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RESEARCH OF THE MINERAL FOULING COMPOSITION AND REMOVAL METHOD IN BAUXITE DIGESTION PROCESS

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Abstract

In the digestion process of diasporic bauxite, due to precipitation of silicon and titanium compounds, a hard, dense mineral fouling are formed at the digestion device wall, causing heat transfer coefficient decrease. The phases of mineral fouling were analyzed by X-diffraction analysis, infrared spectroscopy, scanning electron microscopy and thermal analysis. In view of mineral characteristics of Chinese high silica and hard to digest diasporic bauxite, the mineral composition and microstructure of the silicon titanium mineral fouling have been analyzed. The mineral fouling prevention and removal methods have been studied. Using bauxite slurry pre-desilication and pre-detitanation we can effectively reduce and prevent the mineral fouling formation; and application of acid leaching can soften the hard and dense silicon titanium mineral fouling, and by high pressure water washing, the mineral fouling can be easily washed away.

1. Preface

The enhanced digestion technology can greatly reduce the energy consumption in alumina production, improve the heat utilization rate, strengthen production, raise economic benefits. However, because of silicon titanium mineral precipitation in the bauxite digestion process, on the device wall the hard material is formed, causing the serious reduction of the heat transfer coefficient, seriously affecting the normal operation of equipment. Therefore, elimination and prevention of scaling allows strengthening the alumina production process, improving productivity, reducing the energy consumption, and also improves the digestion through application of indirect heating pipeline.

Many countries have done a lot of research on removal of mineral fouling in recent years, but, due to the different types of ores, process conditions are different, therefore, the mineral foulingprevention and removal methods are not the same. There are following kinds of mineral foulingprevention and removal methods. Removal methods are: (1) acid leaching method, (2) high pressure water washing method, (3) mechanical cleaning method. Preventing methods are: (1) slurry fully pre-desilication, (2) organic compound coating, (3) ultrasonic and electromagnetic field treatment method. At present, the main industrially applied mineral fouling removal methods are acid leaching, high pressure water cleaning and mechanical cleaning. In China the removal mineral fouling in reactor is mainly provided by artificial vibration and beating method, this method is difficult to apply for mineral fouling removal in indirect heating digestion.

In view of the digestion characteristics of high silica diasporic bauxite, using indirect heat transfer digestion technology, mineral fouling problem will be more outstanding. Accordingly, for successful development and application of this advanced technology, more efficient methods of fouling preventing and cleaning up are required. This paper is dedicated to do more comprehensive study, to explore suitable for China's national conditions technical measures in order to reduce mineral fouling, extend the production cycle, to strengthen production, improve the heat utilization rate, reduce the heat consumption, raise economic benefits.

2. Experimental method

2.1. Apparatus and method

The ore is grabbed into a hopper, mixed with lime and caustic by wet grinding in ball mill. Classifier overflow is fed into the desilication tank, pre-desilicated at 95°C for 6 hours, pre-desilication slurry is pumped into the indirect pre-heater for preheating at flow of8m^3/hr. In the 1 to 8 stages pre-heaters are heated with evaporation steam, ninth stage pre-heater is heated with molten salt, thus the slurry is preheated to a digestion temperature, from the ninth stage pre-heater slurry is fed into ten stay tank, further to digestion. The digestion slurry is evaporatedat8 flashing stages, and then enters in the dilution tank.

2.2 Experimental materials

Chemical composition of bauxite digestion liquor is shown in Table 1.Lime chemical composition (lime mixed with incompletely burnt limestone): CaO 71.08%; MgO 6.85%. The silica forms in Chinese diasporic bauxite are presented in Table 2.

