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PREHEATERS AND DIGESTERS IN THE BAYER DIGESTION PROCESS

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Abstract

The existing preheaters and digesters applied in Bayer digestion processes are classified and investigated in this paper. The characteristics and mineral compositions of bauxite to be processed have great effects on the performance and operational efficiency of the preheaters and digesters. Therefore, the design concept and selection principle of Bayer digestion facilities and whole systems should be considered thoroughly on the basis of analysis of chemical and mineral compositions of bauxites and the study results of the behaviors of the minerals in bauxites in the preheating and digestion process.

Introduction

Bayer digestion is the key process of alumina production, which plays an important role in cycle efficiency, productivity and energy consumption of the whole production system. The design concept of a digestion system has to satisfy all the technological requirements for bauxite digestion. The digestion preheaters are the main facility to ensure reaching the required digestion temperature by indirect preheating.

The indirect preheating and intensified digestion process should be applied for the Bayer digestion systems of bauxite in order to save energy and increase efficiency. The key points are to preheat bauxite slurry or liquor to reasonably high temperatures by indirect preheating technology and to keep the high temperature bauxite slurry for enough retention time. This technology has to be applied especially for bauxites containing diaspore and boehmite.

Various types of Bayer digestion processes and relevant preheaters and digesters have been developed in the alumina refineries by scientists and engineers in the world for different kinds of bauxite. Numerous operating conditions and parameters, such as diameters and lengths of equipment, agitators, temperatures and preheating media etc., are selected for design of the equipment to treat the bauxite with different compositions and properties. The Bayer digestion processes and equipment are continuously developed, improved and updated to obtain higher and higher production efficiencies and to save energy.

Existing digestion processes, preheaters and digesters are discussed in this paper. The important influence of the compositions and properties of bauxite and liquor on the processes and equipment operation are investigated and the optimization of the process design is pointed out as well.

Classification And Characteristics Of Digestion Processes And Equipment

In general Bayer digestion processes can be classified as two types: a two-stream process and a single stream process. The main difference is in the preheating methods. The bauxite slurry is heated to the final temperature for the single process and in the two stream process, liquor is heated to an elevated temperature and mixed with high percentage solids bauxite slurry before or within the first digester [1].

Preheaters In Bayer Digestion Processes

The process objective of digestion preheaters is to achieve high heat transfer efficiency and long operation cycle times. The types used for preheating slurry or liquor can be classified as single tube or multi-tube. Depending on the type of preheater, the heat transfer media can be steam (including fresh steam and steam from flash tanks), molten salts or organic media. Table I shows the classification of preheaters and their characteristics.

Table I Classification of Preheaters and Their Characteristics

Items	Tube (Single)	Multi-tube	
		Media Outside	Media Inside
Heating Media	Steam, Molten Salts or Organic Media	Fresh and Spent Steam	Fresh and Spent Steam
Slurry (Liquor) Flow	Plug Flow, Fast	Parallel to Tubes	Vertical to Tubes
Heat Transfer Areas and Unit Investment	Smaller Areas	Bigger Areas, Smaller Unit Investment	Bigger Areas, Smaller Unit Investment
Heating Efficiency	Less Scaling, Higher Efficiency	Higher Scaling, Lower Efficiency	Higher Scaling, Lower Efficiency
Operation Cycle Time	Longer	Shorter	Shorter
Pump Pressure	Higher	Lower	Much Lower

Compared with multi-tube preheaters, the slurry in single tube preheaters flows much faster to promote the transfer of heat through the tube wall and at the same time makes the scaling process slower. Nevertheless, the multi-tube preheaters have the advantage of larger heat transfer areas and lower unit investment. The operating cycle time and technical performance of preheaters depend on the scaling problem.

For the two-stream process, the preheaters are used for heating liquor. Scale formation and corrosion problems can take place depending on the caustic and silica concentrations in liquor. The situation becomes much different in China owing to the higher caustic concentrations of spent liquor in Bayer digestion.

Bayer Digesters

There are two types of digesters: tube digesters and autoclave digesters. Table II shows the classification and characteristics of different types of digesters.

