



Crystallization of gibbsite from synthetic chromate leaching solution in sub-molten salt process

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Abstract: For the clean and economical production of chromium compounds, it is crucial to remove aluminates from chromate alkali solutions and utilize aluminum-containing compounds. In this work, carbonization was used to remove aluminates from a synthetic chromate leaching solution containing a high K_2O/Al_2O_3 mole ratio. The influence of reaction temperature, carbonization time, flow rate of carbon dioxide, and seed ratio on the precipitation of Al was investigated. The optimal output was obtained under the following experimental conditions: a reaction temperature of 50 °C, a carbonization time of 100 min, a carbon dioxide flow rate of 0.1 L/min, and a seed ratio of 1.0. Gibbsite was obtained following carbonization. The structure and morphology of the gibbsite were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and laser particle size analyzer. The particle size distribution and morphology of the gibbsite were significantly influenced by the experimental conditions. The gibbsite had a mean particle size (d_{50}) of 16.72 μm . The thermal decomposition of the gibbsite was analyzed by XRD and the decomposition path was determined. The obtained coarse $\alpha\text{-Al}_2\text{O}_3$ precipitate, which contains 0.08% Cr_2O_3 and 0.10% K_2O , was suitable for subsequent utilization.

Key words: gibbsite; secondary nucleation; carbonization; chromate leaching solution

1 Introduction

Chromium-containing compounds have attracted considerable interest owing to their diverse applications. The conventional process used to produce chromium compounds, namely the lime free roasting process, which uses molten sodium carbonate to treat chromite ore, causes serious pollution [1,2]. Recently, a sub-molten salt process to treat chromite ore for chromate production was developed by the Institute of Process Engineering, Chinese Academy of Sciences [3]. This process eliminates pollution and yields an improved chromium recovery. In the sub-molten salt process, NaOH and KOH are used as the raw materials. However, KOH system is deemed more suitable to treat as it offers several advantages over the NaOH system. The process using the KOH system can be operated at 320 °C compared with 500 °C in the case of the NaOH system,

enabling energy savings. Moreover, at high alkali concentrations, it is easier to separate most Al from the $K_2O\text{-}Al_2O_3$ system (KS) compared with that from the $Na_2O\text{-}Al_2O_3$ system (NS) [4,5]. However, some aluminates remain in the KS system, which influence the quality of the chromium product. Therefore, the removal of aluminates from the chromate leaching solution is crucial in the production of chromium compounds.

Accordingly, many methods have been utilized to precipitate Al from the chromate leaching solution obtained from the lime free roasting process. For example, silica-containing compounds are often added to remove Al. Specifically, the Allied Chemical Corporation removed Al using a soluble-silica compound [6], by employing an easy and feasible process. However, the filtration of products is somewhat difficult because of the high viscosity of the silica-containing compounds. Moreover, chromium-containing slag is produced during the operation, causing

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environmental pollution. In other methods, Al is precipitated by changing the pH of the solution. The Allied Chemical Corporation precipitated Al through acidification of the chromate solution by adding dichromate [7]. Nevertheless, this is a time-consuming method. LI et al [8–10] used NaHCO_3 to change the pH of the sodium aluminate solution, which resulted in the precipitation of $\text{Al}(\text{OH})_3$. In all the aforementioned methods, Al was precipitated from the NS.

There are many differences between the chromate leaching solution KS and NS. According to alumina industry terminologies, the caustic and aluminum concentrations in the chromate solution are expressed as grams of M_2O (M: Na or K) per liter and grams of Al_2O_3 per liter, respectively. The first and the most important difference is the concentration of alkali carbonate and hydroxide species. The concentration of Na_2O in NS is 8–20 g/L, whereas, the concentration of K_2O in KS is about 77.2 g/L. The caustic of KS is higher than that of NS. The composition of the chromate solution, such as the concentration of alkali, affects the precipitation of Al and the morphology of $\text{Al}(\text{OH})_3$ [11,12]. The second difference is the $\text{M}_2\text{O}/\text{Al}_2\text{O}_3$ (M: Na or K) mole ratio in the solutions. The Al concentration in NS (~ 8 g/L) is lower than that in KS (~ 17 g/L). A high $\text{M}_2\text{O}/\text{Al}_2\text{O}_3$ mole ratio makes the precipitation of $\text{Al}(\text{OH})_3$ difficult [13]; therefore, it is more difficult to precipitate $\text{Al}(\text{OH})_3$ from KS containing a high $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio than from NS. Another difference is the variety of alkali metal ions utilized, which play a pivotal role in the precipitation of Al [14,15]. LI et al [14] observed that compared with K^+ ions, Na^+ ions provide greater stability for the formation and densification of Al^{3+} -containing, supramolecular clusters that grow more rapidly into $\text{Al}(\text{OH})_3$ crystallites. Therefore, it is important to investigate the precipitation of Al from KS.

CO_2 reutilization is a promising option for decreasing CO_2 emission and hence preventing environmental pollution [16,17]. In order to separate aluminates from chromate leaching solution in the sub-molten salt process and to reduce CO_2 emission, a high efficiency method that uses CO_2 to change the pH of the solution for Al precipitation, namely carbonization, was proposed by our research group. In this study, the effects of reaction temperature, carbonization time, flow rate of carbon dioxide, and seed ratio (the mass ratio of Al_2O_3 in the seed to Al_2O_3 in the solution) on the precipitation of Al from synthetic chromate leaching solution containing a high $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio were investigated. Cluster gibbsite with a narrow particle size distribution was obtained by optimizing the reaction conditions. The thermal decomposition of the gibbsite to Al_2O_3 was also studied.

