

Reaction behavior and mechanism of anatase in digestion process of diasporic bauxite

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Abstract: Based on the study of influence of temperature, digestion time, amount of CaO added and composition of aluminate solution on reaction behavior of pure anatase in high-pressure digestion process of bauxite, reaction mechanism of anatase was preliminarily determined. Anatase first reacts with caustic soda to produce Na_2TiO_3 , then the resultant Na_2TiO_3 reacts with $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$ resulting from the reaction of CaO with sodium aluminate solution to produce $\text{CaO}\cdot 2\text{TiO}_2\cdot \text{H}_2\text{O}$ which eventually converts into CaTiO_3 . Higher temperature, concentration of free Na_2O_k (the caustic soda uncombined with aluminate anions in the form of Na_2O) and molar ratio of CaO to TiO_2 are favorable to the conversion of $\text{CaO}\cdot 2\text{TiO}_2\cdot \text{H}_2\text{O}$ to CaTiO_3 . And $\text{Al}(\text{OH})_4^-$ shows the function of a catalyzer in the reaction of anatase with caustic soda with or without CaO added during the digestion process of diasporic bauxite.

Key words: anatase; hydroxy calcium titanate; calcium titanate; high-pressure digestion; reaction mechanism

1 Introduction

There is 2%–4% of TiO_2 mainly in the form of anatase, rutile or brookite in almost all kinds of bauxite[1–3]. In the digestion process at relatively low temperature for gibbsitic bauxite, chemical reactions between these titanium-containing minerals and components of aluminate solution will not take place. But as for the digestion of diasporic bauxite in China, higher digestion temperature ranging from 210 °C to 270 °C is required. In this case, titanium-containing minerals will react with components of aluminate solution. According to the results reported in Refs.[4–5], sodium titanates with different compositions produced by the reaction of titanium-containing mineral with caustic soda appear in a dense thin film covering on the surface of bauxite particles. The film can prevent diasporite from contacting with caustic solution, which significantly lowers the extraction rate of alumina from diasporic bauxite. In order to eliminate the inhibition effect of titanium-containing mineral, lime is always added to the original slurry in the high pressure digestion process for diasporic bauxite in the alumina industry.

With the addition of lime in the digestion process, titanium-containing minerals react with calcium-bearing compounds to produce calcium-titanium compounds, such as $\text{CaO}\cdot\text{TiO}_2$ and $\text{CaO}\cdot 2\text{TiO}_2\cdot \text{H}_2\text{O}$ [6]. These compounds usually form substantial scale which is rather difficult to be cleaned up on the surface of heat exchanger during the bauxite digestion process so as to increase energy consumption and cause wastage of equipments productivity[7].

Up to now, although some research work was carried out on the composition, crystal morphology and lattice parameters of calcium-titanium compounds in the red mud[5], it is still unclear about the formation conditions of calcium-titanium compounds and reaction mechanism of titanium-containing minerals with the additive of lime in the alkaline aluminate solution. Therefore, it is of great importance to theoretically make clear the reaction behavior and mechanism of anatase in Bayer high-pressure digestion process of diasporic bauxite for scale control and removal to reduce manufacture cost and improve equipment efficiency.

However, as there are so many other minerals besides diasporite and anatase in bauxite ore, such as limestone, kaolinite, illite, hematite, goethite, etc, the

chemical reactions and influencing factors are complex during high-pressure digestion process of diasporic bauxite, which is one of the reasons that the reaction mechanism of anatase in high-pressure digestion process of bauxite has not yet been revealed clearly. So, it is necessary to employ pure titanium-containing mineral to explore the reaction mechanism of titanium-containing mineral in high-pressure digestion process of diasporic bauxite. With consideration of the presence state and the sequence of reaction ability of titanium-containing minerals with caustic soda[8], anatase, the most representative titanium-containing mineral present in diasporic bauxite in China, was chosen as the starting material in this research work.