Table II Classification and Characteristics of Different Digesters

Items	Tube Digesters	Autoclaves in Series	
		No Agitators	With Agitators
Slurry Flow Types	Plug	Irregular	Back Mixing
Average Digestion Time	Shorter	Longer	Longer
Pump Pressure	Higher	Lower	Lower
Digestion Time Distribution	Same, No Distribution	No Regulation	Homogeneous, Some Distribution
Caustic Concentration Change	Homogeneous Change	Not Homogeneous	Almost Same in Every Autoclave
Scale Effects On Digestion	Greater	Smaller	Smaller

Compared with autoclave digesters, tube digesters are of a plug type flow where there is no back mixing. This is a better condition for digestion of alumina out of bauxite. The problem with tube digester technology is that the digestion time is often very limited due to the small volume in the tubes, and consequently the digestion temperature has to be raised to dissolve alumina in the shorter holding times. Raising the temperature, however, is limited by the design of digester tubes and pumps for higher pressures. In addition, any small amount of scale formed will shorten greatly the digestion time because of the relatively small volume of digesters.

Autoclave digesters can be classified as autoclaves with and without agitators. In the autoclaves with agitators, the bauxite slurry is homogeneously mixed which reduces the initial digestion rate when compared with tube digesters. In un-agitated autoclaves the same digestion rate problem exists. In addition, some bigger bauxite particles will rapidly fall from top to bottom resulting in a shorter digestion time for those coarser fractions of bauxite and a decrease in digestion efficiency.

The average digestion times and digester volumes of autoclaves are much greater than tube digesters so that longer periods can be allowed between scale removals and the equipment investment in pumps and power consumption can be reduced.

The Digestion Processes

The classification and characteristics of all the kinds of digestion technology are shown in Table III.

Behavior Of Impurities Minerals in Bauxite And Additives In The Preheating And Digestion Processes

The main reaction conditions and products in the preheating and digestion processes are shown in Table IV, in which CTH is calcium hydroxytitanate and CASH is hydrogarnet.

In the preheating and digestion processes, the impurity minerals in bauxite and additives, such as lime, will react with liquor and with each other to consume caustic soda and alumina. Some products can precipitate on the preheating area surface to form scale [2,3]

Table III. Classification and Characteristics of Digestion Technology

Classification	Single Stream			Two Stream	
	Tube	Tube and Autoclave Preheating	Tube Heating and Retention Autoclaves	Liquor Preheating	Liquor Preheating, Part Slurry Preheating
Preheater Types	Tubes	Tube and Multi-Tubes in Autoclaves	Tubes	Multi-Tubes	Multi-Tubes(Liquor) Single-Tubes(Slurry)
Digester Types	Tubes	Autoclaves with Agitators	Autoclaves in Series	Autoclaves With Agitators	Retention Autoclaves in Series
Heating Media	Molten Salts or Organic	Steam	Molten Salts or Organic	Steam	Steam
Digestion Temperature	Very High ~280℃	High ~260℃	High ~260℃	Lower 240~250℃	High ~260℃
Digestion Time	Shorter	Longer	Longer	Longer	Longer
Pumps Requirements	High Pressure	Middle Pressure	Middle Pressure	Two Middle Pressure Pumps	Two Middle Pressure Pumps

Table IV Main Reaction Conditions and Products of Bauxite Minerals and Additives in Preheating and Digestion Process

Minerals	Si- Minerals				Fe- Minerals		Ti-Minerals	Lime additive		
	Kaolinite	Pyro-phyllite	Illite	Chamo-site	Fe_2O_3	FeOOH	Anatase Rutile	CaO	$CaCO_3$	MgO
Reaction Tem., °C	95-100	150-210	>180	>280	No	>180 (Form Fe_2O_3)	>180 (With Lime)	Low Tempe-rature	>240 (Carbona-tion)	>180
Products	Sodalite, Cancrinite	Same To Left	Same to Left	Same to Left	No	Fe_2O_3	$CaTiO_3$ CTH*	CASH	CASH**	$Mg(OH)_2$
Scale Possibility	Red mud Seed	Big	Big	Small	Small	Small	Big	Big	Big	Big

* CTH----Calcium Hydroxytitanate; ** CASH----Hydrogarnet

Silica-Containing Minerals

Kaolinite in bauxite can easily react with liquor at about 95°C so that the predesilication of slurry at 90-100°C will remove most of the kaolinite.