2 Experimental

2.1 Chemicals

$\text{Al}(\text{OH})_3$, KOH, K_2CO_3 , and K_2CrO_4 were analytical reagent grade (Guangdong Xilong Chemical Co., Ltd., China). Carbon dioxide (99.99%) was obtained from the Sinopharm Chemical Reagent Beijing Co., Ltd., China. Super-purified water from a Millipore Milli-Q machine was used in the content analysis. The chromate leaching solution was synthesized according to the solution for industry production; the concentrations of the components are listed in Table 1. To prepare the synthetic chromate leaching solution, a known mass of KOH was first dissolved in Milli-Q water in a 1 L caustic-resistant polytetrafluoroethylene vessel, followed by slow addition of a known mass of aluminum hydroxide. After complete dissolution, the solution was filtered twice through a caustic-resistant 0.22 μm Teflon membrane. Known masses of potassium chromate and potassium carbonate were dissolved in the solution according to Table 1, which was stored in a Teflon bottle.

Table 1 Composition of chromate leaching solution

Component	Concentration/($\text{g}\cdot\text{L}^{-1}$)
Al_2O_3	80
K_2CrO_4	78
K_2CO_3	200
KOH	17

2.2 Experiments

The experiments were performed in a three-necked flask with a glass lid having the necessary openings for a mechanical stirrer, a Pt thermocouple and a pH electrode.

0.25 L of the synthetic chromate leaching solution was stirred with seed crystals in the reactor. The flask was placed in a heated oil bath, and the temperature of the bath was monitored by a thermometer dipped into the oil. The slurry was mechanically stirred at 150 r/min using Teflon-coated paddles to ensure that the slurry was sufficiently suspended. After the slurry reached the desired temperature, a mixture of N_2 and CO_2 was bubbled at various flow rates, and then, the required experiments were performed. The CO_2 volume fraction was fixed at 25%. The flow rate was measured and controlled by a rotary flow meter.

After carbonization, the slurry was filtered through a Buchner funnel, and the filter cake was washed with deionized water for 30 min at 90 °C. The filtrate and precipitate were separately collected and analyzed to determine the precipitation of Al from the synthetic chromate leaching solution.

The dried precipitates were calcined in a corundum

crucible in an oxidizing atmosphere in a programmed electric furnace for 2 h at the maximum temperature, from 200 °C to 1300 °C.

2.3 Analytical procedures

The residual concentration of Al in the filtrate was analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 5300DV, Perkin Elmer). The precipitation of Al was calculated as follows:

$$Y=(1-c_rV_r/c_iV_i)\times 100\% \quad (1)$$

where c_i and c_r are the initial and residual concentrations of Al, respectively. V_i and V_r are the initial and residual volumes of the solution, respectively.

The elemental contents of the solids were measured by fusion with fluxes, dissolution in HCl and analysis of diluted solution using ICP-OES. The impurity content was calculated as follows:

$$X=(cV/m)\times 100\% \quad (2)$$

where X is the impurity content, c is the concentration of impurities in the diluted solution, V is the volume of diluted solution, and m is the mass of the precipitates.

2.4 Characterization

The particle size distributions (PSD) of the dried precipitates were measured by a Malvern Mastersizer Hydro 2000MU instrument, with water as the dispersion agent. The morphologies of the precipitates were observed by scanning electron microscopy (SEM, JSM-7001F+INCA X-MAX). For surface morphology observations by SEM, the precipitates obtained from the experiments were sputter-coated with carbon. Phase identification was performed by comparing the powder diffraction patterns of the precipitates using X-ray diffractometer (XRD, X'Pert Pro MPD, Panalytical Co.; 40 kV, 30 mA) with Cu K_{α} radiation.

3 Results and discussion

3.1 Precipitation of $\text{Al}(\text{OH})_3$

3.1.1 Effect of carbonization time

The effect of time on the precipitation of Al from the synthetic chromate leaching solution was investigated at a CO_2 flow rate of 0.1 L/min, a carbonization temperature of 50 °C, and a seed ratio of 1.0 (Fig. 1). The precipitation of Al increased from 17.84% to 95.12% when the carbonization time increased from 80 min to 100 min, demonstrating fast precipitation kinetics. The effect of carbonization time on Al precipitation became less pronounced beyond 100 min, and a further increase in the carbonization time did not enhance precipitation. Therefore, the carbonization time of 100 min was considered to be optimal and used in the subsequent experiments to

minimize energy consumption. The concentration of Al in the solution decreased to 0.43 g/L, which met the industry requirements for the production of high-quality chromium compounds [18]. The precipitates obtained from the synthetic chromate leaching solution after 100 min of carbonization were gibbsite, as determined by XRD (Fig. 2). The Cr_2O_3 and K_2O contents in the

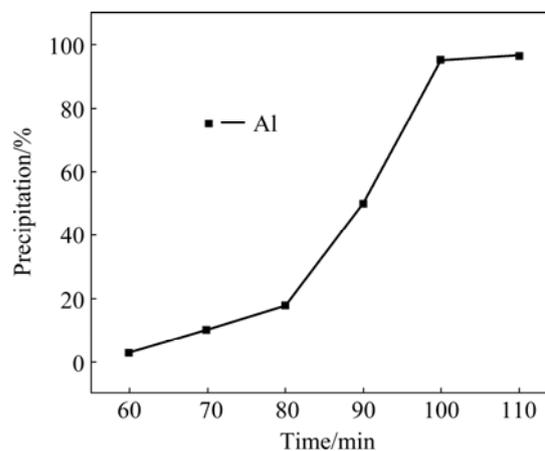


Fig. 1 Effect of time on precipitation of Al

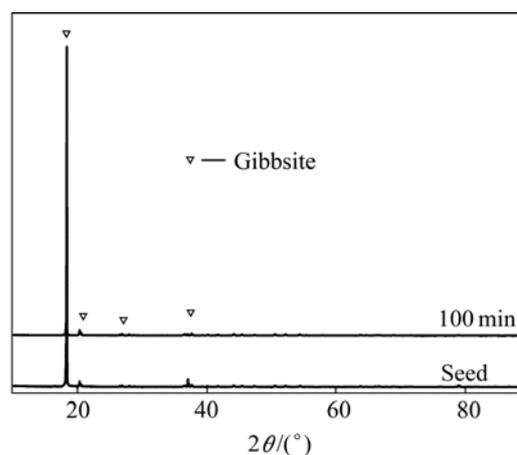


Fig. 2 XRD patterns of seed and precipitates

gibbsite were determined to be 0.05% and 0.06%, respectively.