2 Experimental

2.1 Materials

TiO₂ powder was a chemical reagent in the phase of anatase; NaOH and Na₂CO₃ were reagents with analytically pure grade; Sodium aluminate solution was synthesized in laboratory by heating the mixture of NaOH and Al(OH)₃ with analytically pure grade; and CaO was prepared by calcination of Ca(OH)₂ with analytically pure grade at 800 °C for 2 h.

2.2 Methods

Digestion operations of anatase were carried out in high-pressure autoclaves (made in Machine Factory of Central South University, China) with mixed nitrate molten salts as heating medium. The resultant slurry from digestion process was abruptly cooled down by cold water, then filtered by vacuum pump, and washed with boiling water three times. The filter cake was dried at 95–105 °C, and finally weighed by electrical balance with a accuracy of 0.1 g. Then 0.50 g of filter cake was put into 100 mL hydrochloric acid solution with a volume ratio of hydrogen chlorine to water of 1, then heated at 100 °C for 15 min in thermostat and filtered while it was hot. The concentration of titanium dissolved in hydrochloric acid was measured by H₂O₂ colorimeter with 7230G spectrometer (Shanghai Analytical Apparatus Company, China).

Symbol $\omega(\text{Ti})$ represents mass ratio of TiO₂ dissolved in hydrochloric acid to the total amount of TiO₂ present in the anatase added. Na₂O_k represents caustic soda (NaOH) in the form of Na₂O in alkali aluminate solution, and free Na₂O_k represents the caustic soda uncombined with aluminate anions in the form of Na₂O. Na₂O_c represents sodium carbonate (Na₂CO₃) in the form of Na₂O.

3 Results and discussion

3.1 Influence of temperature and time on reaction behavior of anatase

It was reported that the apparent activation energy of de-titanization in diasporic bauxite digestion slurry is 84.4 kJ/mol in the temperature range of 180–260 °C, and surface chemical reaction is the controlling step of the de-titanization reaction in this temperature range[9–11]. Temperature and time have great influence on reaction ability and solubility of all minerals present in bauxite, and on the composition of scale and scaling speed during the bauxite digestion process. Composition of scale formed by Ti-containing minerals varies with temperature and time, such as CaO·2TiO₂·H₂O, titanium-containing hydrogarnet, and perovskite.

Fig.1 shows the influence of temperature on $\omega(\text{Ti})$. It is obviously that $\omega(\text{Ti})$ first increases slowly to reach its maximum and then decreases sharply with the increase of temperature. When temperature is lower than 180 °C, $\omega(\text{Ti})$ increases with the increase of time; when temperature is higher than 180 °C, $\omega(\text{Ti})$ first increases and then decreases with the prolongation of time.

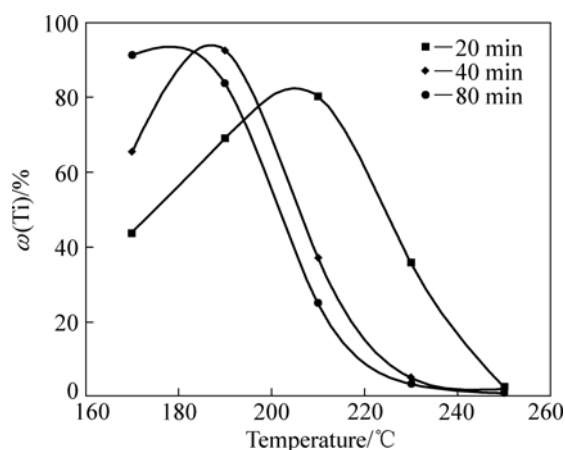


Fig.1 Influence of temperature on $\omega(\text{Ti})$ of residue resulting from reaction of anatase with alkaline aluminate solution ($\rho(\text{Na}_2\text{O}_k)=233.11 \text{ g/L}$, $\rho(\text{Al}_2\text{O}_3)=183.01 \text{ g/L}$, $n(\text{CaO})/n(\text{TiO}_2)=1.0$)

Fig.2 represents XRD patterns of residue obtained at different digestion temperatures for various time. When digestion temperature is lower than 200 °C, the main phases of residue are CaO·2TiO₂·H₂O and 3CaO·Al₂O₃·6H₂O with a small amount of CaTiO₃ as shown in Fig.2(a), and CaO·2TiO₂·H₂O converts into more stable CaTiO₃ at higher digestion temperature and longer time, as shown in Fig.2(b).

