

High Iron Diasporic Bauxite Processing Study

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Abstract

A new approach was applied to processing high iron diasporic bauxite which involves firstly pre-processing at low temperature with high α K liquor and then digesting at high temperature with recycled mother liquor. The pre-processing and digestion conditions which affect A/S and N/S of the red mud generated were explored. The bauxite was pre-processed at conditions of 150 °C, NK = 260 g/L and 9% lime addition, before being digested at 260 °C for 60 minutes, resulting in an A/S in the red mud produced of 0.74, with an N/S of 0.12. The pre-processed bauxite and the red mud were analyzed by XRF, XRD and SEM-EDS. The main Silica mineral of both the pre-processed bauxite and the red mud was a hydrogarnet where Al was substituted by Fe and Ti. It was concluded that this hydrogarnet is formed in pre-processing, that it is stable through digestion, resulted in improved diasporic digestion, and is the reason why A/S and N/S in the red mud generated is greatly reduced under the conditions of pre-processing and digestion.

Keywords: Low temperature pre-processing, high temperature digestion, high iron diasporic bauxite, Al substituted by Fe and Ti hydrogarnet.

Definitions of terms:

"A/S": mass ratio of Al₂O₃ to SiO₂ in the solid

"N/S": mass ratio of Na₂O to SiO₂ in the solid

" α K ": molar ratio of caustic Na₂O to Al₂O₃ in liquor

"burden α K ": the α K used to calculate bauxite charge

"NK": caustic concentration of the liquor (as Na₂O)

"NT": total Na₂O concentration of the liquor

1. Introduction

The removal of soluble silica minerals in the pre-desilication and digestion steps is critical in alumina production in the alkali Bayer process due to the silicate ion's effect on scaling and product quality later in the process. Silica minerals in red mud following the Bayer process when feeding diasporic bauxite are mainly Na₂O·Al₂O₃·1.7SiO₂·nH₂O, where $n \leq 2$ [1,2]. The lowest A/S of red mud in the Bayer process is only 1 in theory, and the N/S of the red mud is 0.608. With the ore A/S decreased, the losses of Al₂O₃ and Na₂O to red mud will increase, and more so the loss of Na₂O. The silica minerals will be changed into CaO·Al₂O₃·nSiO₂·(6-2n)H₂O, where $n \leq 1$ [3], when additional lime is added into Bayer process. This is referred to in China as the "Lime Bayer Process".

The basis of the method for reducing desilication losses by the use of lime was examined in the work of Klan [4] on the reduction in soda losses through the formation of calcium silicates. This process was further developed and patented by Cresswell and Milne of Comalco [5,6,7] in publications between 1982 and 1984. Similar processes were developed in Eastern Europe and Russia and reported by Zoldi et al., 1987 [8], Medvedev et al., 2003 [9], Solymar et al., 1997 [10].

The use of lime with the specific intent of forming hydrogarnets has been further developed in China and reported in 2002 by Gu et al. [11], and Zhao et al., [12]. In a "Lime Bayer" process, the A/S of the red mud is usually above 1.4, and N/S could be 0 in theory. It is suitable to deal with A/S 5-6 of diasporic bauxite. In 2009 Smith [13] points out that as the grade of the bauxite declines, the loss of alumina will greatly increase when the A/S is lower than 4.5, and it is difficult to achieve a real recovery rate of 70% alumina. As the diasporic bauxite ore grade decreases, the Al₂O₃ content will drop, and the Fe₂O₃ content will increase. If silica minerals are transformed into iron hydrogarnet minerals (3CaO·Fe₂O₃·nSiO₂·H₂O) as the main component of red mud, alumina recovery will be greatly enhanced and alkali consumption will be greatly reduced [1,8].

In the high pressure hydration method put forward by the Soviet Union, not only the formation conditions of the hydrated sodium calcium silicate desilication product Na₂O·2CaO·2SiO₂·H₂O, but also generation of iron hydrogarnet were studied in detail. The relationship between the caustic molecular ratio and the saturation coefficient of SiO₂ and the ratio of Fe replacing Al in the iron hydrogarnet (3CaO·Fe₂O₃·nSiO₂·mH₂O) were examined at 280 °C. The work showed that as the caustic molecular ratio increased, the content of hydrogarnet increased, and gradually transformed into iron based products, until eventually close to complete formation of Fe₂O₃ hydrogarnet would be obtained in sodium aluminate solution with $\alpha K = 12\sim 30$.