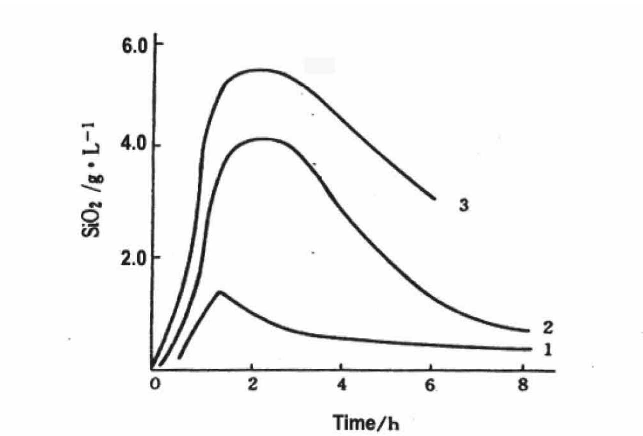

Figure 1. Predesilication Curves of Kaolinite at 95°C
1— Na_2O 140g/l; 2—Na_2O 200g/l; 3—Na_2O 240g/l

Figure 1 shows there is an induction period at the beginning of kaolinite predesilication. The higher the caustic concentration is the higher the top silica concentration becomes. The pyrophyllite in diasporic bauxite reacts with liquor slowly at temperatures of 95-105°C, while the reaction rate increases sharply in the temperature range of 150-210°C, and there is an even faster reaction rate when the temperature reaches about 220°C [3].

The illite in diasporic bauxite reacts slowly at the temperatures below 180°C. And the reaction rate increases sharply at temperatures above 180°C. Some bigger grains or fractions of illite can be found remaining in red mud after digestion, which proves that illite dissolves in liquor only gradually at the higher temperatures (See Fig.2) [4].

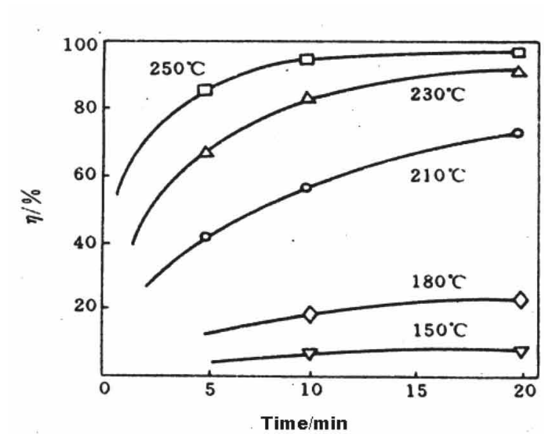

Figure 2 Reaction Efficiency of Illite in Spent Liquor at Different Temperatures

Chamosite and well-crystallized quartz react very slowly in sodium aluminate solutions even at temperatures up to 280°C, and in fact they are inert minerals under the common digestion conditions [5].

SiO_2 dissolved in sodium aluminate solution can be precipitated as Si-containing minerals (for example, as sodalite etc.) to form scale during the preheating process of the liquor when the SiO_2 concentration reaches up to or above the SiO_2 equilibrium concentration. Dissolved SiO_2 in liquor will precipitate by the kinetic effect of time/temperature during preheating. The scale precipitation process depends on SiO_2 supersaturation extent in the liquor and the concentrations of all relevant ions as well.

Ti- Containing Minerals

Anatase and rutile in diasporic bauxite react to a very small extent in spent liquor without additives (see Fig.3). Only if additives such as lime are added will the Ti-minerals in bauxite react quickly with the additives. The reaction rate is very slow at the temperatures below 150°C and increases sharply as the temperature rises to the range of 150~220°C. The reaction efficiency of Ti-minerals will reach above 50% when the retention time is 30 minutes at a temperature of 220°C (see Fig. 4) [6].

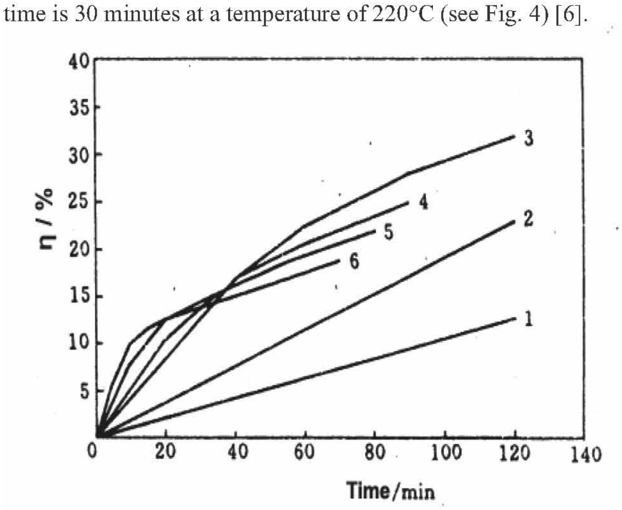

Figure 3 Reaction Efficiency of Rutile Without Lime at Different Temperatures
1---182°C; 2---202°C; 3---221°C; 4---242°C; 5---262°C; 6---280°C