CaTiO₃ in the phase of perovskite is the most stable phase of titanium-containing compounds in residue in the digestion process of diasporic bauxite, which is also the main component of scale formed on the surface of heat exchanger in alumina refinery. Well crystallized CaTiO₃ dissolves completely only in hydrofluoric acid, and with a small solubility in boiling hydrochloric acid[12–14],

while poor crystallized CaTiO_3 , Na_2TiO_3 and $\text{CaO} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$ can completely dissolve in the boiling hydrochloric acid solution. With increasing the digestion temperature and time, more CaTiO_3 with better crystallization degree is produced, which leads to the decreases of $\omega(\text{Ti})$ rapidly. So, it should be noted that $\omega(\text{Ti})$ is not always a reliable parameter to characterize reaction degree of titanium-containing mineral, which is different from the common knowledge.

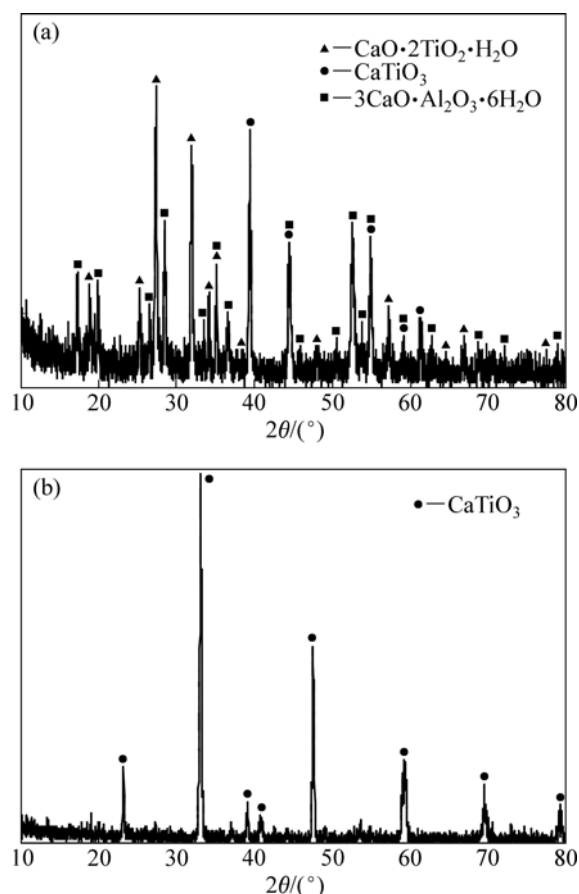


Fig.2 XRD patterns of residue prepared under different conditions ($\rho(\text{Na}_2\text{O}_k)=233.11 \text{ g/L}$, $\rho(\text{Al}_2\text{O}_3)=183.01 \text{ g/L}$, $n(\text{CaO})/n(\text{TiO}_2)=1.0$): (a) 170 °C, 40 min; (b) 250 °C, 80 min

3.2 Influence of composition of sodium aluminate solution on reaction behavior of anatase

When concentration of Na_2O_k or free Na_2O_k is fixed, influence of concentration of Al_2O_3 on reaction behavior of anatase is shown in Fig.3(a). $\omega(\text{Ti})$ is almost invariable with the increase of concentration of Al_2O_3 while concentration of free Na_2O_k is fixed. However, when concentration of Na_2O_k is fixed, $\omega(\text{Ti})$ decreases with the increase of concentration of Al_2O_3 . It may be explained that the concentration of free Na_2O_k decreases with the increase of concentration of Al_2O_3 in the alkaline aluminate solution. And it is the same case in Fig.3(b). The reason will be discussed later in detail.

