

S^{2-} behaviors analysis in leaching SrS and precipitating high purity $SrCO_3$ by reduction-decomposition process^①

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Abstract: A new preparation method (reduction-decomposition process) for high purity $SrCO_3$ was investigated, which mainly includes four processes: reduction, leaching, purification and precipitation. The affecting factors about S^{2-} behaviors in leaching process and the effects of variables on purity and particle sizes distribution of $SrCO_3$ were analyzed theoretically and practically. It is concluded that with the increase of temperature or decrease of pH value in leaching process, the strontium recovery increases, but SrS decomposes and hydrogen sulphide (H_2S) gas discharges. The purity of $SrCO_3$ is dependent on dissolution-recrystallization times, for example, the purity of $SrCO_3$ is as high as 99.97% when it is recrystallized three times. Besides, the solution concentration of $Sr(OH)_2$ and flow rate of CO_2 have important effects on particle size distribution of $SrCO_3$ particles, especially, the particle sizes of $SrCO_3$ mainly distribute in 0.1 - 1.0 μm when the flow rate of CO_2 is about 2 000 mL/min and other parameters are invariable.

Key words: strontium carbonate; high purity; reduction-decomposition process; behavior analysis

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1 INTRODUCTION

Strontium compounds, especially, strontium carbonate ($SrCO_3$), are important industrial reagents. $SrCO_3$ (technical grade > 95.0%) has two main commercial applications: (1) as an additive for producing glass for color television tubes, computer display, industrial monitors, etc; (2) as a constituent of ferrite magnets for small DC motor. Other applications of $SrCO_3$ are in production of iridescent and special glasses, pigment, paints, strontium metal, etc^[1-4]. In recent years, with the development of science and technology, the demand of high purity $SrCO_3$ (> 99.0%) is increasing greatly in many fields such as a constituent of PTC thermal resistor in electronic industry^[5-8], strontium ferrite magnets with high properties^[9, 10], strontium superconducting tapes^[11], strontium sensor^[12], strontium electrode materials^[13], chemical reagent for analysis.

Technical grade $SrCO_3$ (> 95.0%) is mainly produced by double-decomposition process, by reductive process, known as the black ash process for celestite ore (main $SrSO_4$), or by decomposition process for strontianite ore (main $SrCO_3$). As for high purity $SrCO_3$ (> 99.0%), most of it is produced with technical grade $SrCO_3$ by purifying. One process is that

the technical grade $SrCO_3$ is first dissolved in chlorhydric acid (HCl) or nitric acid (HNO_3), then purified through chemical process, and then precipitated by sodium carbonate, ammonium carbonate or ammonium bicarbonate to produce high purity $SrCO_3$ ^[5-7]. Another process is that the technical grade $SrCO_3$ is boasted at 1 250 °C to produce SrO, which dissolves in hot water to form $Sr(OH)_2$ solution, then $Sr(OH)_2$ is purified by dissolution-recrystallization process (physical method) and carbonated with CO_2 which is produced in boasting process^[8, 14, 15].

However, the existing production flow for producing high purity $SrCO_3$ is too complicated and consumes a series of chemical products (HCl, HNO_3 , sulphate, etc), which causes high production cost and environmental pollution. Accordingly, manufacturing process for high purity $SrCO_3$ with low cost should be investigated, which can decrease production cost and environmental pollution.

A new preparation method for high purity $SrCO_3$, known as "Reduction-decomposition process", has been studied. The leaching process, purification process and precipitation process are mainly discussed. The S^{2-} behaviors in leaching SrS and the particle size distribution of $SrCO_3$ are also analyzed.

2 EXPERIMENTAL

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2.1 Preparing SrS

The black ash containing SrS used in this study was prepared by the reductive process of celestite concentrate having 93.70% SrSO₄, 1.72% CaSO₄, 1.95% BaSO₄, 0.87% SiO₂, 0.40% Fe₂O₃, brown coal and calcium chloride (CaCl₂) at 1 050 °C for 1 h. In the reductive roasting process, the proportion of celestite concentrate, brown coal and CaCl₂ (catalytic agent) was about 100: 60: 0.5, and the admixtures of them were ground in ball mill until the grains sizes were between 100 ~ 120 mesh, which were measured by standard test sieves^[16, 17]. It was demonstrated that the 95.5% black ash was soluble in hot water (75 ~ 85 °C) and about 4.5% of it was insoluble through chemical analysis.