The unimodal particle size distribution (PSD) of the seed crystals (median particle size (d_{50}) of 13.67 μm) is shown in Fig. 3. In contrast, the precipitates obtained from the synthetic chromate leaching solution after 80 min of carbonization exhibited a bimodal PSD. This was possibly due to attrition from the parent crystals owing to mechanical contact and fluid shearing. The findings indicate that 0.2–1 μm crystals were produced as a result of secondary nucleation during crystallization. The percent of total crystals in the 2–5 μm particle size range decreased as the carbonization time increased, suggesting the agglomeration of these crystals with larger crystals. The d_{50} value increased and the PSD curve narrowed as the carbonization time increased from

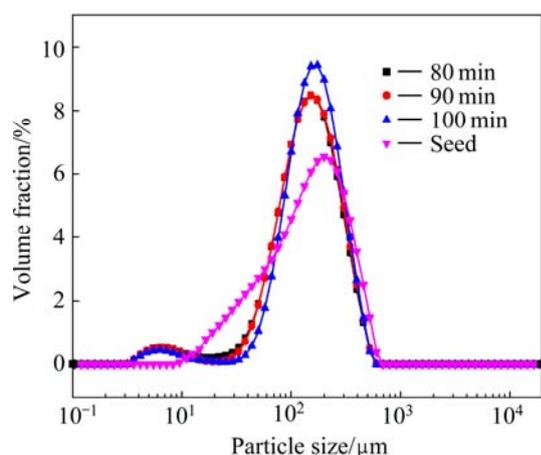


Fig. 3 PSDs of precipitates obtained for different carbonization time

80 to 100 min, as shown in Fig. 3, demonstrating the growth of the crystals.

SEM images of the precipitates (Fig. 4) revealed the existence of different developmental stages in the formation of new crystal surface layers in the synthetic chromate leaching solution during carbonization. The surface of the seed crystals (Fig. 4(a)) became rough shortly after contacting the liquor, as depicted in Fig. 4(b). After 70 min of crystallization, several microscopic protrusions (potential secondary nuclei) were apparent on the surfaces of the seed crystals (Fig. 4(c)). The random formation of protrusions as a result of crystal growth appeared to be consistent with the surface nucleation mechanism [19]. Large numbers of discrete hexagonal particles were found attached to the parent seed grown in the synthetic chromate leaching

