is processed in a Bayer refinery. Another path is Bayer processing of low-grade bauxite and subsequent treatment of the red mud produced. One way to treat red mud is to recover caustic and alumina from Bayer red mud by sintering referred to as the 'Series' method, or 'Improved Innovative Series Method' [4]. In addition to these options, a 'Hydrochemical Series Process' for the recovery of caustic and alumina from Bayer red mud using a high molecular ratio alkaline solution [5, 6] has been proposed.

This paper introduces the technical basis of the Hydrochemical Series Process, the results achieved by treating three low-grade bauxites with high molecular ratio alkali solution, and the results of industrial testwork. The particular application to high-iron bauxites for caustic recovery from Bayer red mud is examined.

## 2. Hydrochemical Series Process Testwork

To test and demonstrate the Hydrochemical Series process, the lower grade bauxite ores were first processed in a simulated Bayer process digestion, before mud settling and washing. The resulting Bayer red mud (or 'bauxite residue') was then treated by a hydrochemical extraction process which includes digestion in a high caustic/low alumina liquor, with the addition of lime at normal temperature and pressure to leach alumina and liberate caustic soda from the Bayer red mud.

The lime solids or 'dealuminising slag' produced from the digestion/extraction of the Bayer red mud is recycled to the Bayer digestion, as a substitute for the usual digestion lime addition. The aim of the Bayer digestion is then to maximize recovery of alumina from both the primary bauxite ore and dealuminized slag. To simulate these steps, the next batch of Bayer red mud was treated by recirculation, and the dealuminized slag was added into the Bayer digestion step as an additive. The caustic soda required to maintain liquor caustic for the whole Bayer cycle is added into the red mud dissolution step. The process flowchart is shown in Figure 1.