A hydrothermal method was studied in Hungary where desilication product in red mud is also dominated by iron hydrogarnet. Liu et al reported in 2003 [14] that most of the silica in bauxite can be changed into iron hydrogarnet if being processed with the additives of hydrated calcium ferrite, or calcium ferrite (Li et al, 2006, 2007, 2010) [15,16].

A new method for desilication of high iron bauxite is proposed in this paper, where the A/S of red mud can be reduced to below 0.8 and N/S dropped to below 0.15 by the addition of lime, without other additives. High iron bauxite is first pretreated with high αK liquor, the solid phase after pre-treatment is then digested with Bayer recycling mother liquor. Following this treatment, A/S and N/S in the red mud can be lowered. The solids after pre-treatment and red mud are analyzed and studied by x-ray fluorescence, x-ray diffraction, scanning electron microscopy and energy spectrum analysis. It shows that when the bauxite PG was pretreated with lime in high αK liquor, hydrogarnet was generated where Fe and Ti is substituted for Al. This approach can not only promote diasporic digestion, but the desilication products formed are stable through the digestion process, with the desilication product in the red mud being mainly hydrogarnet where Al is substituted by Fe and Ti. This is the primary mechanism explaining why the bauxite with high iron content studied, pretreated only with lime before digestion, can result in low A/S and N/S of the resulting red mud. This paper introduces the bauxite pretreatment, and subsequent digestion conditions to optimise this process.

2. Experimental

2.1. Materials

2.1.1. Bauxite

The bauxite used is a high ferrous bauxite referred to here as "PG". It was spot-sampled from the plant, and prepared by sub-sampling, mixing and milling. Its chemical and mineralogical composition is shown in Table 1.

Table. 1 Chemical and mineralogical composition of PG (mass fraction, %).

Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	LOI
57.54	4.16	18.83	3.79	0.26	0.09	0.03	0.06	15.24
Diaspore	Gibbsite	Kaolinite	Hematite	Goethite	Anatase	Rutile	Quartz	
60.2	5.0	7.8	9.0	11.3	2.9	0.9	trace	

2.1.2. Recycling Mother Liquor for Bayer Digestion

It is adjusted with spent liquor spot-sampled from the plant. Its main composition is N_T 252.97g/L, N_K 228g/L, Al₂O₃ 127g/L, α_K2.95.

2.1.3. Lime

Lime was spot-sampled from the plant. Its total calcia (CaO_T) was 91.17%, and available calcia (CaO_A) was 89.24%.

2.1.4. High α_K Liquor for Bauxite Pre-processing

Liquor was adjusted to the target concentration with liquid caustic soda (sampled from the plant), and deionized water.

2.2. Test Programme

High iron diasporic bauxite was first pre-processed with high α_K liquor and lime at the reported conditions, before the slurry is separated. The solids are digested with recycling mother liquor. The process of bauxite pre-processing and digestion is seen in Figure 1. The procedure has two steps: 1) Bauxite is pre-processed with high α_K liquor; 2) Pre-processed bauxite is digested with recycling mother liquor.