Table 1. The composition of Digestion Liquor(g/L)

Composition	Na_2O_T*	Al_2O	Na_2O_K	$\alpha_k(Na_2O_K/Al_2O_3)$**
Content (%)	251.6	127.3	235.2	3.04

Notes: *Na_2O_T=Na_2O_K+Na_2O_C; **caustic ratio is represented by molar weights the compounds

Table 2. The silica mineral forms in bauxite

Mineral	kaolinite	illite	chlorite	quartz	other
Content (%)	59.5	23.2	5.6	9.3	2.4

3. Experimental results and discussion

3.1. Desilication and titanium removing test

In the process of alumina production, titanium silicate mineral digestion behavior has a great effect on mineral fouling of alumina production. Test is conducted in casing indirect heater, pre-desilication slurry is heated from 95 °C to about 260 °C, then fed to holding tank for further digestion. The study is focused on investigation of titanium and silicate mineral behavior in the heating process, prompting some rules of mineral fouling.

The test results show that, kaolinite digestion is easily conducted in alkaline solution, with normal pressure. In the range160 °C~260 °C, illite, chlorite, quartz are gradually digested in alkaline solution with the increase of temperature;below160 °C no reaction is observed.

Changes of concentration of SiO_2 and desilication rate have similar features, i.e. SiO_2 concentration increases slowly for digestion of kaolinite, which is due to the small of residual kaolinite content, rapid movement of slurry and slow heating. SiO_2 concentration increased dramatically in the later stages, which is the result of illite minerals digestion, and sharp temperature rise. In the preheating process, the dissolution rate of silicon mineral is greater than SiO_2 precipitation rate in solution. As the result of changes in SiO_2 concentration and desilication ratio feature, silicon mineral fouling is mild before ninth stage pre-heater.

In the ninth stage pre-heater, although the desilication rate may cause mineral fouling formation, but because the SiO_2 concentration in the solution is also increasing, so, mineral fouling is milder than expected, as shown in Figure1 and Figure2.

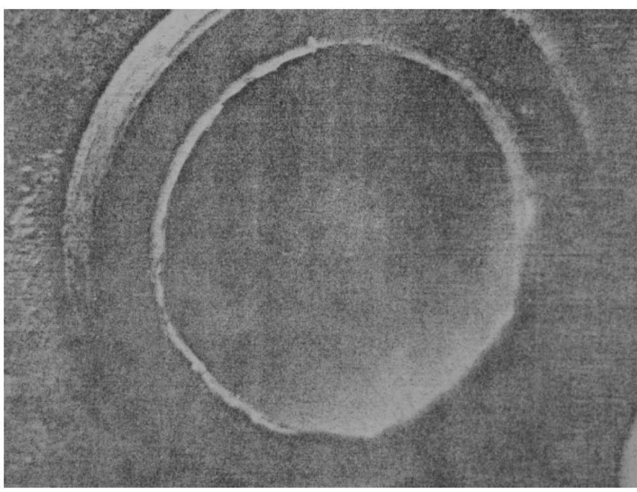

Figure 1. Low temperature pre-heater mineral fouling

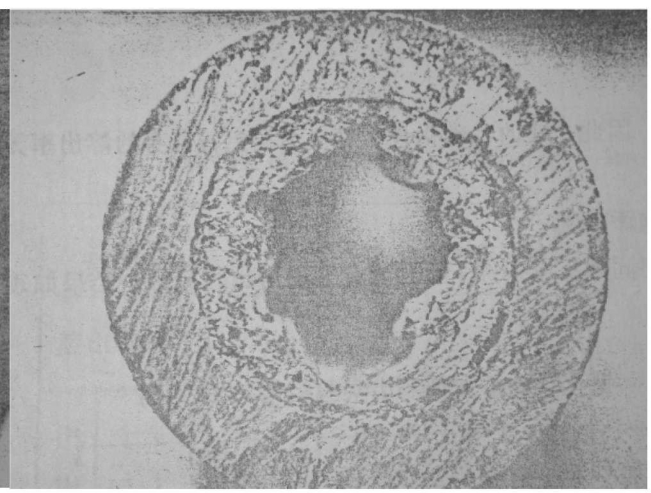

Figure 2. Higher temperature mineral fouling

3.2. Titanium removing test

In China's bauxite ore, TiO_2 is mainly presented by anatase and rutile, which accounted 98.4% of the TiO_2 total amount. Other forms of $TiO_2$are presented in a very small amount of white titanium and colloidal TiO_2. As anatase particles are small and widely dispersed, that is improving the reaction and titanium extraction rate from bauxite can reach 85%.