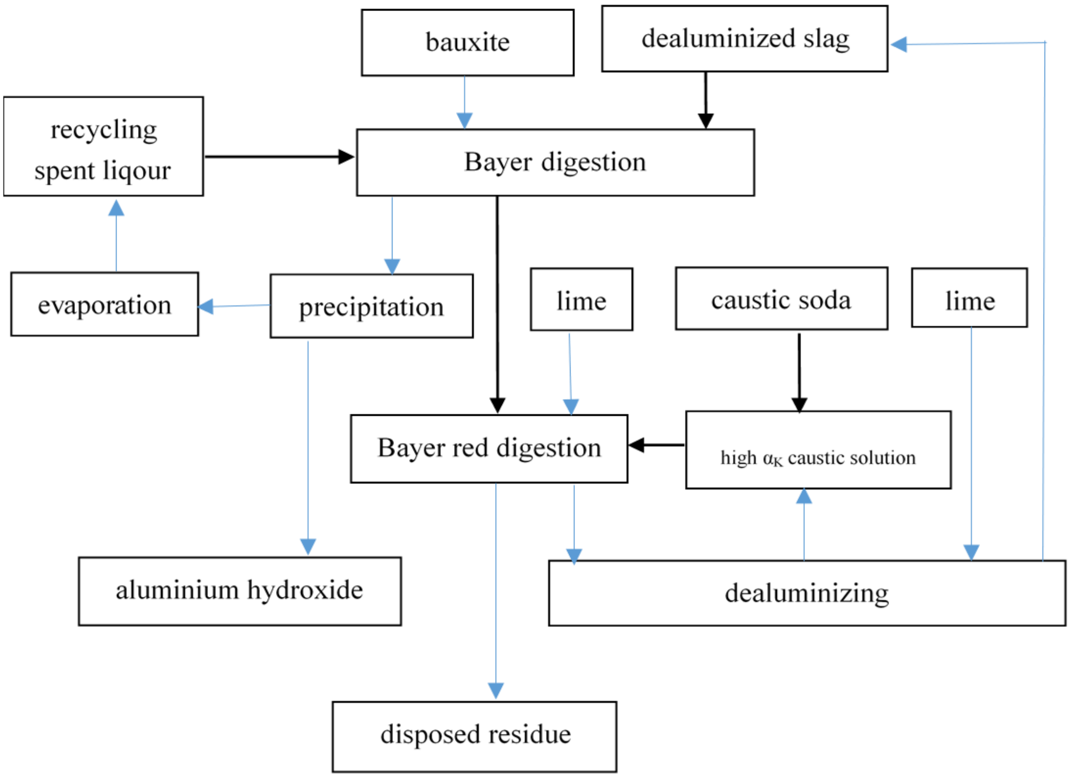


**Figure 1. Process flowchart.**

The key to the process is that caustic soda and alumina can be recovered effectively by hydrochemical treatment of Bayer red mud with a high $\alpha_K$ (high $Na_2O$/low $Al_2O_3$) Bayer liquor, with the red mud A/S reduced to less than 0.8, and N/S to below 0.1. The results from the treatment of Bayer red mud from three different bauxites is described below.

## 3. Results of Hydrochemical Series Process Testwork

The chemical composition of the three bauxites (A, B and C) treated by the Hydrochemical Series Process is shown in Table 1. Tests were performed with a Bayer liquor $N_K$ (caustic as $Na_2O$) of 130 g/L, and a temperature of 260 °C. The addition rates of lime, expressed as a C/S ratio ($CaO:SiO_2$) to the Bayer red muds tested was 0.4, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.4, 2.8.

The relationship between A/S ($Al_2O_3$:$SiO_2$) and C/S of the red muds after treatment are shown in figures 2, 3 and 4, and the relationship between N/S ($Na_2O$:$SiO_2$) and C/S are shown in Figures 5, 6 and 7.

**Table 1. Main chemical composition of bauxite.**

| Bauxite | $Al_2O_3$ (%) | $SiO_2$ (%) | $Fe_2O_3$ (%) | $TiO_2$ (%) | $K_2O$ (%) | CaO (%) | MgO (%) | A/S |
|---|---|---|---|---|---|---|---|---|
| A | 60.89 | 12.01 | 6.76 | 2.86 | 1.25 | 0.61 | 0.34 | 5.07 |
| B | 61.12 | 14.28 | 7.11 | 2.34 | 0.52 | 0.073 | 0.46 | 4.28 |
| C | 58.66 | 14.14 | 8.81 | 2.31 | 0.51 | 0.08 | 0.52 | 4.15 |