2.2 SrS leaching process

The leaching of SrS was carried out in reaction vessel immersed in a temperature controlled water bath in order to keep constant temperature (± 0.1 °C). When the distilled water temperature in reactor reached the desired value (25, 35, 45, 60, 75, 85, 90, 95, 98, 100 °C), the black ash with 8 times water was added into reactor. At the same time, the agitator stirred for 90 min at a constant speed of 1 000 r/min at intervals of 5 min. After water leaching, the slurry was filtered by filter paper, residues were washed with hot distilled water, dried at 150 °C for 3 h, and weighed by TG328A model analytic balance (± 0.0001 g). The leaching liquor was sealed and kept in temperature controlled water bath to avoid Sr(OH)₂ separating out from the solution. The black ash was leached two times in this experiment. During the leaching, gases (containing water-vapor) spilled from the reactor were collected and absorbed by lead acetate solution (Pb(C₂H₃O₂)₂, 0.2 mol/L) to measure the spillage factor of S²⁻. The lead acetate solution was also filtered, then the residue was washed by distilled water and dried at 120 °C until no more mass reduction was measured and weighed by analytic balance.

2.3 Strontium hydroxide (Sr(OH)₂) purification

After leaching, the molar concentration of Sr²⁺ was analyzed, and then sodium hydroxide (NaOH, chemical reagent), calculated by Eqn. (1), was added into leaching liquor. After that, the leaching liquor was heated to 100 °C for 30 min, then filtered, and cooled down to room temperature (25 °C), and the strontium hydroxide crystal (Sr(OH)₂•8H₂O) precipitated from the leaching liquor. Sr(OH)₂•8H₂O crystals were filtered and washed, then dissolved in hot distilled water and boiled at 100 °C for 30 min, at last, filtered again and cooled down to 25 °C. Repeat the dissolution-filtration-cooling process again, then the high purity Sr(OH)₂ solution was

prepared.

$$m(\text{NaOH}) = 80 \times \frac{m_1}{184} \times A \times (105\% \sim 110\%) \quad (1)$$

where $m(\text{NaOH})$ is the mass of NaOH, g; m_1 is the mass of celestite concentrate, g; and A is SrSO₄ content in celestite concentrate, %.

2.4 Preparing high purity SrCO₃

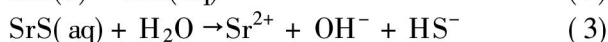
Precipitation by using CO₂ was carried out in reactor immersed in a temperature controlled water bath, and the reactive temperature was 95 °C in this study. When the temperature of Sr(OH)₂ solution reached 95 °C, carbon dioxide (CO₂, industrial grade) was sparged into solution. The flow rate of CO₂ was 100, 300, 500, 700, 900, 1 000, 1 200, 1 500, 2 000, 2 500 mL/min and the reaction time was about 15 min in this experiment. Precipitations of SrCO₃ were filtered, washed by distilled water, then dried at 150 °C until no more mass reduction was measured.

Precipitation (SrCO₃) was analyzed by using WFX-IB model FAAS (flame atomic absorption spectroscopy); strontium standard solution (according to GB9723-88, China) was used to prepare desired solution for calibration. The phase compositions of precipitates were measured by D/MAX model X-ray Diffractometer (XRD). Particle size distributions of the precipitates were measured by CAPA-300 model particle-size analyzer. The precipitate was dispersed in acetone by using ultrasonic wave, coated with a thin layer of gold, then observed in an AMRAY scanning electron microscope (SEM).