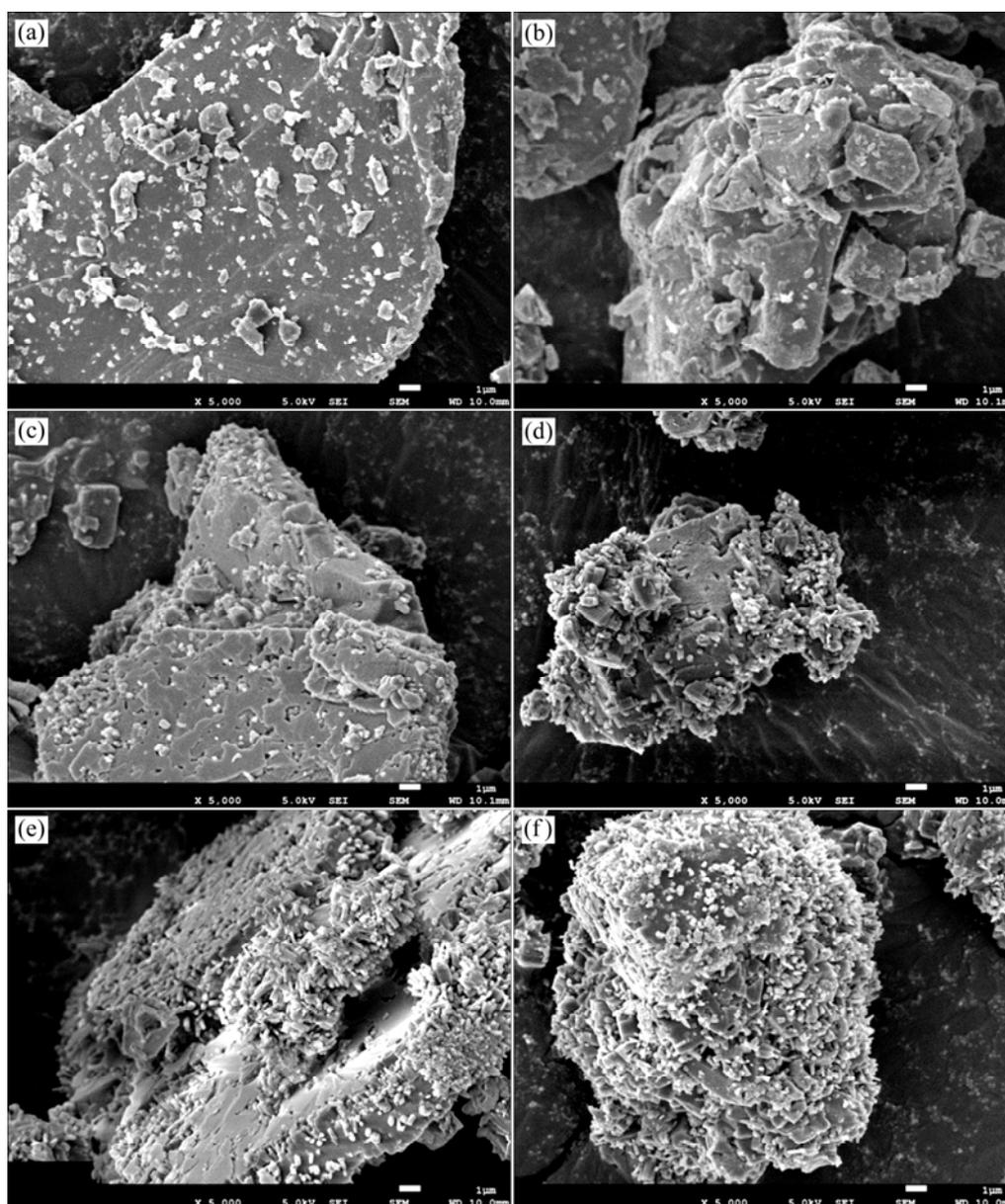


Fig. 4 SEM images of precipitates during carbonization at 0 min (a), 60 min (b), 70 min (c), 80 min (d), 90 min (e), and 100 min (f)

solution at 80 min (Fig. 4(d)). After 90 min (Fig. 4(e)), the texture of the precipitates seemed to be coarser compared with that after 70 min. The seed surfaces were covered by the hexagonal particles at 100 min (Fig. 4(f)). Figure 4 also shows that the small particles adhered instantly on the surface of the large particles following a collision between them, thus demonstrating the agglomeration of the crystals. The growth of the protrusions and the agglomeration of the seed caused the growth of the particles. The different concentrations of alkali aluminate possibly led to the difference in the d_{50} values and morphology of the particles compared with those reported in the literatures [8–10]. Because of the low concentration of the potassium aluminate in the synthetic chromate leaching solution, there is not sufficient Al to promote the growth of gibbsite crystals at the late carbonization stage. However, in the leaching solution containing a high concentration of sodium aluminate, continuous agglomeration led to coarse particles.

3.1.2 Effect of temperature

The effect of temperature on the precipitation of Al from the synthetic chromate leaching solution was investigated at a CO_2 flow rate of 0.1 L/min, a carbonization time of 100 min, and a seed ratio of 1.0

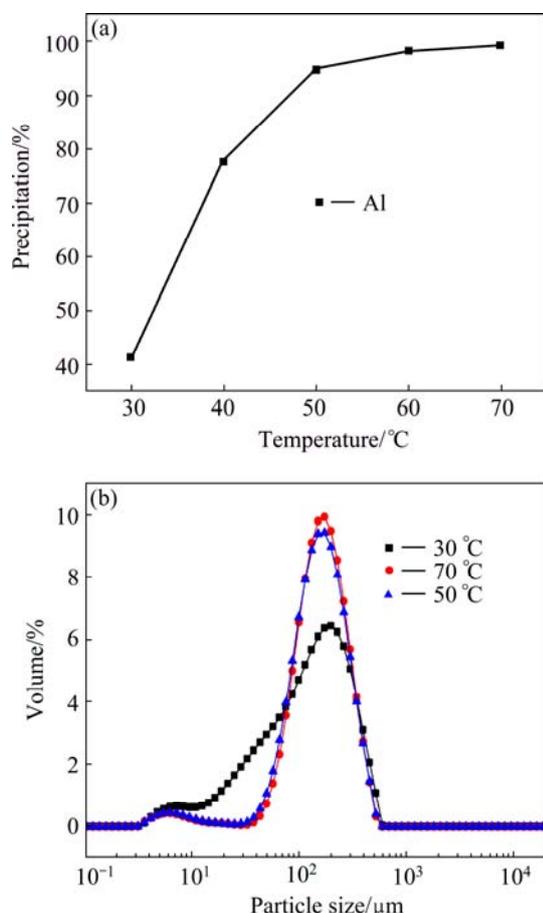


Fig. 5 Effect of temperature on precipitation of Al (a) and PSDs of precipitates prepared at different temperatures (b)

(Fig. 5(a)). Increasing temperature enhanced the precipitation of Al from the chromate leaching solution (Fig. 5(a)). The precipitation of Al was approximately 41.28% at 30 °C for 100 min, while it was approximately 95.12% at 50 °C under the same conditions. The reaction rate increased with increasing temperature, leading to greater precipitation of Al.

The bimodal PSDs of the precipitates indicate that secondary nucleation occurred at different temperatures. CHEN [15] and GAO [20] have investigated the effect of temperature on the particle size of precipitate, which indicated that the degree of agglomeration increased with increasing the temperature [15,20]. WEI et al [21] observed a similar trend in the temperature range of 50–70 °C [21]. The percent of total crystals in the 2–5 μm range changed slightly at 30 °C, possibly because of a low degree of agglomeration. The d_{50} increased and the PSD curve narrowed significantly as the temperature was increased from 30 to 70 °C, as shown in Fig. 5(b).

The plate gibbsite particles precipitated at 30 °C (Fig. 6(a)) and a number of small particles were observed on the seed crystal surfaces. However, the particles formed at 50 °C and 70 °C (Fig. 4(f), Fig. 6(b)) were lamellar crystals covered by small particles. This supports the agglomeration of gibbsite precipitates in the system. The collision and surface integration rates increase with temperature, and particles can be incorporated more quickly into the growing agglomerate at higher temperatures.