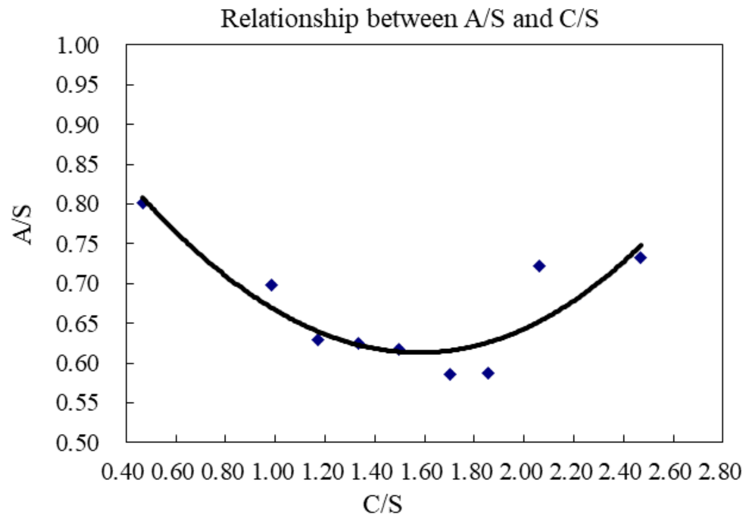


**Figure 2. Relationship between A/S and C/S of treated red mud (bauxite A).**

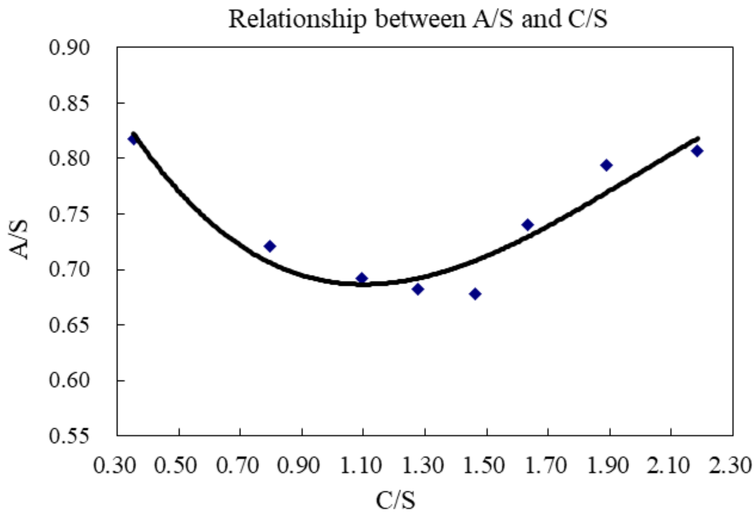


**Figure 3. Relationship between A/S and C/S of treated red mud (bauxite B).**

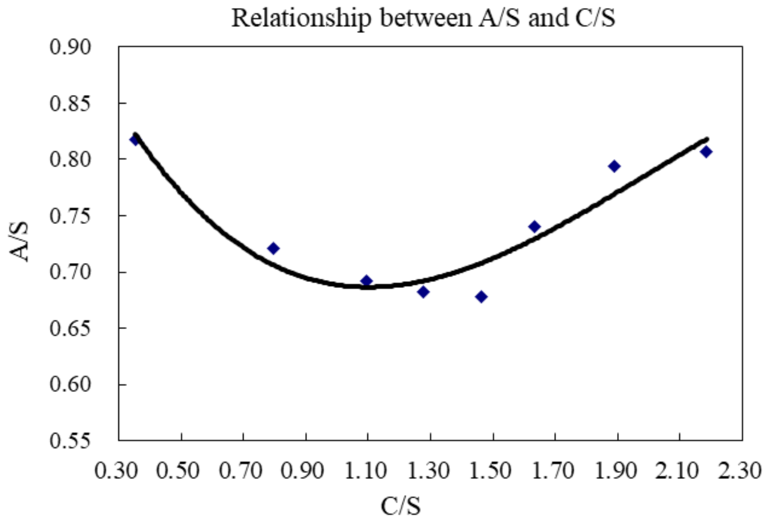


**Figure 4. Relationship between A/S and C/S of treated red mud (bauxite C).**

As can be seen from Figures 2, 3 and 4, under the same experimental conditions, the relationship between A/S and C/S is "V"-shaped for the Bayer red mud after hydrochemical treatment. With increased lime addition, the A/S of the red mud is decreased to a minimum, after which it increases again. The response to increasing lime addition in the 3 treated red muds was similar, except that the lowest A/S achieved and the amount of lime added at the lowest point were different. The A/S achieved from ores A, B and C being 0.59, 0.68 and 0.61, respectively.