In the low-temperature preheating stage (less than 200~220°C), soluble form of titanium is mainly anatase. With high temperature 220~260°C, rutile particles also began to participate in the reaction.

According to above the test results of desilication and titanium removing show some regularity of the mineral fouling:

(1) At preheating below 180°C the mineral fouling is small;

(2) At temperatures higher than 180 °C the mineral fouling at heating surfaces gradually grows, however, because the SiO_2 concentration in the solution is not reduced, mineral fouling rate is lower than expected;

(3) The rate of desilication and titanium removing increase gradually at 180°C, the removal rate of silicon and titanium are associated with the mineral composition of silicon and titanium, more with the increasing rate of temperature, so, the control of heating rate can control the mineral fouling rate.

3.3 Structure and composition of mineral fouling

Mineral fouling from the pre-heater was removed using a screwdriver, washed two times with alcohol, dried and crushed in agate mortar. The samples were used for chemical and phase analysis. The components of the mineral fouling are shown in Figure3 and Figure 4.

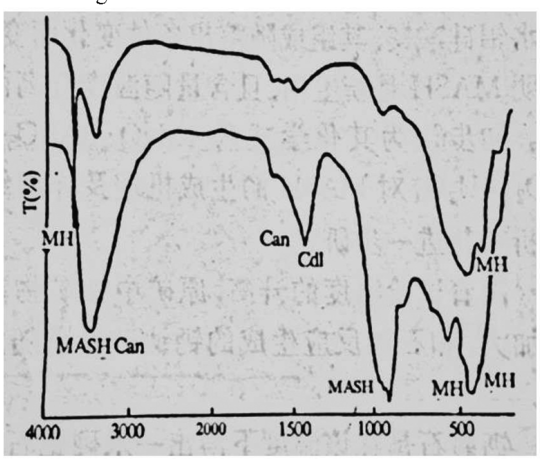

Figure 3. FTIR pattern of the mineral fouling

The mineral fouling in sleeve pipe pre-heater is composed of silicon slag mineral fouling (mainly cancrinite), magnesium slag mineral fouling [hydrated silicon magnesium aluminate and Mg $(OH)_2$] and titanium slag mineral fouling (calcium titanate and hydroxy calcium titanate).

Till the preheating temperature reaches 180 °C, due to the fact that reaction rate of titanium minerals is very slow, TiO_2 conversion rate is very low, even at this temperature, there is a small amount of mineral fouling formed in sleeve pipe pre-heater, it is composed of silicon and magnesium, but when titanium mineral fouling occurs, it is mainly in form of hydroxyl calcium titanate, the mineral fouling is easy to clean.