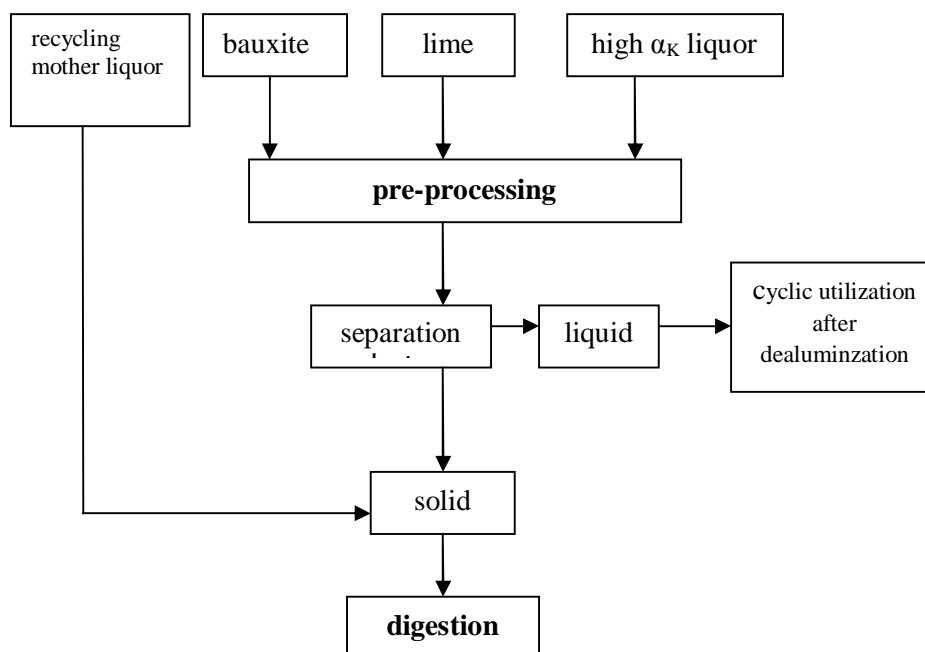


Figure 1. Process flow for bauxite pre-processing and digestion.

2.2.1. Bauxite Pre-processed with High α K Liquor

Pre-processing tests were done in steel bombs heated in a glycerin bath. The steel bombs were filled with 100mL of high α K liquor and the required bauxite and lime, before being loaded into the glycerin bath. After the target time, the bombs were withdrawn, and the pre-processed slurry was filtered. The filtrate was analyzed for Al_2O_3 and Na_2O . The filter cake was washed with hot water, then dried ready for next digestion.

Tests for bauxite pre-processed using different lime addition, solid contents and NK were done to select optimum pre-processing conditions.

2.2.2 Pre-processed Bauxite Digestion with Recycling Mother Liquor

Digestion tests were also done using steel bombs in a molten salt bath. Steel bombs were filled with 50mL of recycling mother liquor and the required pre-processed bauxite, before being put into the molten salt bath. After the target time, the bombs were withdrawn and the digestion slurry filtered. The filtrate was analyzed for main chemical compositions, and the filter cake (red mud) was washed with hot water, then dried for analysis for its chemical and mineralogical composition. Digestion tests with pre-processed bauxite at different digestion α K and temperatures were done to select optimum digestion conditions.

2.3. Analysis Method

The chemical composition of liquors including NT, NK, Al_2O_3 and SiO_2 were analyzed. NT and NK was determined by acid - alkali titration. Al_2O_3 was determined by EDTA titration. SiO_2 is analysed by silica-molybdenum complexation with a spectrophotometric finish. The chemical composition (including Al_2O_3 , SiO_2 , Fe_2O_3 , TiO_2 , K_2O , Na_2O , CaO , MgO and LOI), and mineralogy of the solids were analyzed. Solids analysis was by X-ray fluorescence (XRF). Mineralogy was by X-ray diffraction (XRD) and SEM-EDS.

3. Results and Discussion

3.1. The Effects of Pre-processing Conditions to A/S and N/S of the Red Mud

To select optimum pre-processing conditions, tests were done to determine which pre-processing conditions such as lime addition, solid contents, caustic soda concentration affected the A/S and N/S of the red mud. For these tests, the concentration of the recycling mother liquor for Bayer digestion was constant, with $N_T = 252.97g/L$, $N_K = 228g/L$, $Al_2O_3 = 127g/L$, $\alpha_K = 2.95$. Digestion temperature was $260\text{ }^\circ\text{C}$, digestion time was 60 minutes.

3.1.1. The Effects of Lime Addition to A/S and N/S of the Red Mud

At the conditions of 105°C , 120 min, NK of 260g/L, solid content of 100g/L, lime additions of 5, 7, 9, 11 and 13%, bauxite pre-processing tests and pre-processed bauxite digestion tests were conducted. The relationship between lime addition and A/S of red mud is seen in Figure 2, and between lime addition and red mud N/S in Figure 3.