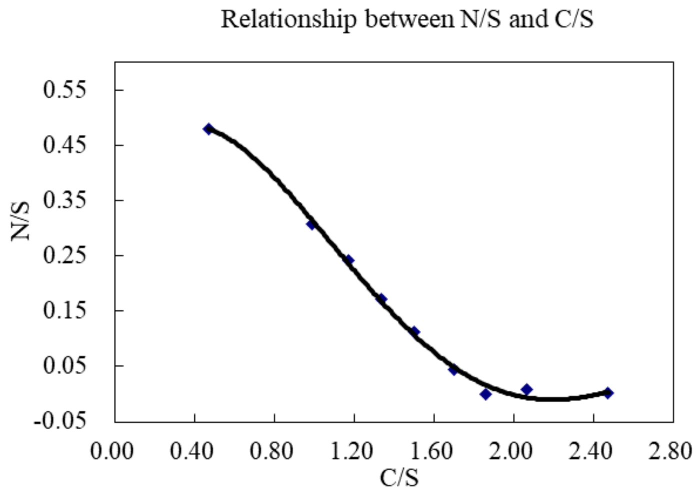


**Figure 5. Relationship between N/S and C/S of the treated red mud (bauxite A).**

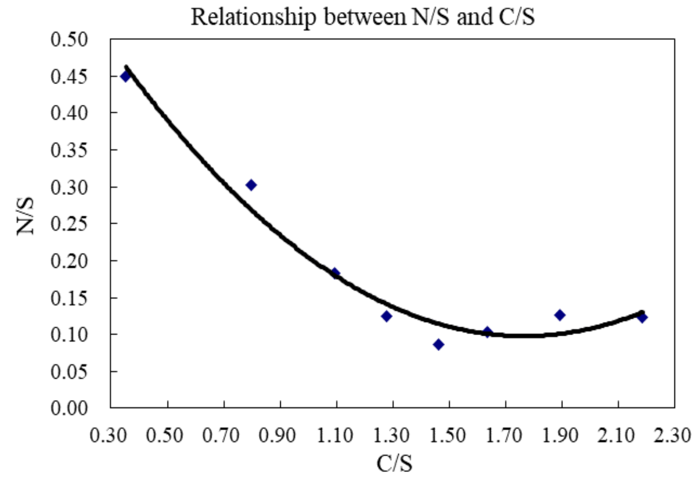


**Figure 6. Relationship between N/S and C/S of the treated red mud (bauxite B).**

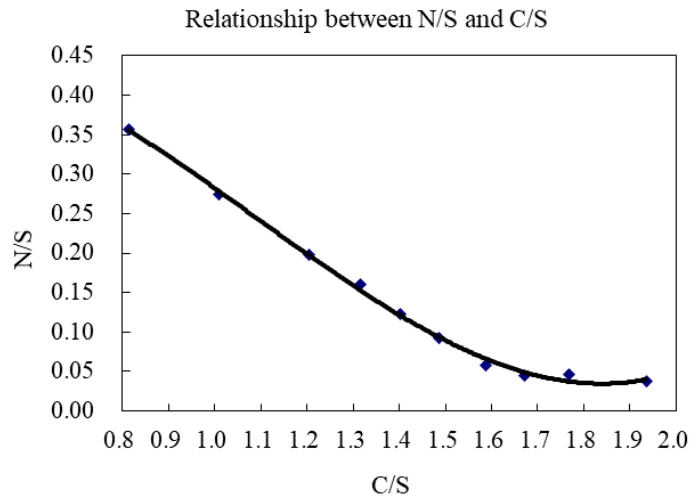


**Figure 7. Relationship between N/S and C/S of the treated red mud (bauxite C).**

From Figures 5, 6 and 7, it can be seen that the N/S of the treated red muds decreased more or less linearly with increasing lime addition, before reaching a minimum and remaining relatively unchanged (or increasing slightly) with further lime addition. While the response of the N/S to increased lime addition is similar in all 3 cases, the minimum N/S achieved (0.05,0.09,0.05 for ores A,B and C respectively), and the amounts of lime added at that point are also different.

## 4. Hydrochemical Series Process Industrial Test and Results

The principles of the Hydrochemical Series Process were defined from the results of the laboratory experiments using a high $\alpha_K$ Bayer liquor extraction, and the dealuminization and recycling of de-aluminizing slag to substitute for lime in the primary Bayer digestion testwork. Based on these results, the flowsheet and feasibility of the Hydrochemical Series process for alumina production was confirmed.

A full-process industrial scale (14 $m^3$/h) test of the Hydrochemical Series Process was carried out in the Zhengzhou Non-ferrous Metals Research Institute from September to December 2009. Two sets of existing Bayer digestion systems were used, one for the primary Bayer digestion, and the other for the hydrochemical treatment of the red mud produced from the primary Bayer digestion.

A new settler/washer system was added to carry out Bayer settling/washing, while the original settling/washing area was used for settling/washing of the treated red mud slurry. New equipment was installed for dealuminization, filtration of dealuminized slag and delivery of circulating liqour to the hydrochemical process.