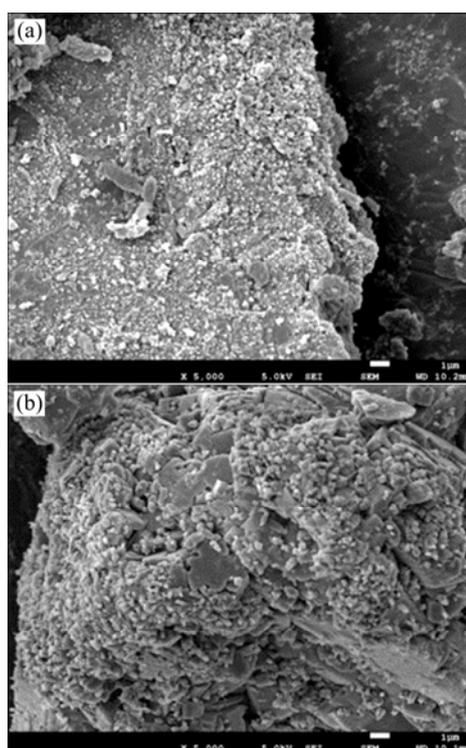


Fig. 6 SEM images of precipitates after carbonization at 30 °C (a) and 70 °C (b)

3.1.3 Effect of seed ratio

The influence of the seed ratio in the range from 0 to 1.0 on the precipitation of Al was investigated with a seed median particle size below 14 μm (Fig. 7). The precipitation of Al increased from 52.26% to 95.12% with 100 min of carbonization time. The precipitates obtained using the seed ratio of 0 were confirmed to be bayerite (Fig. 8). At a seed ratio of 0.4, the constituent of the precipitate was identified to be gibbsite from the XRD pattern, thus confirming that the seeds facilitate the formation of gibbsite from $\text{Al}(\text{OH})_4^-$ but not bayerite.

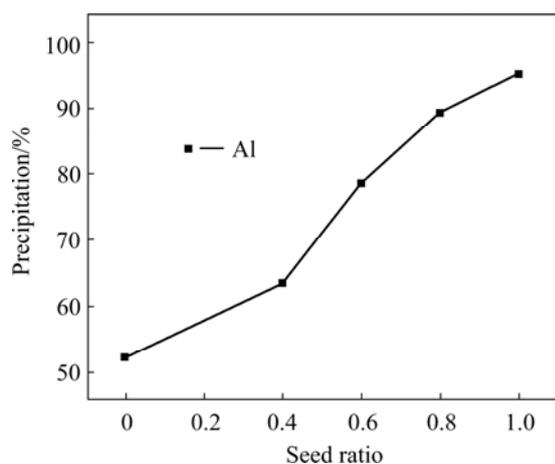


Fig. 7 Effect of seed ratio on precipitation of Al

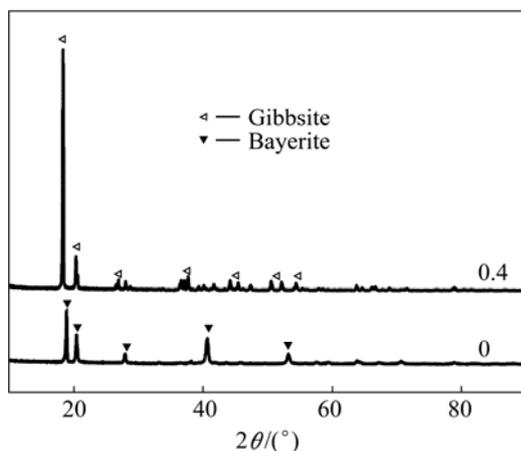


Fig. 8 XRD patterns of precipitates after carbonization at seed ratios of 0.4 and 0

The d_{50} (25.47 μm) of bayerite was larger than that of gibbsite (14.43 μm) obtained with the seed ratio of 0.4 (Fig. 9). Figure 9 also shows that d_{50} increased from 14.43 μm to 16.72 μm as the seed ratio was increased from 0.4 to 1.0.

As seen in Fig. 10(a), conical frustum-shaped bayerite particles were obtained from the synthetic chromate alkali solutions at a seed ratio of 0. A large number of frustums were connected by their edges and consisted of several thin plates. This was quite different from the preparation of bayerite using NaHCO_3 to

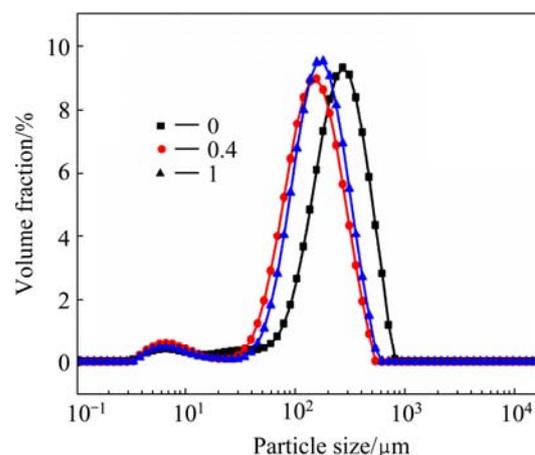


Fig. 9 PSDs of precipitates prepared at different seed ratios

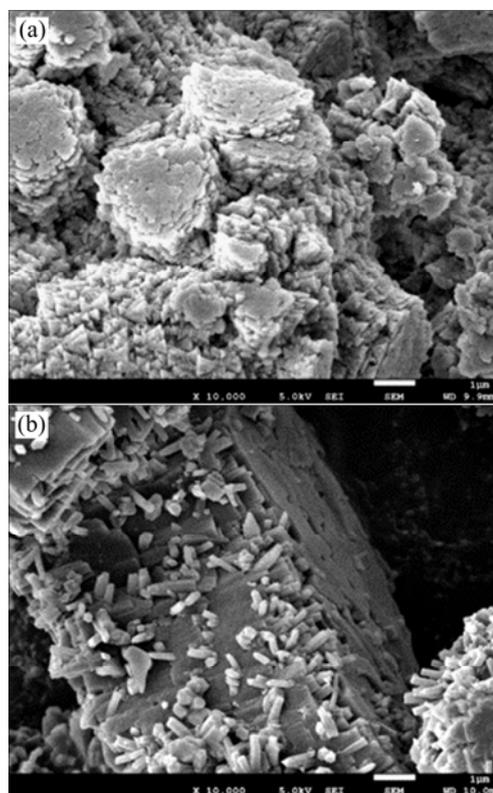


Fig. 10 SEM images of precipitates after carbonization at seed ratio of 0 (a) and 0.4 (b)

neutralize aluminate solution, where spherical bayerite was obtained [9]. Fewer hexagonal particles (Fig. 10(b)) were attached to the seed at the seed ratio of 0.4, as compared to that at the seed ratio of 1.0 (Fig. 4(f)). The decreased precipitation Al led to the smaller d_{50} and incomplete growth of the particles.