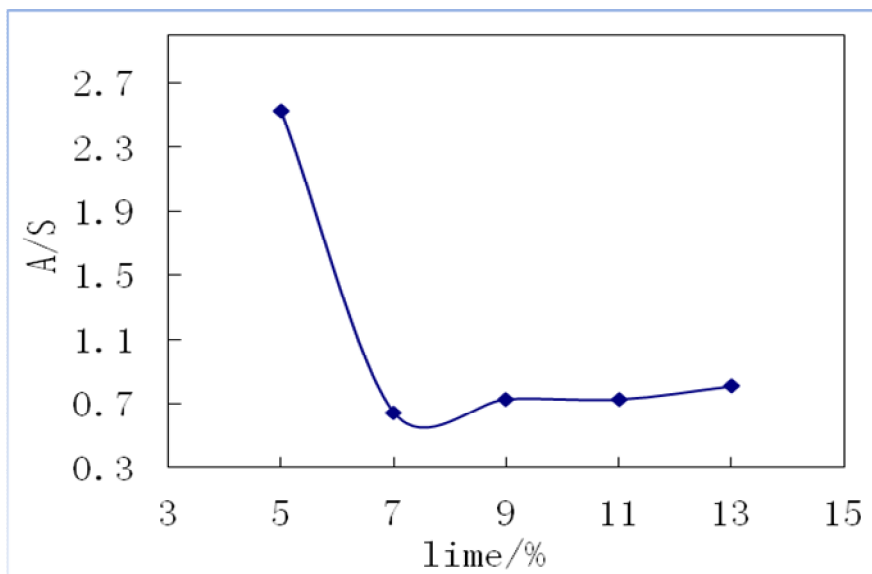


Figure 2. Effect of different lime additions on red mud A/S.

It can be seen from Figure 2 that as lime addition is increased, the A/S of red mud quickly decreases until lime addition reaches 7%, after which A/S changes only slightly. Appropriate lime addition is therefore in the range of 7 – 11 %, at which the A/S of the red mud is under 0.8.

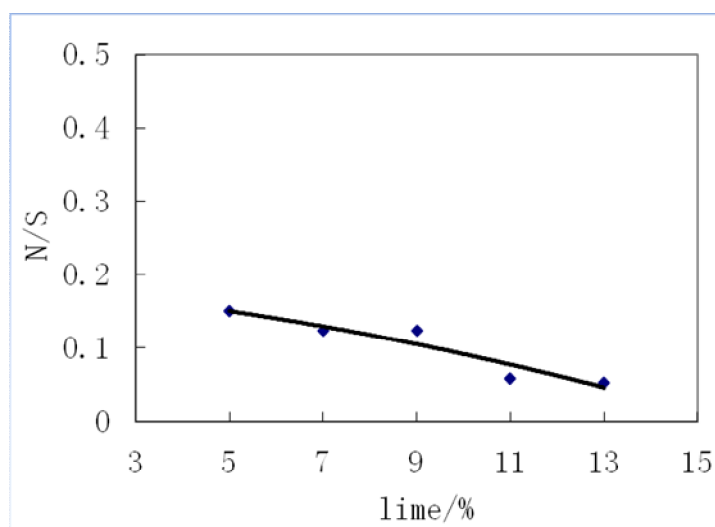


Figure 3. Effect of different lime additions to N/S of red mud.

It can be seen from Figure 3 that N/S of the red mud decreased slowly, as lime addition is increased. Under the range of test conditions, N/S of the red mud is always under 0.15. When lime addition is 7%, A/S of the red mud is 0.65, N/S is 0.12.

3.1.2. The Effect of Solid Content on Red Mud A /S and N/S

At the conditions of 150°C, 120 mins, N_K of 260g/L, lime addition of 9%, and solid contents of 100, 150, 200, 250g/L, bauxite pre-processing tests and pre-processed bauxite digestion tests were conducted. The relationships between solid content and A/S of the red mud is seen in Figure 4, while the relationship between solid content and N/S is seen in Figure 5.