An industrial test using bauxite with an A/S of 4.3 was completed, including continuous dealuminization of the high $\alpha_K$ liquor and Bayer digestion using dealuminized slag instead of lime. The full process included settling/washing of both the Bayer red mud and Hydrochemical treatment slurry.

The full-process industrial test ran steadily for 45 days. During this period, the average flow rate of primary Bayer process was 12.5 $m^3$/h, and that of red mud hydrochemical treatment system was 10.5 $m^3$/h. The de-aluminized slag was recycled instead of lime to the Bayer digestion process, achieving an A/S of the red mud produced of 1.01-1.19 at 260 - 265 °C. When the Bayer red mud was treated by the Hydrochemical Series method, the A/S of the treated mud was 0.78 - 0.85 and N/S 0.06 - 0.18 at 256 - 260 °C. The dealuminization (alumina recovery) efficiency can reach about 85% by using lime to dealuminize the high caustic ratio digestion liquor. The slurry settling behaviour of the red mud after hydrochemical treatment was good.

The results of the industrial test show that the Hydrochemical Series Process route is feasible and the process technology is reliable. Material balances, including alkali, water, calcium oxide and red mud in the Hydrochemical Series circulation system was easily achieved. The technology of removing alumina by adding lime to the leachate after hydrochemical treatment of red mud was demonstrated.

As a Bayer digestion additive, dealuminized slag can achieve the same digestion effects as lime, and can be completely digested in the Bayer digestion. A high solid settling and washing technology for the red mud after hydrochemical treatment was developed and demonstrated. Alkali corrosion in the red mud Hydrochemical treatment system was not seen, mainly because a small amount of scale formed by the process plays a protective role in the equipment.

## 5. Silicon Mineral Reactions

To determine the silicon minerals present in the treated red mud, SEM and EDS analysis was carried out. Tables 2 and 3 show the elemental analysis after hydrochemical treatment of red muds from bauxites B and C.

**Table 2. Elemental analysis of bauxite B Bayer red mud after Hydrochemical treatment**
(Treated Red Mud A/S=0.61 N/S=0.15 C/S=1.23)

| **Element** | **Weight Percent** |
|---|---|
| O | 48.66 |
| Al | 5.47 |
| Si | 10.97 |
| Ca | 24.69 |
| Fe | 10.21 |
| **Total** | **100.00** |

**Table 3. Elemental analysis of bauxite C Bayer red mud after Hydrochemical treatment**
（Treated Red Mud A/S=0.65  N/S=0.05  C/S=1.67)

| Element | Weight Percent |
|---|---|
| O | 49.47 |
| Al | 6.06 |
| Si | 10.64 |
| Ca | 24.22 |
| Ti | 2.05 |
| Fe | 7.56 |
| **Total** | **100.00** |

Analysis of the diffraction patterns and SEMs of the treated red mud from the bauxites B and C identified the hydrogarnet $3CaO.Al_2O_3(Fe_2O_3).nSiO_2.(6-2n)H_2O$. The saturation coefficient of $SiO_2$ (or the value of the "n" in the formula "$3CaO.Al_2O_3(Fe_2O_3).nSiO_2.(6-2n)H_2O$") is close to 2. The formation of the high-efficiency desilication product iron-hydrogarnet clearly explains the low A/S and N/S in the treated red mud.

To further study the formation of the iron-hydrogarnet in the Hydrochemical Process, multi-point sampling was carried out in the process of pre-heating and digestion during the industrial test. Figure 8 shows the X-ray diffraction of the solids sampled. Samples were taken at the following points/temperatures; 1. 8# preheat-exit (170 °C); 2. 1# reaction vessel (230 °C); 3. 10# preheat-outlet (260 °C); 4: 9# reaction vessel (256 °C).