3.1.4 Effect of CO_2 flow rate

Given the theoretical flow rate of CO_2 is 0.086 L/min, we investigated the precipitation of Al as a function of CO_2 flow rate in the range from 0.04 L/min to 0.1 L/min, as shown in Fig. 11(a). The precipitation of Al was favored at high CO_2 flow rates. The precipitation

of Al was approximately 2.12% at the CO₂ flow rate of 0.04 L/min with a carbonization time of 100 min. It reached approximately 97.35% at the CO₂ flow rate of 0.12 mL/min under the same conditions.

The crystal growth was attributed to the decrease of pH due to the continuous bubbling of CO₂ into the solution with increasing carbonization time. The PSD of the gibbsite particles was very sensitive to the flow rate of CO₂, as shown in Fig. 11(b). Faster flow rates led to narrower PSD curves of the gibbsite particles and larger d_{50} values. The SEM results (Fig. 12) showed that several microscopic protrusions were present on the surfaces of the seed crystals at the CO₂ flow rate of 0.04 L/min. When the CO₂ flow rate was increased to 0.1 L/min (Fig. 4(f)), many hexagonal particles agglomerated on the seed. The morphology of the gibbsite changed slightly as the CO₂ flow rate was increased from 0.1 L/min to 0.12 L/min (Fig. 4(f), Fig. 12(c)).

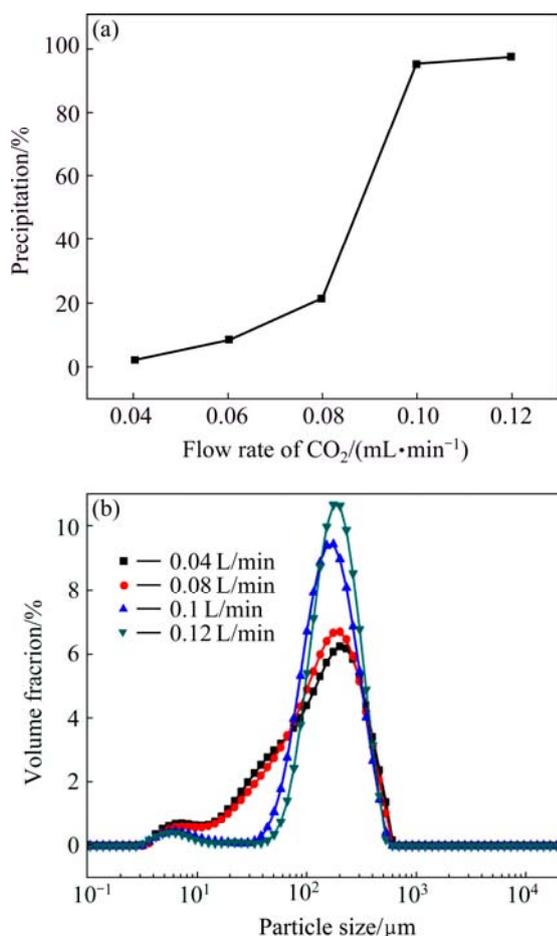


Fig. 11 Effect of flow rate of CO₂ on precipitation of Al (a) and PSDs of precipitates prepared at different flow rates of CO₂ (b)

3.1.5 Effect of K₂CrO₄ concentration

The influence of the K₂CrO₄ concentration on the precipitation of Al was investigated from 0 to 200 g/L at

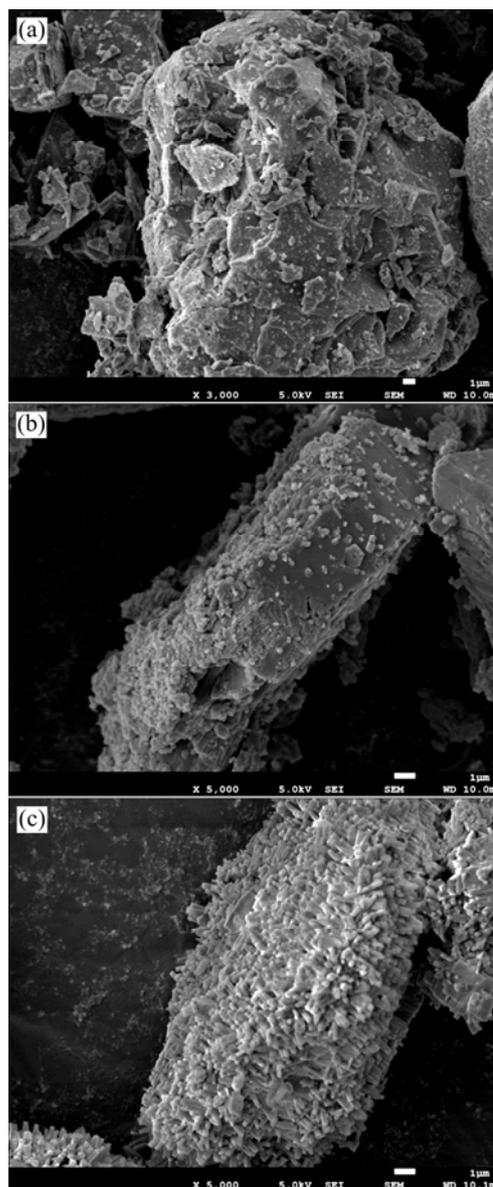


Fig. 12 SEM images of precipitates after carbonization at flow rates of CO₂ of 0.04 L/min (a), 0.08 L/min (b) and 0.12 L/min (c)

a carbonization time of 100 min, a carbonization temperature of 50 °C, a seed ratio of 1.0, and a CO₂ flow rate of 0.1 L/min (Fig. 13(a)). The precipitation of Al decreased from 98.89% to 95.12% as the K₂CrO₄ concentration was increased from 0 to 200 g/L. This may be caused by the longer induction period in the chromate leaching solution compared with that in potassium aluminate [21].