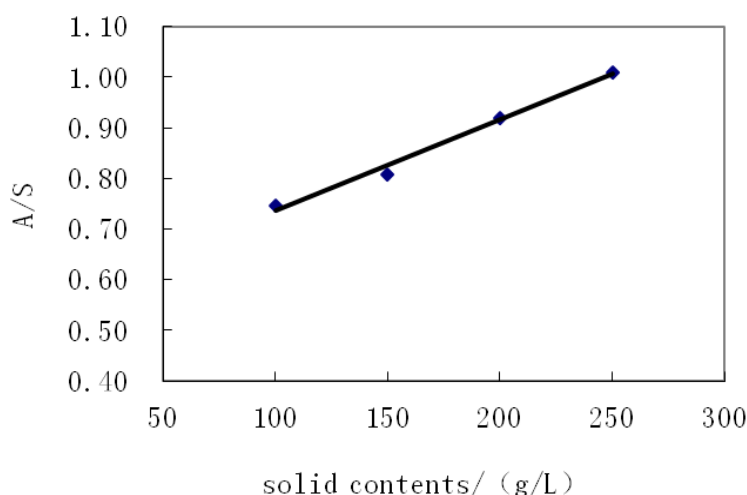


Figure 4. Effect of different pre-processing solid contents to A/S of the red mud.

It can be seen from Figure 4 that the A/S of the mud also decreased, as pre-processing solid contents are decreased. When solid contents are ≤ 200 g/L, the red mud A/S reaches below 0.9.

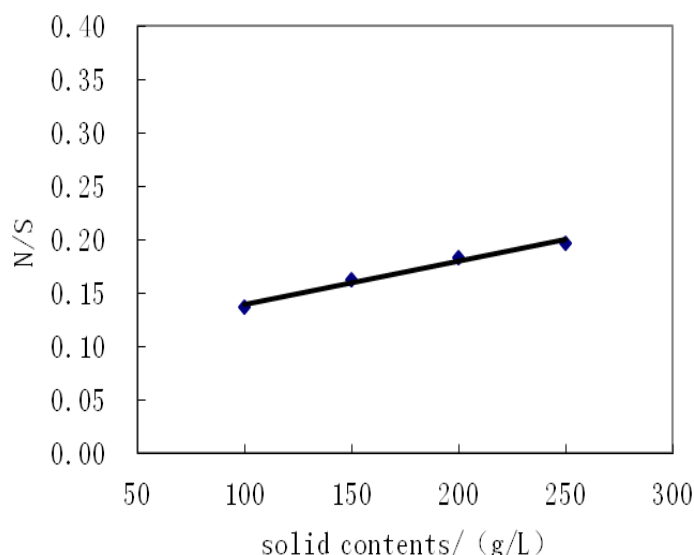


Figure 5. Effect of different pre-processing solid contents on red mud N/S.

It can be seen from Figure 5 that N/S of the red mud decreased slowly with decreasing pre-processing solid contents. At the test conditions, N/S of the red mud can reach below 0.25.

3.1.3. The Effects of Pre-processing Caustic Concentration on Red Mud A/S and N/S

Bauxite pre-processing and pre-processed bauxite digestion tests were conducted at the conditions of 150°C, 120min, solid content 100g/L, lime addition 9%, and caustic soda concentrations (N_K) of 100, 200, 300, 400g/L. The relationship between caustic soda concentration (N_K) and A/S of the red mud is seen in Figure 6, and the relationship between N_K and N/S is seen in Figure 7.

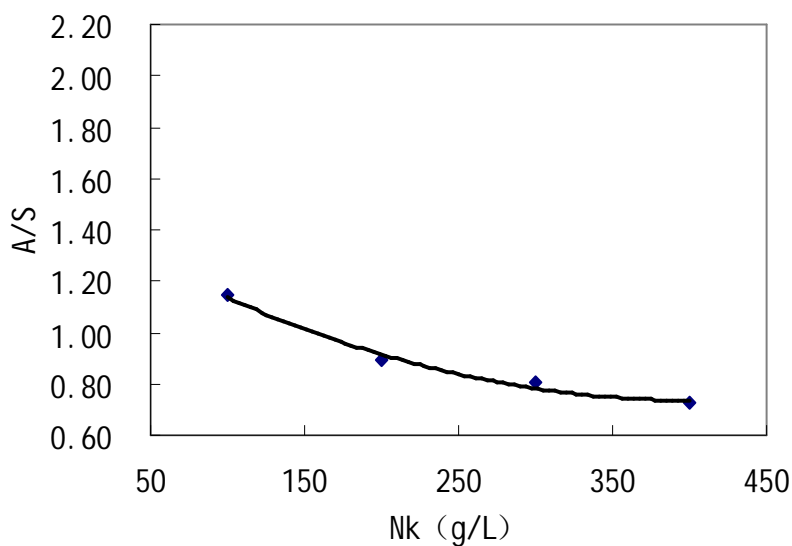


Figure 6. Effect of pre-processing liquor N_K on A/S of red mud.