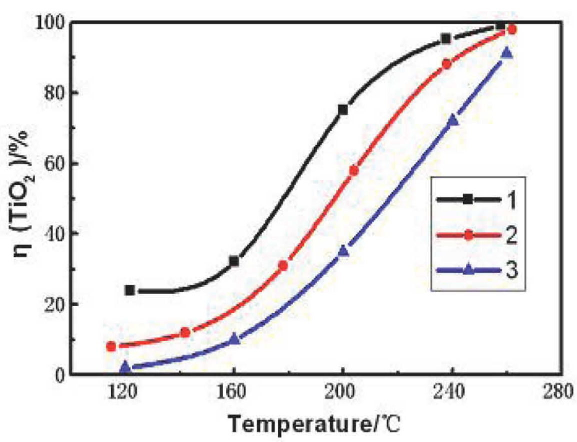

Figure 4 Reaction Efficiency of TiO_2 in Bauxite With Lime Addition at Different Temperatures With Reaction Time of 30 Minutes
1-bauxite 1, 2-bauxite 2, 3-bauxite 3,

Fe-Containing Minerals

Fe-containing minerals exist in bauxite mostly as hematite and in small amounts as goethite. Hematite does not react in digestion process and the goethite can be dehydrated and changed to inert hematite during high temperature digestion. Some amount of Al-containing goethite can be decomposed under the conditions of high temperature digestion with addition of lime, as a result of which the Al element existing in goethite is transferred into liquor.

Lime Additive

Lime is an effective digestion additive for diasporic bauxite and contains CaO, MgO and remaining $CaCO_3$. CaO can form hydrogarnet at predesilication temperatures (~100°C) and react quickly with TiO_2 in bauxite at higher temperatures (>180°C). As a result, calcium titanate or calcium hydroxytitanate is formed and the inhibition effect of TiO_2 on the digestion of diaspore is eliminated [7]. $CaCO_3$ remaining in lime plays an important role in the carbonation reaction with sodium aluminate solution at the higher digestion temperatures, which causes Al_2O_3 and caustic soda consumptions:

$$2NaOH + CaCO_3 = NaCO_3 + Ca(OH)_2 \quad (1)$$

$$3Ca(OH)_2 + 2NaAl(OH)_4 + aq \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + 2NaOH + aq \quad (2)$$

MgO

The small amount of MgO, commonly existing in lime, can react in liquor to produce such compounds as $Mg(OH)_2$ and magnesium hydroaluminosilicate which in turn can form scale on the indirect preheating surface in preheaters [8,9,10]. It can be seen from Figure 5 that the $Mg(OH)_2$ solubility in sodium aluminate solution is nearly zero when the temperature reaches 180°C.

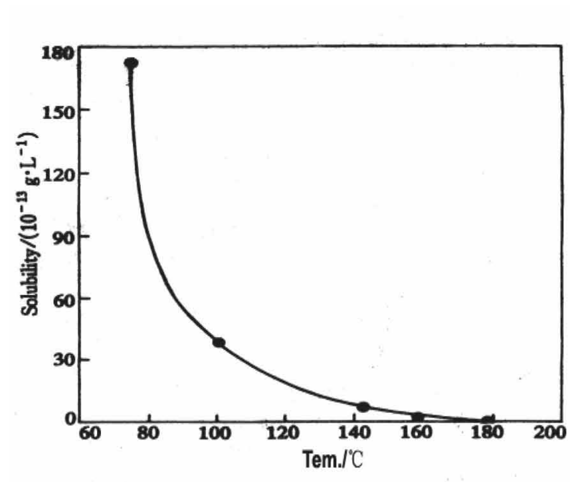

Figure 5 Solubility of $Mg(OH)_2$ in Bayer Liquor at Different Temperatures

New Design Concept of Bayer Process and Equipment

Scale - Key Problem Of Bayer Digestion Process And Equipment

High temperature and indirect preheating equipment must be used to raise the temperature of spent liquor or bauxite slurry up to the target values in order to achieve the digestion conditions needed to reduce energy consumption and raise production efficiency.