The d_{50} of the gibbsite particles increased with the increase of K₂CrO₄ concentration, as shown in Fig. 13(b). The supersaturation of KAIO₂ decreased with the increase of K₂CrO₄ concentration [21]. Therefore, at a high K₂CrO₄ concentration, the degree of supersaturation of KAIO₂ was low, which resulted in the formation of

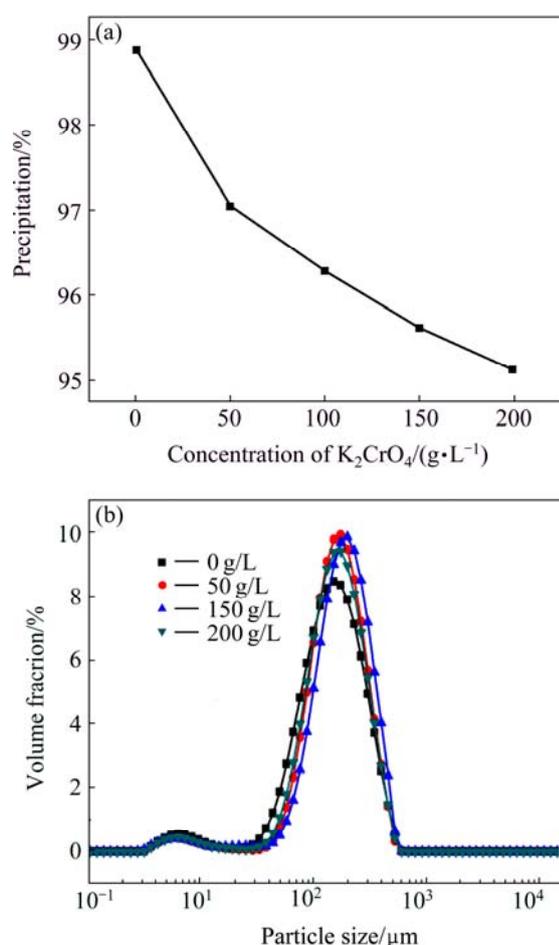


Fig. 13 Effect of K_2CrO_4 concentration on precipitation of Al (a) and PSDs of precipitates prepared at different K_2CrO_4 concentrations (b)

larger particles. However, because of low concentration of Al and the approximate precipitation of Al, the PSD curves and d_{50} values of the gibbsite particles obtained at different K_2CrO_4 concentrations were similar. As can be seen in Fig. 14, the morphology of the particles was also affected slightly by K_2CrO_4 concentration.

In summary, the optimum carbonization conditions were as follows: a carbonization time of 100 min, a carbonization temperature of 50 °C, a seed ratio of 1.0, and a CO_2 flow rate of 0.1 L/min. The precipitation of Al reached 95.12% under these conditions. Most of Al was removed from the synthetic chromate leaching solution in the sub-molten salt process.

3.2 Thermal decomposition

Thermal decomposition of the gibbsite particles prepared from the carbonization of the synthetic chromate leaching solution was carried out. Following the heat treatment of the gibbsite particles, the phases were characterized by XRD. The XRD patterns of the calcined samples are shown in Fig. 15(a). Upon

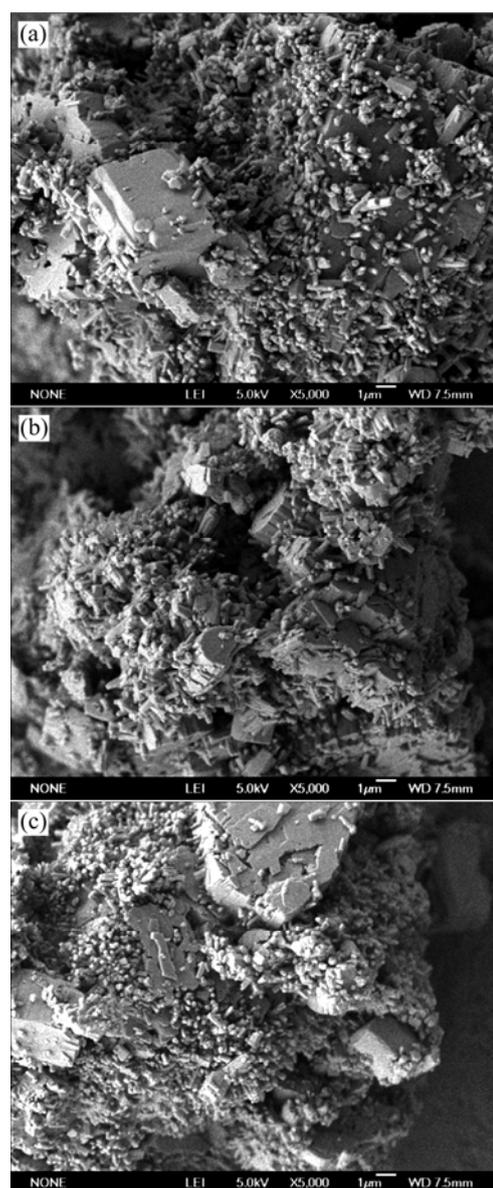


Fig. 14 SEM images of precipitates after carbonization at K_2CrO_4 concentrations of 0 g/L (a), 50 g/L and (b) 150 g/L (c)