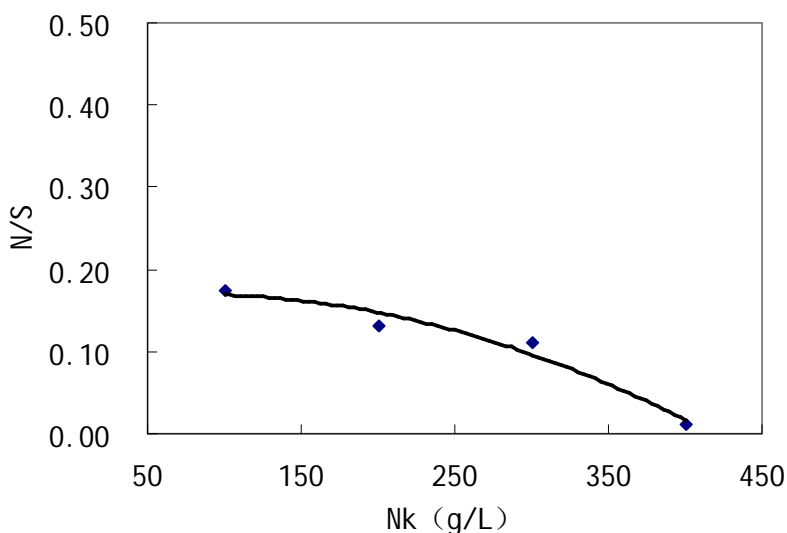


Figure 7. Effect of pre-processing liquor N_K on N/S of red mud.

It can be seen from Figure 6 and Figure 7, that as pre-processing caustic soda concentration N_K is increased at the test conditions, A/S and N/S of the red mud is decreased. When pre-processing caustic soda concentration $N_K \geq 200$ g/L, A/S of the red mud is below 0.8 and N/S of the red mud is always below 0.2.

As pre-processing caustic soda concentration N_K is increased, it is difficult that the pre-processed slurry to be filtrated. So appropriate N_K is in range of 200–280g/L.

3.2. The Effect of Digesting Conditions on A/S and N/S of Red Mud

To select appropriate Bayer digestion conditions, tests were done that digestion α_K , temperature affect A/S and N/S of the red mud. Pre-processing conditions: 150°C, 120 min, NK 260g/L (which is adjusted with liquid caustic soda), solid contents 100g/L, lime addition 9%.

3.2.1. The Effects of Digestion α_K to A/S and N/S of the Red Mud

Bauxite pre-processing were done at the conditions of NK 260g/L, solid content 100g/L, 150°C, 120min, lime addition 9%, followed by digestion of the solids at conditions of 260°C, 60min, burden α_K 1.4, 1.45, 1.5, 1.55, 1.6, 1.65, 1.7, 1.8. The relationship between digestion α_K and A/S of the red mud is seen in Figure 8.