3 RESULTS AND DISCUSSION

3.1 Leaching chemistry

SrS was dissolved and hydrolyzed in hot water as follows^[2]:



As the leaching reaction progresses, the pH value of the pulp is increasing gradually from 7 (neutral value) to 11.5 ~ 12.5 (alkaline value) because of increasing of [OH⁻] in solution. At the same time, precipitation is produced in lead acetate solution, which proves that H₂S gases are produced during leaching process. The ionizable equations are the following:



$$K_{a1} = 10^{-13} (25\text{ }^\circ\text{C})$$



$$K_{a2} = 10^{-7} (25\text{ }^\circ\text{C})$$



At 25 °C, the molar concentration of sulfide ions

and molecule, c_{total} , is calculated as

$$c_{\text{total}} = [\text{H}_2\text{S}(\text{aq})] + [\text{HS}^-] + [\text{S}^{2-}] \quad (7)$$

The molar fractions of $\text{H}_2\text{S}(\text{aq})$, β_1 (relative to c_{total}), is calculated as

$$\beta_1 = \frac{[\text{H}_2\text{S}(\text{aq})]}{c_{\text{total}}} = \left[1 + \frac{K_{a2}}{[\text{H}^+]} + \frac{K_{a1} \cdot K_{a2}}{[\text{H}^+]^2} \right]^{-1} \quad (8)$$

Similarly, the molar fractions of HS^- and S^{2-} (β_2 and β_3) are calculated respectively as

$$\beta_2 = \frac{[\text{HS}^-]}{c_{\text{total}}} = \left[\frac{[\text{H}^+]}{K_{a2}} + 1 + \frac{K_{a1}}{[\text{H}^+]} \right]^{-1} \quad (9)$$

$$\beta_3 = \frac{[\text{S}^{2-}]}{c_{\text{total}}} = \left[\frac{[\text{H}^+]^2}{K_{a1} \cdot K_{a2}} + \frac{[\text{H}^+]}{K_{a1}} + 1 \right]^{-1} \quad (10)$$

From above equations, the relative molar fractions of H_2S , HS^- and S^{2-} in equilibrium depend on the pH value of leaching liquor, as shown in Fig. 1. From Fig. 1, $\text{H}_2\text{S}(\text{aq})$ or H_2S gas does not exist basically in solution when pH value is over 9 at 25 °C.

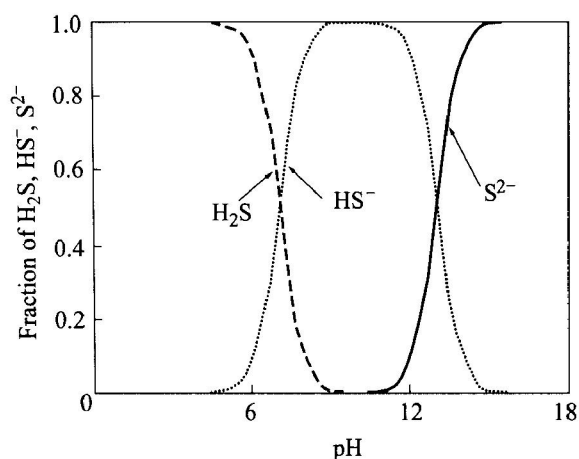
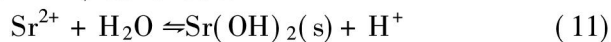


Fig. 1 Relationship of molar fractions of H_2S , HS^- and S^{2-} with pH at 25 °C

But, when the $\text{pH} > 14$, strontium hydroxide ($\text{Sr}(\text{OH})_2$) will precipitate from the leaching liquor^[2, 18], as follows:



$$K = 3.55 \times 10^{-29} (25^\circ \text{C})$$

$$\lg[\text{Sr}^{2+}] = 28.45 - 2\text{pH} \quad (12)$$

3.2 Effect of temperature on leaching

Hydrolytic reaction of SrS is a kind of heat-absorbing reaction, as shown in reaction (3); therefore, the equilibrium of reaction (3) is shifted to the right when the leaching temperature increases. In addition, the solubility of strontium hydroxide ($\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$) in water varies greatly at different temperature: solubility of it at 20 °C and 100 °C is given as 0.69 g and 24.2 g per 100 g water respectively^[8]. When temperature reaches a critical value, $\text{Sr}(\text{OH})_2$ will dissolve completely, therefore, the recovery of Sr^{2+} (R_{Sr} , %), which is calculated according to Eqn. (13), increases with temperature increas-

ing in leaching process, as shown in Fig. 2.

$$R_{\text{Sr}} = \frac{184m_2}{148m_1 \times A} \times 100\% \quad (13)$$

where m_1 is the mass of celestite concentrate, g; m_2 is the mass of SrCO_3 , g; and A is the SrSO_4 content in celestite concentrate, %.