calcination of the samples at 200 °C, the gibbsite peaks were maintained and peaks corresponding to $AlOOH$ appeared. Upon calcination at 300 °C, the $AlOOH$ peaks were retained, while the peaks corresponding to gibbsite disappeared. The XRD patterns suggested that $\gamma-Al_2O_3$ was the main phase at 500 °C. Calcination of the samples at 700 °C did not alter the position or intensity of the $\gamma-Al_2O_3$ peaks. After calcination at 1000 °C, the peaks attributed to $\gamma-Al_2O_3$ disappeared and those attributed to $\theta-Al_2O_3$ appeared; these peaks did not shift, but became narrower with increasing calcination temperature. The narrowing of the XRD peaks was attributed to an increase in the crystallite fraction, which was directly related to the increase in particle size. The XRD patterns showed that $\theta-Al_2O_3$ and $\alpha-Al_2O_3$ were the main phases

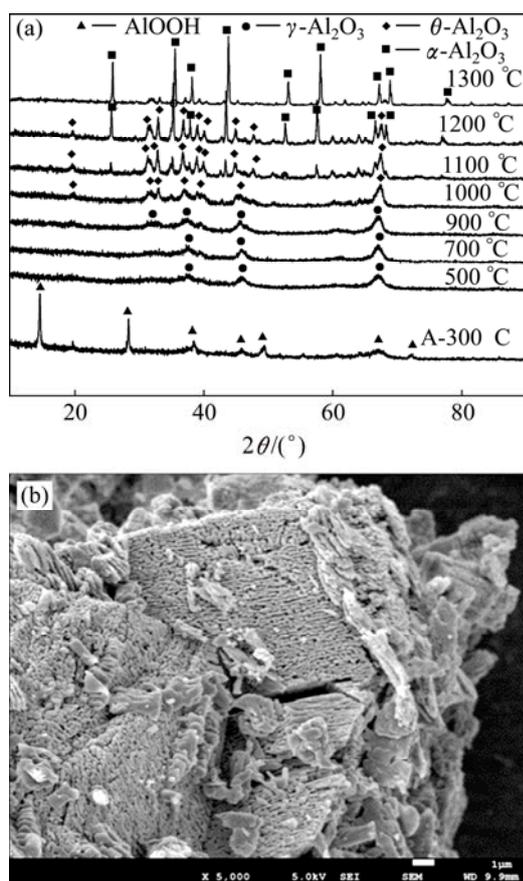


Fig. 15 XRD patterns of gibbsite samples calcined at various temperatures for 2 h (a) and SEM image of α - Al_2O_3 crystals (b)

of the samples calcined at 1200 °C. Upon calcination of the samples calcined at 1300 °C, θ - Al_2O_3 was converted to α - Al_2O_3 . The phase analysis revealed the decomposition path of the gibbsite particles. The thermodynamically stable form of aluminum oxide was formed via the metastable form according to the following sequence: gibbsite \rightarrow boehmite \rightarrow γ - Al_2O_3 \rightarrow δ - Al_2O_3 \rightarrow θ - Al_2O_3 \rightarrow α - Al_2O_3 . The XRD results agree with those reported in Ref. [9] for the calcination of bayerite at different temperatures. Lamellar α - Al_2O_3 was obtained after calcination at 1300 °C, as shown in Fig. 15(b). The Cr_2O_3 and K_2O contents in α - Al_2O_3 were 0.08% and 0.10%, respectively.

4 Conclusions

1) The optimal conditions for $\text{Al}(\text{OH})_3$ precipitation from synthetic chromate leaching solution by carbonization were investigated. The precipitation of $\text{Al}(\text{OH})_3$ reached 95.12% at a reaction temperature of 50 °C, a carbonization time of 100 min, a CO_2 flow rate of 0.1 L/min, and a seed ratio of 1.0. After carbonization, the concentration of Al in the chromate leaching solution met the industrial requirements.

2) Cluster gibbsite was obtained from the synthetic

chromate leaching solution in the sub-molten salt process. The mean particle size of gibbsite was 16.72 μm under the optimized conditions.

3) Lamellar α - Al_2O_3 was obtained after calcination at 1300 °C. The thermal decomposition of gibbsite to α - Al_2O_3 was identified in this work, and it occurred via the following sequence: β - $\text{Al}(\text{OH})_3$ \rightarrow AlOOH \rightarrow γ - Al_2O_3 \rightarrow θ - Al_2O_3 \rightarrow α - Al_2O_3 .

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亚熔盐法铬酸盐模拟浸出液中三水铝石的结晶行为

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摘要: 除去铬酸钾溶液中的铝并实现铝化合物的再利用是实现清洁、经济地生产铬盐的关键步骤。采用碳分的方法从配制的高 $\text{K}_2\text{O}/\text{Al}$ 摩尔比铬酸钾溶液中去铝。考察反应温度、碳分时间、 CO_2 流量、晶种系数对铝沉淀率的影响。优化反应条件为: 反应温度为 $50\text{ }^\circ\text{C}$, 碳分时间为 100 min , CO_2 流量为 0.1 L/min , 晶种系数为 1.0 。碳分产物为三水铝石。采用 X 射线衍射仪、扫描电镜和激光粒度仪对产物的结构和形貌进行表征。实验结果表明, 产物的粒度和形貌受实验条件影响明显。产物的平均粒径为 $16.72\text{ }\mu\text{m}$ 。对三水铝石的热分解路径进行研究。产物 $\alpha\text{-Al}_2\text{O}_3$ 含少量杂质($0.08\%\text{ Cr}_2\text{O}_3$ 和 $0.10\%\text{ K}_2\text{O}$), 适于后续利用。

关键词: 三水铝石; 二次成核; 碳分; 铬酸钾溶液

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