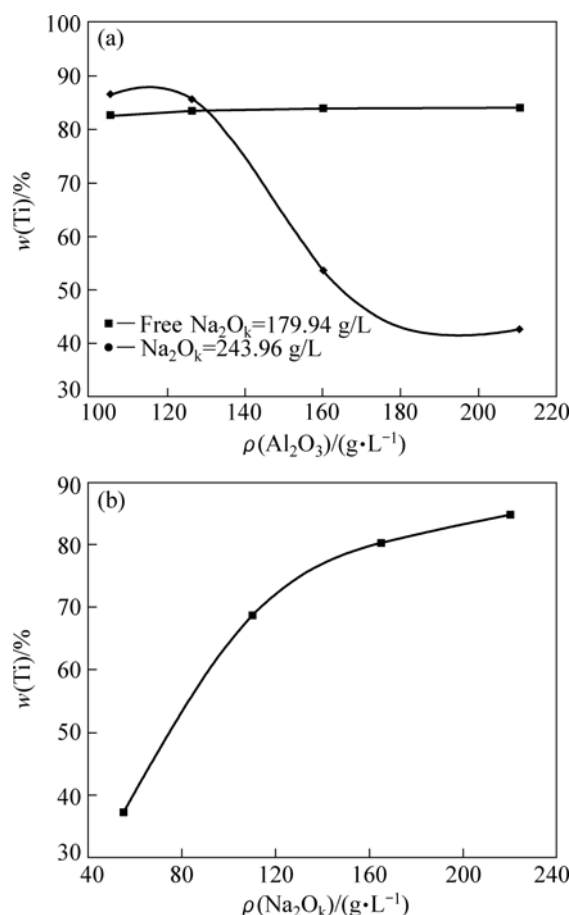


Fig.3 Influence of composition of sodium aluminate solution on $\omega(\text{Ti})$: (a) 180 °C, 30 min, $n(\text{CaO})/n(\text{TiO}_2)=1.0$; (b) $\rho(\text{Al}_2\text{O}_3)=183.01 \text{ g/L}$, 180 °C, 30 min, $n(\text{CaO})/n(\text{TiO}_2)=1.0$

3.3 Influence of molar ratio of CaO to TiO_2 on reaction behavior of anatase in sodium aluminate solution

During the high-pressure digestion process, Na_2TiO_3 isolates diasporite from caustic soda so as to inhibit digestion of alumina in the diasporic bauxite. Calcium aluminate hydrate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$) is rapidly produced once CaO is added to the aluminate solution, then other reactions may take place. As for the familiar compounds, $\text{CaO} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$ and CaTiO_3 , theoretical molar ratios of CaO to TiO_2 are 0.5 and 1.0. Research on the phase transformation of silicon-containing and titanium-containing minerals in high-pressure digestion proves that TiO_2 mainly converts into $\text{CaO} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$ when molar ratio of CaO to TiO_2 is less than 0.76, and that $\text{CaO} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$ becomes unstable and changes into more stable calcium-titanium compound gradually if more CaO is added[15–19].

Fig.4 indicates the relationship between $\omega(\text{Ti})$ and molar ratio of CaO to TiO_2 . $\omega(\text{Ti})$ increases with the increase of molar ratio of CaO to TiO_2 with relatively low concentration of free Na_2O_k , whereas $\omega(\text{Ti})$ first

increases and then decreases with the increase of molar ratio of CaO to TiO_2 under the condition of high concentration of free Na_2O_k . For example, $w(\text{Ti})$ decreases from 84.70% to 35.63% with molar ratio correspondingly ranging from 0.5 to 3.0 when concentration of free Na_2O_k is fixed at 220 g/L. Fig.5