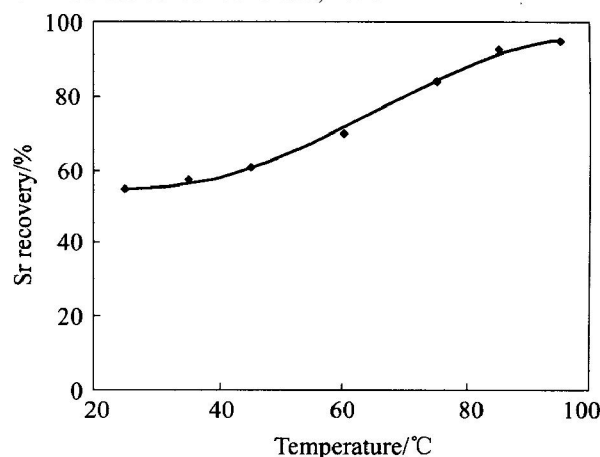


Fig. 2 Effect of temperature on dissolution of SrS (Precipitating SrCO_3 from leaching liquor directly)

When the leaching temperature increases, the S^{2-} concentration ($[\text{S}^{2-}]$) increases, which causes the equilibrium of reactions (4), (5), (6) to shift to the left, resulting in that H_2S gases evolve out from the leaching liquor. The higher the temperature, the more the H_2S gases separate out. Fig. 3 shows the relationship between temperature and spillage factor of S^{2-} , φ_s , which is calculated as

$$\varphi_s = \frac{32m_4}{239m_3 \times B} \times 100\% \quad (14)$$

where m_3 is the mass of black ash, g; m_4 is the mass of PbS precipitation, g; B is the S content in black ash, %. It is shown that the recovery of Sr^{2+} is high ($> 93\%$) while the spillage factor of S^{2-} is very low ($< 0.2\%$) at 80–85 °C (as shown in

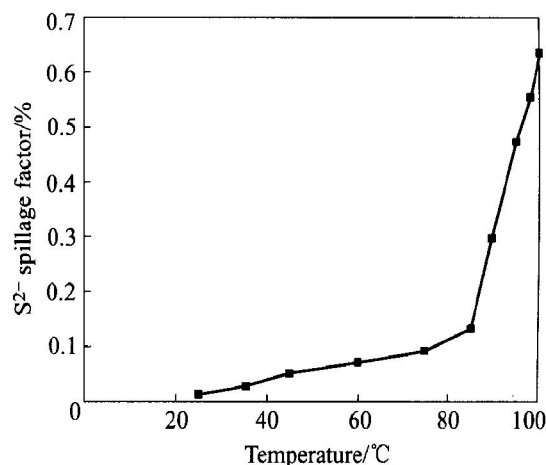
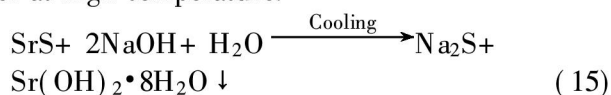


Fig. 3 Effect of temperature on spillage factor of S^{2-}

Fig. 2 and Fig. 3). Therefore, leaching SrS at 80 ~ 85 °C is optimal. In industrial manufacture, the separated H₂S gases can be collected by alkaline solution (NaOH, Ca(OH)₂, etc).