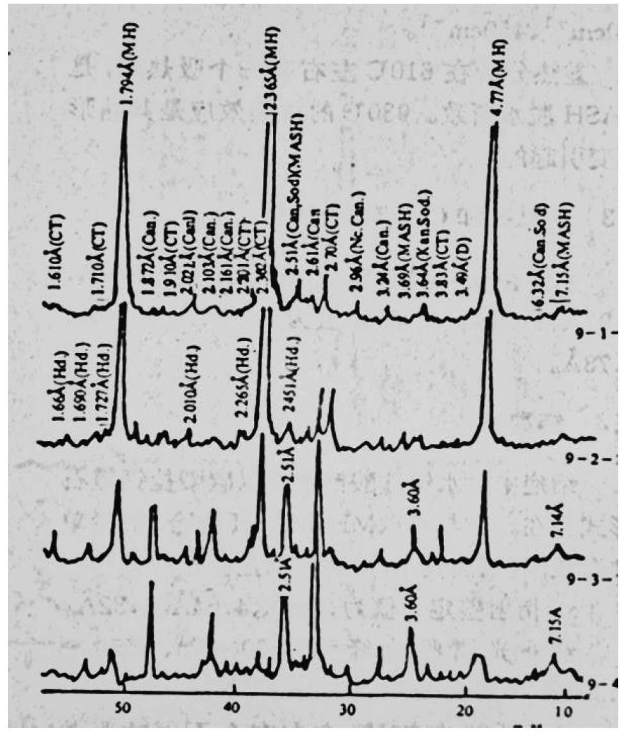

Figure 4. X-ray diffraction of the mineral fouling

With temperature higher than 260 °C, the mineral fouling is composed of magnesium slag and perovskite, although perovskite mineral fouling is difficult to clean, but the magnesium slag is easy to clean with acid, as the magnesium slag was cleaning the perovskite structure became loose, the mineral fouling cleaning is not difficult.

The MgO in ore and lime addition is the source of the MgO of calcium and magnesium mineral fouling. Because the mineral fouling of magnesium slag is easy to clean with acid, it make mineral fouling more soft and easily to clean. By reducing MgO content in raw materials, we can reduce the scaling rate, but the mineral fouling becomes hard, difficult to clean.

3.4 Mineral foulingcleaning method and results

As mentioned before, because there is a small amount of MgO in the raw materials, the mineral fouling structure becomes loose. This mineral fouling can effectively remove by pickling and water jet cleaning.

Table 3. The phase composition of mineral fouling at pre-heater

Composition (%)	sodium silicate slag	hydrating garnet	perovskite	$Mg(OH)_2$	magnesium silicon slag	Boehmite
Low temperature pre-heater scale	42	9	0	4	29	6
Higher temperature pre-heater scale	13	0	45	15	14	0

Hydraulic cleaning by CM-3 type hydraulic pump, rated 40 kW, feed rate of 1.5 m^3/hr., maximum discharge pressure is 700Kg/cm^2, nozzle diameter 26mm, flow beam diameter is less than 1.5mm.

Experiments were conducted at 180°Cand 260 °C pre-heater, the phase composition is shown in the table 3.

The results show that 180°C preheated mineral fouling can be easily cleaned off with 10% sulfuric acid pickling for 90 minutes at 40 °C, the temperature is the most important factor influencing pickling in the range of research (temperature 45～75 °C, the sulfuric acid 5 ~ 15%, 90 ~ 270 minutes). With increasing temperature, mineral foulingcleaning rate increase, followed by the catalyst, with the extension of time, sulfuric acid concentration increase, mineral foulingcleaning rate also increases.

For high temperature preheating mineral fouling, its digestion rate is up to 78% in 10%HCl pickling for 5 hours and adding the catalyst. Without the presence of a catalyst, digestion rate of the preheating mineral fouling reduce to only 42%. From the dissolved components, mineral fouling of sodium, aluminum mineral is more easily digested, the digestion rate can reach more than 90%. Calcium titanate is difficult to be dissolved, without the presence of a catalyst, calcium titanate basically not digested, only adding catalyst, calcium titanate was dissolved by 40%.

4. Conclusion

4.1 In the pre-heater below 180°Cthe mineral fouling is slow. The rate of desilication and titanium removing increase steeply at 180 °C, the removing rate of silicon and titanium are associated with the mineral composition of silicon and titanium.

4.2 The mineral fouling in sleeve pipe pre-heater is composed of silicon slag mineral fouling (mainly cancrinite), magnesium slag mineral fouling [hydrated silicon magnesium aluminate and $Mg(OH)_2$] and titanium slag mineral fouling (calcium titanate and hydroxy calcium titanate).

4.3 With temperature higher than 260 °C, the mineral fouling is composed of magnesium slag and perovskite, because magnesium slag cleaning, make the perovskite structure became loose, therefore, the mineral fouling cleaning is not difficult.

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