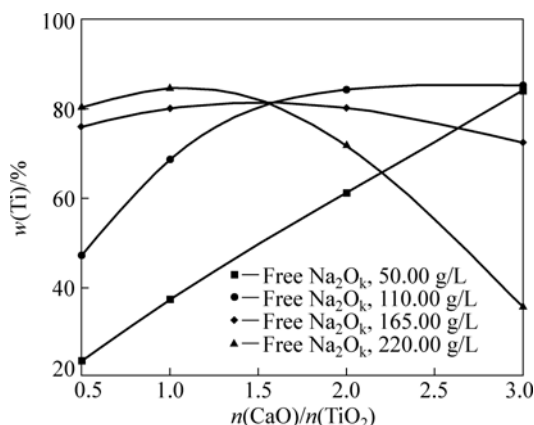


Fig.4 Influence of molar ratio of CaO to TiO_2 on $w(\text{Ti})$ ($\rho(\text{Al}_2\text{O}_3)=180.94$ g/L, 180°C for 30 min)

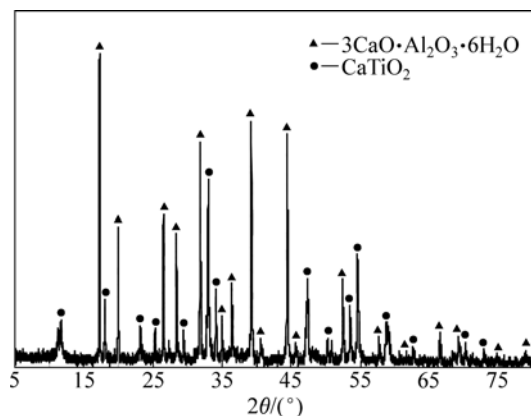


Fig.5 XRD pattern of residue prepared with high molar ratio of CaO to TiO_2 and high concentration of free Na_2O_k ($\rho(\text{Al}_2\text{O}_3)=180.94$ g/L, $n(\text{CaO})/n(\text{TiO}_2)=3.0$, $\rho(\text{free Na}_2\text{O}_k)=220$ g/L, 180°C , 30 min)

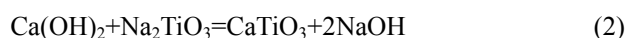
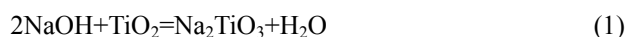
shows the XRD pattern of residue obtained under the following conditions: the molar ratio of CaO to TiO_2 is 3, and the concentration of free Na_2O_k is 220 g/L. It can be revealed that $\text{CaO} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$ changes into more stable CaTiO_3 which is hard to dissolve in hydrochloric acid.

3.4 Reaction mechanism of anatase in high-pressure digestion process

In order to explore the reaction laws and its mechanism of titanium-containing mineral during high-pressure digestion process of diasporic bauxite, digestion experiments of anatase in different solutions were carried out at 180°C for 60 min. Experimental results are listed in Table 1.

From results listed in Table 1 and the reaction behaviors of anatase discussed above, reaction mechanism of anatase in sodium aluminate solution during the high-pressure digestion process can be presumably determined as follows.

1) Neither soda (Na_2CO_3) nor $\text{Ca}(\text{OH})_2$ can react with anatase under the experimental conditions. However, anatase can react with NaOH to form Na_2TiO_3 which may further react with $\text{Ca}(\text{OH})_2$ to form CaTiO_3 if CaO is added to the system, as shown in reactions (1) and (2):

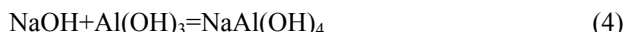
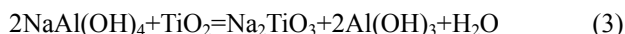


2) Aluminate anion seems to remarkably catalyze reactions of anatase with caustic soda solution. Results of experiment 3 and experiment 4 show that, under the almost same concentrations of free Na_2O_k (Na_2O_k 116.00 g/L), $w(\text{Ti})$ increases from 3.05% to 37.88% in the presence of aluminate anion without CaO, and $w(\text{Ti})$ also increases from 7.16% to 84.87% in the presence of aluminate anion when CaO is added with molar ratio of CaO to TiO_2 of 1. So, the conclusion can be drawn that aluminate anions plays catalysis role in the reaction process. The catalysis mechanism of aluminate anions