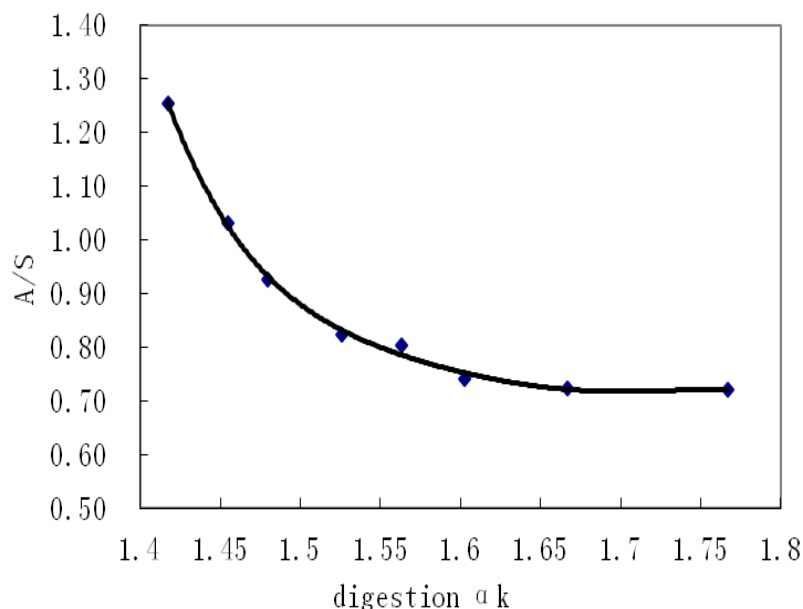


Figure 8. Relationship between digestion α_K and A/S of the red mud.

It can be seen from Figure 8 that as digestion α_K is increased, the A/S of red mud is decreased. When digestion α_K is above 1.5, the A/S of the mud is relatively flat, below 0.8.

3.2.2. The Effect of Digestion Temperature on A/S and N/S of Red Mud

At the digestion conditions of 60 minutes, 260, 270, 280°C, pre-processed bauxite digestion tests were conducted. Key test results are seen in Table 2.

Table 2. Effect of different digestion temperatures on A/S and N/S of red mud.

No. of red mud	temperature (°C)	Mass fraction(%)					A/S	N/S	C/S
		Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	Na ₂ O	CaO			
PG-1-6	260	6.08	8.20	44.85	0.98	21.47	0.74	0.12	2.62
PG-4-4	270	5.91	8.13	45.05	0.80	21.52	0.73	0.10	2.65
PG-8-4	280	5.57	8.62	45.48	0.85	21.66	0.65	0.10	2.51

It can be seen from Table 2 that as temperature is increased, the A/S of the red mud is lowered, while N/S is steady.

3.3. Silica Mineral Behaviour During Pre-processing and Digestion

The tests results show that the best results (reduction of mud A/S and N/S to 0.74 and 0.12 respectively) can be achieved when the high ferrous bauxite " PG" is pre-processed under the conditions of NK = 260g/L, solid content = 100g/L, 150°C, 120 min and 9% lime addition, and

when this pre-processed bauxite is then digested at 260°C for 60 mins. When diasporic bauxite is processed in Bayer process at high temperature, the A/S of the red mud is usually above 1. The typical formula of its silica- mineral is $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 1.7\text{SiO}_2 \cdot n\text{H}_2\text{O}$ (A/S=1, N/S=0.608).

As more lime is added to reduce soda consumption, the dominant silica-mineral in the red mud will turn into hydrogarnet ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot (6-2n)\text{H}_2\text{O}$). The A/S of the red mud is well above 1, when the maximum n is 1, A/S is 1.7 and with lime addition increased, A/S is increased and N/S is decreased. But in the process studied here, the A/S of the red mud is 0.74, and with increased lime addition, A/S is changed slightly and N/S is decreased.

The pre-processed bauxite and the red mud were analyzed by XRF, XRD, SEM-EDS to examine what reactions occurred in the course of pre-processing and digestion. The main chemical components of the two samples BG (Bauxite PG after pre-processing) and RD (red mud) are seen in Table 3. The XRD spectrum of both are shown in Figure 9. Elemental composition of BG by SEM-EDS is seen in Table 4, and for RD (red mud) in Table 5.

Table 3. Chemical composition of BG and RD samples.

No	Mass fraction(%)								A/S	N/S	C/S
	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O	Na_2O	CaO	MgO			
BG	28.75	5.96	31.28	4.86	0.00	0.58	15.03	0.27	4.83	0.098	2.52
RD	6.08	8.20	44.85	6.90	0.023	0.98	21.47	0.42	0.74	0.12	2.62