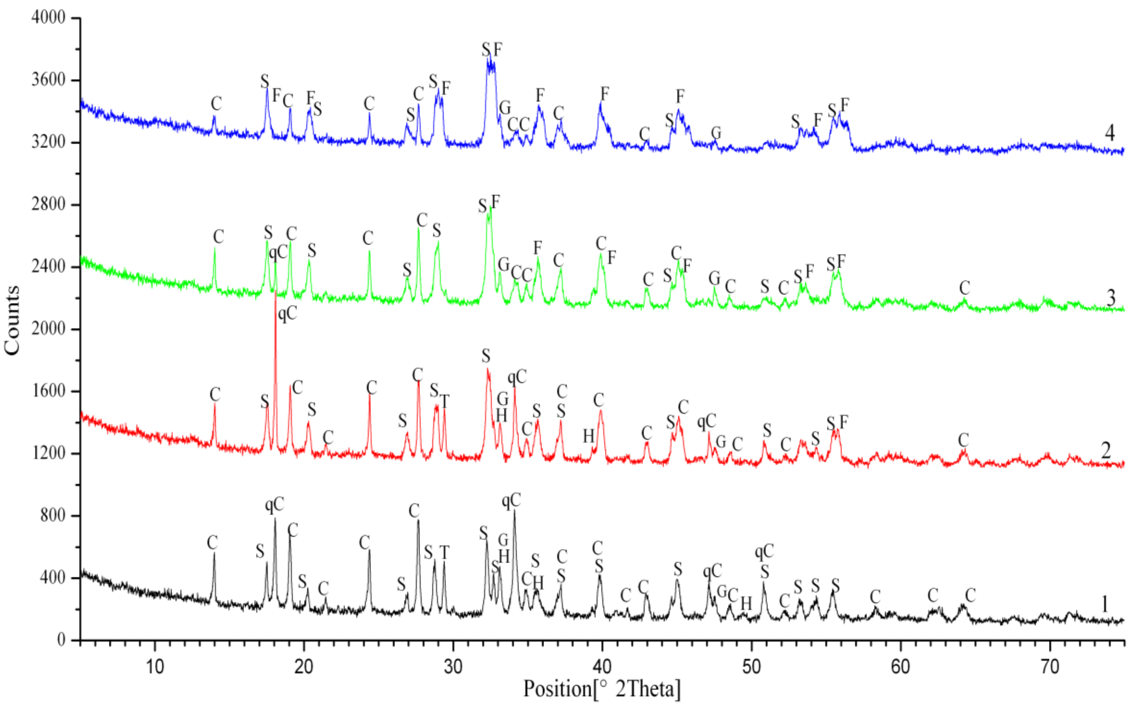


**Figure 8. XRD plot of the solid phase for the first sampling.**
C: Cancrinite; S: hydrogarnet; qC: $Ca(OH)_2$; H: hematite; G: perovskite; F: Fe-hydrogarnet; T: $CaCO_3$.

As can be seen in X Ray diffractograms 1 to 4 in Figure 10, the cancrinite (C) peak decreased gradually, while Fe-hydrogarnet (F) began to form in 1# vessel, and increased gradually. Most of silica mineral cancrinite in the Bayer red mud was transformed into the Fe substituted Al hydrogarnet during the hydrochemical treatment, confirming that this is the main mechanism for the reduced A/S and N/S in treated mud.

To examine the effect of available $Fe_2O_3$ on Fe-hydrogarnet formation, experiments were done adding different amounts of $Fe_2O_3$ reagent to bauxite was carried out. It was found that increased $Fe_2O_3$ content was beneficial to decrease N/S and A/S of the treated red mud. Subsequently, the high-iron bauxite and the high iron Bayer red mud were treated in the hydrochemical process, and good test results were obtained, as detailed below.

## 6. Progress in Hydrochemical Series Process Development

### 6.1 Effect of $Fe_2O_3$ on A/S and N/S of Treated Red Mud after Hydrochemical Treatment

The Bayer red mud from bauxite D was hydrochemically treated with different additions of $Fe_2O_3$ reagent. The chemical composition of bauxite used (HN) and its Bayer red mud can be found in Table 4. The hydrochemical treatment was carried out under the conditions of a temperature of 260 °C, lime addition rate of C/S 1.4, and iron oxide content of 10.15 % (by adding $Fe_2O_3$ reagent). The main results are shown in table 5.