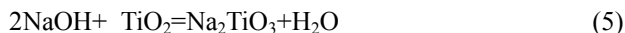
Table 1 Reaction behavior of anatase in different solutions

Experiment No.	Solution	Composition	Molar ratio of CaO to TiO_2	$w(\text{Ti})/\%$	Product in solid phase
1	Pure water		0	0	Anatase
			1	0	Anatase, $\text{Ca}(\text{OH})_2$
2	Sodium carbonate	$\rho(\text{Na}_2\text{O}_k)=117.31$ g/L	0	0	Anatase
			1	0	Anatase, CaCO_3
3	Caustic soda	$\rho(\text{Free Na}_2\text{O}_k)=115.95$ g/L	0	3.05	Anatase, Na_2TiO_3
			1	7.16	Anatase, CaTiO_3 , $\text{Ca}(\text{OH})_2$
4	Sodium aluminate	$\rho(\text{Na}_2\text{O}_k)=243.96$ g/L	0	37.88	Anatase, Na_2TiO_3
		$\rho(\text{Free Na}_2\text{O}_k)=116.00$ g/L	1	84.87	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, $\text{CaO} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$, CaTiO_3
		$\rho(\text{Al}_2\text{O}_3)=210.65$ g/L			
		$\rho(\text{Na}_2\text{O}_k)=329.98$ g/L			
		$\rho(\text{Free Na}_2\text{O}_k)=220.00$ g/L	3	35.63	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, CaTiO_3
		$\rho(\text{Al}_2\text{O}_3)=180.94$ g/L			

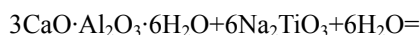
could be explained as follows:



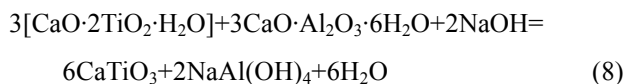
The total reaction can be expressed as



3) Hydroxy calcium titanate ($\text{CaO} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$) is the product of reaction of Na_2TiO_3 with calcium aluminate hydrate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$) resulting from the reaction of CaO added with sodium aluminate solution, as shown in chemical reactions (6) and (7):



Calcium titanate (CaTiO_3) may be formed from two ways. One is from reaction of Na_2TiO_3 and $\text{Ca}(\text{OH})_2$, and the other is from reaction of $\text{CaO} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$ with $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ and NaOH , as shown in chemical reaction (8):



According to the theoretical calculation, reaction (8) may take place only if molar ratio of CaO to TiO_2 is more than 0.5. Result from experiment 4 in Table 1 also indicates that more $\text{CaO} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$ converts into CaTiO_3 , which results in the decrease of $\omega(\text{Ti})$, if molar ratio of CaO to TiO_2 is 3. From the discussion mentioned above, conclusion can be made that elevating the digestion temperature, prolonging the duration time, increasing concentration of free Na_2O_k and molar ratio of CaO to TiO_2 favor the conversion of $\text{CaO} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$ to CaTiO_3 .

4 Conclusions

1) In sodium aluminate solution, aluminate anion has a catalysis function for reaction of anatase with caustic soda.

2) During high-pressure digestion process of diasporic bauxite, the reaction degree of anatase depends on the concentration of free Na_2O_k rather than the concentration of Al_2O_3 , so long as there is aluminate anions in alkali solution.

3) Anatase first reacts with free Na_2O_k to form Na_2TiO_3 which further reacts with $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ to produce $\text{CaO} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$, and $\text{CaO} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$ eventually changes into CaTiO_3 . Moreover, higher temperature, longer time, higher concentration of free Na_2O_k and molar ratio of CaO to TiO_2 all favor the conversion of $\text{CaO} \cdot 2\text{TiO}_2 \cdot \text{H}_2\text{O}$ to CaTiO_3 .

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