Reactions in the spent liquor or bauxite slurry take place to form solid products precipitated on the preheating surface as scale. As a result the heat transfer coefficient is reduced, the operating cycle period is shortened, and the equipment capital investment is increased.

It is can be seen in Table V that the heat transfer coefficient will be dropped by about 50% if the scale formed is as thick as 1mm.

Table V Influence of Scaling on Heat Transfer Coefficient

Scale Thickness (mm)	No	0.5	1.0	2.0
Comparative Heat Transfer Coefficient (%)	100	65	50	15

Scale formed in the preheating process of spent liquor is simply sodalite or cancrinite. The mineralogy of scale formed from bauxite slurry, however, is very complicated.

Table VI Main Scale Mineral Composition in Preheating and Digestion of Bauxite Slurry with Complicated Composition

Temperature Range °C	100~180	180~220	220~260	260~280
Minerals in Scale	Sodalite, CASH**	$Mg(OH)_2$, Cancrinite	$CaTiO_3$, CTH*	$CaTiO_3$, Cancrinite

* CTH—Calcium Hydroxytitanate; **CASH---Hydrogarnet

The Factors That Influence The Optimization Of The Bayer Digestion Process

Lime Additive The main function of lime additive is to eliminate the retarding effect of Ti-minerals on bauxite digestion at high temperatures, which increases the digestion rate of the alumina hydrate in bauxite. Compounds such as $CaTiO_3$ are formed in the process. Lime also reacts with Si-containing minerals during digestion to form hydrogarnet etc. so that the ratio of Na_2O/SiO_2 in red mud and soda consumption are decreased.

An increase of lime dosage is advantageous to decrease the soda consumption when the SiO_2 content is high in bauxite. The optimum lime addition amount must be determined according to the experimental results.

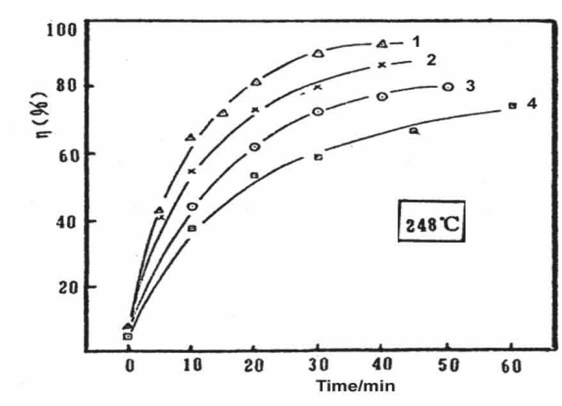

Figure 6 Digestion Curves of Different Sizes of Pingguo Bauxite
1: -45 m 100%; 2: -45 m 50%, 56-75 m 50%;
3: 56-75 m 100%; 4: 100-150 m 100%.

The Influences of Bauxite Grain Sizes It can be seen in Figure 6 that the various sizes of alumina containing minerals in bauxite have quite different digestion rates. During grinding, the bauxite is ground to different sizes of particles so that the ground bauxite size distribution control and application of suitable digestion technology and equipment are very important to achievement of the best digestion performance.

Optimization of Digestion Conditions Such factors, as caustic concentrations, digestion temperatures, time and agitation have great impacts on bauxite digestion performance. The digestion kinetics equation of diasporic bauxite can be expressed as follows:

$$d\eta /dt = K \cdot S[(C_N - C_A)/K_E] = K' \cdot S \cdot N_K[1 - (K_E+1)/(\alpha_K \cdot K_E)] \quad (3)$$

where $d\eta/dt$ is digestion rate; C_N, C_A are caustic and alumina molar concentrations respectively; K_E is equilibrium constant; α_K is caustic molar ratio (Na_2O/Al_2O_3); N_K is caustic concentration (g/l); S is the surface area; K and K' are the constants.

It is shown by the measurements of the apparent activation energy of digestion of diasporic bauxite that the digestion reaction is controlled by surface chemical reactions at temperatures lower than 240°C and is controlled by diffusion processes of ion reactants and products when the temperature is higher than 268°C. The combination of both diffusion and surface chemical reaction processes can be found for the digestion process of diasporic bauxite at 240-268°C [7]. Therefore, the digestion process can be intensified by increasing the digestion temperature to above 268°C and enhancing agitation.