**Table 4. Chemical composition of Bauxite D and Bayer red mud (%).**

| Name | $Al_2O_3$ | $SiO_2$ | $Fe_2O_3$ | $TiO_2$ | $Na_2O$ | CaO | A/S | N/S | C/S |
|---|---|---|---|---|---|---|---|---|---|
| Bauxite D | 60.83 | 14.57 | 4.50 | 3.35 | 0.064 | 0.68 | 4.18 | / | / |
| Red Mud | 24.66 | 24.90 | 7.55 | 5.88 | 13.70 | 10.10 | 0.99 | 0.55 | 0.41 |

**Table 5. The effect of $Fe_2O_3$ addition on A/S and N/S of treated red mud.**

| Test Case | $Fe_2O_3$ (%) | Digestion liquor composition (g/L) | | | | Red mud composition (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $N_T$ | A | $N_K$ | $\alpha_K$ | $Al_2O_3$ | $SiO_2$ | $Na_2O$ | $Fe_2O_3$ | A/S | N/S | C/S |
| D-8-3 | 7 | 144.9 | 12.4 | 140 | 18.6 | 17.02 | 21.19 | 6.11 | 6.54 | 0.80 | 0.29 | 1.34 |
| D-8-7 | 10 | 158.0 | 20.4 | 152 | 12.3 | 14.23 | 22.46 | 4.09 | 9.38 | 0.63 | 0.18 | 1.36 |
| D-8-8 | 15 | 156.7 | 22.6 | 148 | 10.8 | 12.70 | 21.70 | 3.70 | 14.05 | 0.59 | 0.17 | 1.37 |

Note: 7% is without ferric oxide reagent addition.

It can be seen from the table that with increased $Fe_2O_3$, A/S and N/S of the treated red mud decreases. That is to say, the increase of iron oxide content in the Bayer red mud is beneficial to the hydrochemical leaching efficiency.

### 6.2 Results of hydrochemical treatment of high-iron bauxite

The Bayer red mud of bauxite E with A/S: 3.31, $Al_2O_3$: 45.39% and $Fe_2O_3$: 25.66%, was treated at 240 °C for 60 min by Hydrochemical Series process, with the treated red mud found to have an A/S: 0.54, N/S: 0.02, $Al_2O_3$: 8.62 %, $SiO_2$: 15.99 % and $Na_2O$: 0.28 %.

## 7. Application Prospects for the Hydrochemical Series Process

### 7.1 Technical and Economic Comparison

For low-grade bauxite with A/S: 4, $Al_2O_3$: 45 %, $SiO_2$:11.25 %, the Hydrochemical Series treated red mud was calculated to have an A/S: 0.54, N/S: 0.05, and Bayer red mud as A/S: 1 and N/S: 0.3. See Table 6 for the comparison between the Hydrochemical Series Process and Bayer process.

**Table 6. Comparison of Hydrochemical Series and Bayer processes.**

| Process | Bayer process | Hydrochemical Series process |
|---|---|---|
| A/S of the treated red mud | 1 | 0.54 |
| Recovery of $Al_2O_3$ | 75 % | 86.5 % |
| Bauxite consumption t/t $Al_2O_3$ | 2.96 | 2.57 |
| N/S of the treated red mud | 0.3 | 0.05 |
| Chemical soda consumption kg $Na_2O$/t $Al_2O_3$ | 99.9 | 14.4 |

Table 6 shows alumina recovery is much improved at 86.5 %, and dramatically reduced caustic soda consumption of only 14.4 kg $Na_2O$. The alumina recovery is more than 10 % higher, and the caustic soda consumption is less than one-sixth of the Bayer process alone.

### 7.2 Prospects for application

The Hydrochemical Series process is characterized by a low energy consumption, high alumina recovery, low alkali consumption, and due to its lower soda content, the red mud produced can be much more easily utilized. The process is suitable for treating low-grade bauxite, especially high-iron bauxite, and $Na_2O$ recovery from high iron Bayer process red mud .

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