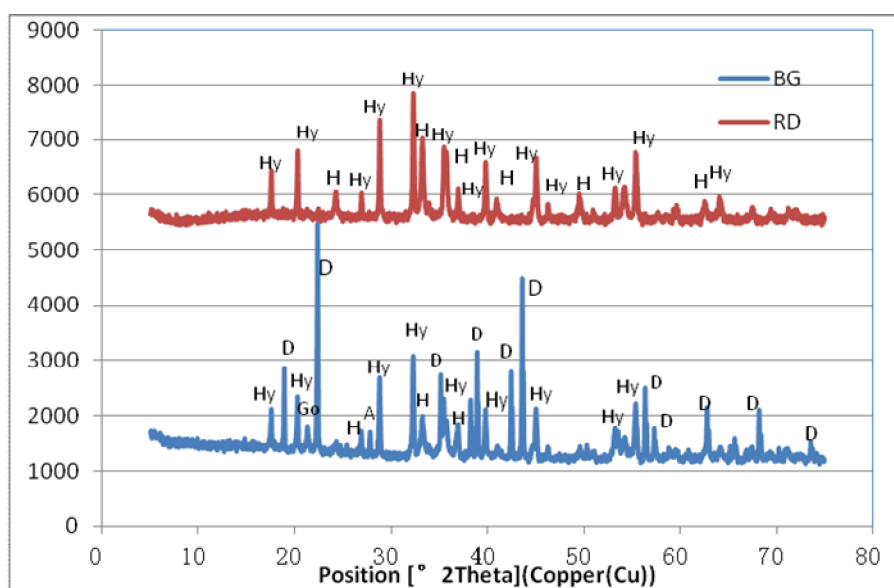


Figure 9. XRD spectrum of BG (Bauxite PG after pre-processing) and RD (red mud).

Note: H: hematite, D: diaspore, A: anatase, Go: goethite, Hy: hydrogarnet
Above: RD (digested red mud sample); Below: BG (pre-processed bauxite sample)

It can be seen from the XRD spectrum that the main differences between processed bauxite (BG) and digested red mud (RD) are that there is a lot of diaspore in the BG, but none in the RD. There are hydrogarnets in both BG and RD.

Table 4. Elemental composition of BG by SEM -EDS.

element	w(%)	x(%)
O	45.05	67.49
Al	3.73	3.31
Si	6.06	5.17
Ca	25.38	15.18
Ti	5.09	2.54
Fe	14.69	6.30
Total	100.00	

Table 5. Elemental composition of RD by SEM -EDS.

Element	w(%)	x(%)
O	46.17	67.68
Al	4.15	3.61
Si	7.30	6.10
Ca	26.77	15.66
Ti	5.61	2.75
Fe	10.00	4.20
Total	100.00	

It can be seen from Tables 4 and 5 that the elemental composition of BG is similar to that of BG, once corrected for diaspore content. It can be concluded that the main desilication products of processed bauxite (BG) are the same as that of digested red mud (RD). By XRD the desilication products are hydrogarnets where Al is substituted by Fe and Ti. This hydrogarnet is generated in pre-processing, and it remains stable in digestion, improves diaspore digestion, and is the reason why A/S and N/S in the red mud is greatly reduced under the conditions of pre-processing and digestion reported here.

4. Conclusions

Because there is high iron in the Bauxite 'PG', a new process can be applied which involves high caustic liquor pre-processing before digestion in mother liquor, resulting in low A/S and N/S of the red mud generated.

In the course of pre-processing, as lime addition is increased up to about 7%, the A/S of the red mud will be reduced. Increasing lime addition past 7 %, does not significantly increase the mud A/S. Increasing caustic concentration and reducing solid content can be effective in reducing the A/S and N/S of the mud.

Bauxite pre-processing tests were conducted under the conditions of N_K of 260g/L, solid content of 100g/L, 150°C, 120 mins and 9% lime addition, followed by pre-processed bauxite digestion under the conditions of 260 °C, 60 mins. Good results were achieved, with the A/S of the red mud 0.74, and N/S of 0.12.

The pre-processed bauxite and the generated red mud were analyzed by XRF, XRD and SEM -EDS. The main silica mineral of the pre-processed bauxite and that of the red mud are both hydrogarnet where Al is substituted by Fe and Ti. It was concluded that the Fe and Ti substituted hydrogarnet is generated in pre-processing, that it remains stable in digestion, also improved diaspore digestion, and is the reason why A/S and N/S in the red mud is greatly reduced under the conditions of pre-processing and digestion described in this paper.

5. Acknowledgements

The author wishes to acknowledge the financial support received from Zhengzhou Non-ferrous Metals Research Institute Co. Ltd of CHALCO. The author also wishes to acknowledge the colleagues who have worked together to complete this project.

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