3.3 Analysis on Sr(OH)₂ purification process

When NaOH is added into the leaching liquor (mainly including SrS), pH value is increased (> 13.5) and Sr(OH)₂·8H₂O will precipitate from the liquor when leaching liquor is cooled down because the solubility of Sr(OH)₂·8H₂O decreases greatly with temperature decreasing (Eqn. (15)). Precipitation of Sr(OH)₂·8H₂O is influenced by the following factors: concentration of leaching liquor, the amount of NaOH, temperature of leaching liquor, holding time, etc. The results demonstrate that the higher temperature of leaching liquor and longer holding time are beneficial to increasing the purity of Sr(OH)₂·8H₂O and decreasing the content of Na⁺ and S²⁻ in Sr(OH)₂·8H₂O because they can dissolve greatly in water at high temperature.



In order to obtain the high purity Sr(OH)₂·8H₂O, the dissolution-recrystallization process was used. In fact, the differences among the solubility of Ba(OH)₂·8H₂O, Sr(OH)₂·8H₂O and Ca(OH)₂ are great, as shown in Table 1^[5,8]. Ca²⁺ can be removed at high temperature because Ca(OH)₂ will precipitate at high temperature. Ba²⁺ can be removed after Sr(OH)₂·8H₂O is recrystallized at low temperature, since Ba²⁺ is reserved in solution.

Table 1 Solubilities of Ba(OH)₂·8H₂O, Sr(OH)₂·8H₂O and Ca(OH)₂ in 100 g water(g)

Temperature/ °C	Ba(OH) ₂ · 8H ₂ O	Sr(OH) ₂ · 8H ₂ O	Ca(OH) ₂
0	1.67	0.35	0.185
20	3.89	0.69	0.165
40	8.02	1.80	0.141
60	20.94	3.13	0.116
80	101.4	7.03	0.094
90	—	13.6	0.085
100	—	24.20	0.077

The dissolution-recrystallization times have an important effect on the purity of SrCO₃, as shown in Table 2. From Table 2, high purity of SrCO₃ satisfies the demand for reagent grade (> 99.0 %, HG3-953-76, China) by dissolving and recrystallizing one times. The XRD pattern of SrCO₃ is depicted in Fig. 4 after being recrystallized two times and precipitated

by CO₂, in which only SrCO₃ is detected. It is demonstrated that the precipitation meets the criterion for producing electronic component (> 99.50 %, TDK standard, Japan) after being dissolved and recrystallized two times. If dissolved and recrystallized three times, the purity of SrCO₃ is as high as 99.97%; but, with the increasing of recrystallizing times, the production cost increases and the recovery factor of Sr decreases.

Table 2 Influence of recrystallizing times on purity of SrCO₃ prepared by CO₂(%)

Recrystallizing times	SrCO ₃	BaO	CaO	Fe ₂ O ₃	Na ₂ O
0	97.48	0.51	0.32	0.007	—
1	99.24	0.12	0.04	0.001	0.05
2	99.73	0.015	0.007	< 0.001	< 0.01
3	99.97	< 0.01	< 0.01	< 0.001	< 0.01

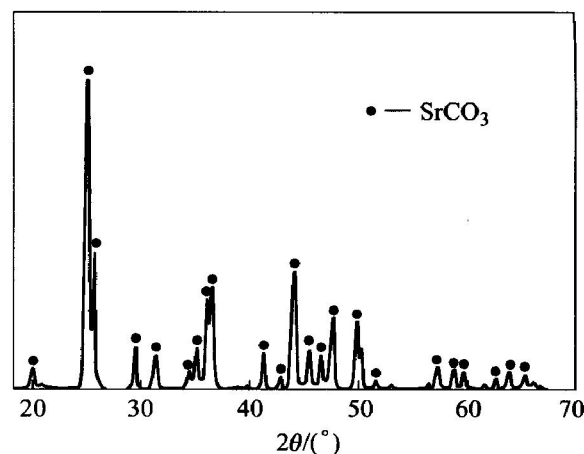


Fig. 4 XRD pattern of SrCO₃ recrystallized two times and precipitated by CO₂

3.4 Effect of flow rate of CO₂ on precipitation

The precipitation process is related with many processing parameters, such as reaction temperature, flow rate of CO₂, solution concentration, reaction time, drying condition, etc.