High Temperature Two Stream Process With Preheating For Both Liquor And Bauxite Slurry

Figure 7 is a flow sheet of a high temperature two stream process with preheating of both liquor and bauxite slurry, which is named the converging stream digestion process [1]. The difference between the traditional two stream process and the converging stream process is that bauxite slurry in the converging stream process is also preheated to about 180°C to further increase the digestion temperature and make the liquor preheating much easier due to its lower temperature rise. The slurry preheating temperature is limited by the scaling rate during slurry preheating.

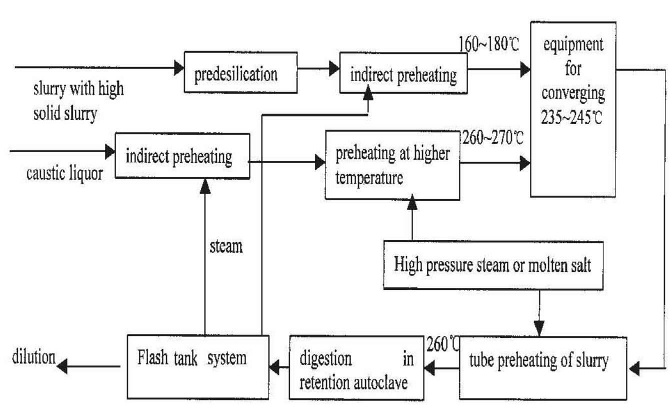

Figure.7 Converging Stream Process Flow Sheet

Retarding Scaling Problems In Preheaters By Adding Seeds

It is shown in Table VII that adding red mud seeds into the bauxite slurry can reduce the SiO_2 concentration in the liquor. The result is that the scaling rate on the preheating surface is slowed down.

Table VII Influences of Adding Red Mud Seeds on SiO_2 Concentrations in Slurry in Preheating Process

No.	Red Mud Addition	Experimental Results (g/l)			
	Dry Red Mud/ Bauxite	N_T	N_K	A	SiO_2
1	0 %	219.0	191.0	108.8	0.71
2	5 %	217.8	190.0	107.5	0.59
3	10 %	217.5	189.0	108.0	0.50
4	0 %	220.3	194.0	113.3	1.08
5	5 %	217.2	188.0	113.4	0.88
6	10 %	217.4	190.0	113.0	0.84

The Processes To Remove Si And Ti Containing Minerals At High Temperatures

Si and Ti containing minerals in bauxite will rapidly react with liquor or additives when bauxite slurry is preheated to certain temperatures, e.g. 220°C. If enough retention time is given to the bauxite slurry during this period for the reactions to be completed, scaling in the following preheating process will be greatly reduced.

New Technological Concept On Fluidized Digestion

The test results show that the coarser grains of alumina containing minerals in bauxite slurry have the greatest influence on the digestion efficiency of the difficult to digest bauxites. In series autoclaves, the bauxite slurry flows from top down and those coarser bauxite grains in the slurry settle down more quickly than others to bring about shorter retention time for coarser grains, which leads to lower digestion efficiency.

On the basis of reaction engineering principles, the new technological concept of fluidized digestion is proposed to overcome this problem. In the fluidized digestion process the bauxite slurry enters into the autoclaves at a position near the autoclave bottoms and the slurry flows up to the top. In this digestion process, the coarser bauxite grains will have a longer retention time in the autoclaves because of their specific gravity. This results in a general optimization of the digestion process for the various sizes of bauxite grains and increases digestion efficiency.

Conclusions

(1) Present indirect preheating and intensified digestion technology and relevant equipment include: Tube preheating and tube digestion, Tube (or Multi-tubes in autoclaves) preheating and digestion in autoclave in series with agitation, Tube preheating and retention autoclave digestion and Two stream (or Converging stream) digestion processes.

(2) Different indirect preheating and intensified digestion technology and relevant equipment can be applied to different kinds of bauxite with various minerals.

(3) The complex behavior of all the minerals in the bauxite, digestion additives and liquor during preheating and digestion of bauxite slurry should all be investigated to optimize preheating and digestion process for a specific bauxite.

(4) Some new concepts on preheating and digestion processes and equipment are proposed for intensifying digestion, reducing scale and improving production efficiency.

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