In this paper, the effect of flow rate of CO₂ on particle sizes was mainly discussed, and the other parameters were fixed as the following: the concentration of (Sr(OH)₂), 0.5 mol/L; reaction temperature, 95 °C; reaction time, 15 min; agitator rate, 1 000 r/min; drying temperature, 150 °C. The relationship between the flow rates of CO₂ and the mean particle size is shown in Fig. 5, in which the mean particle size decreases with the flow rate increasing. The particle sizes of precipitation SrCO₃ are distributed narrowly too, but the precipitation SrCO₃ has agglomerated to some extent, as shown in Fig. 6 and Fig. 7.

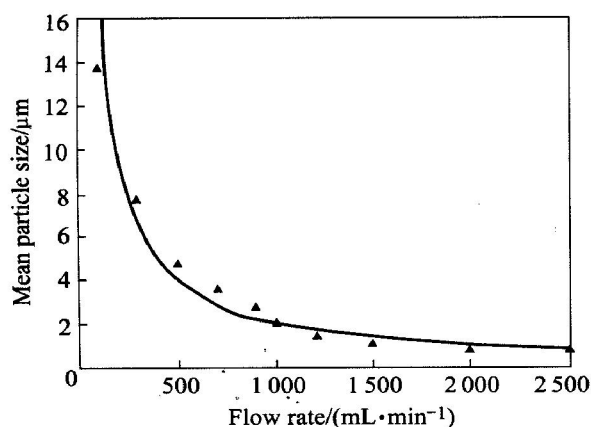


Fig. 5 Relationship between flow rates of CO_2 and mean particle sizes

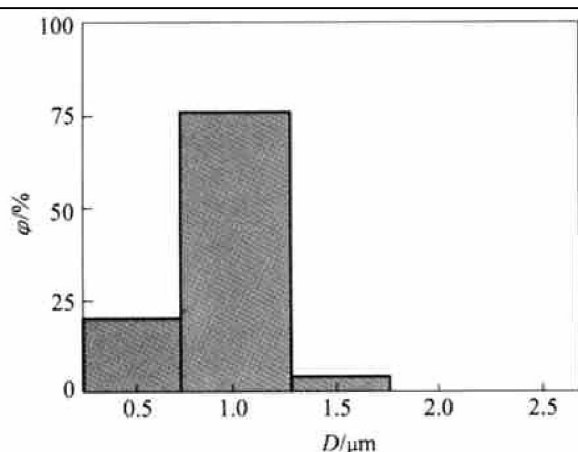


Fig. 6 Particle size distribution of $SrCO_3$ (CO_2 flow rate: $2000 \text{ mL} \cdot \text{min}^{-1}$)

High accurate electronic components demand $SrCO_3$ with small particle sizes ($< 1.0 \mu\text{m}$), particle sizes distributing narrowly and particle shapes close to globular (TDK standard, Japan)^[19]. From Fig. 5, Fig. 6 and Fig. 7, $SrCO_3$ that was prepared by CO_2 and $Sr(OH)_2$ satisfied the TDK standard, when the flow rate of CO_2 was over 2000 mL/min .

4 CONCLUSIONS

1) In leaching process, the strontium recovery and solubility of $Sr(OH)_2$ increase with temperature increasing, but H_2S discharges more when temperature increases. At 25°C , S^{2-} behaviors are also related with pH value of leaching liquor, and H_2S gives off when pH value is lower than 8.

2) $Sr(OH)_2 \cdot 8H_2O$ will precipitate from leaching liquor when NaOH is added and the liquor is cooled down. The purity of $SrCO_3$ increases with the dissolution-recrystallization times increasing. After being dissolved and recrystallized three times, the purity of $SrCO_3$ is as high as 99.97%.

3) The particle sizes of $SrCO_3$ are mainly controlled by the flow rate of CO_2 . The particle sizes of $SrCO_3$ decrease and distribute narrowly with the flow rate increasing when other parameters are unchangeable in precipitation process; especially, the particle sizes of $SrCO_3$ mainly distribute in $0.1 - 1.0 \mu\text{m}$ when the flow rate of CO_2 is about 2000 mL/min .

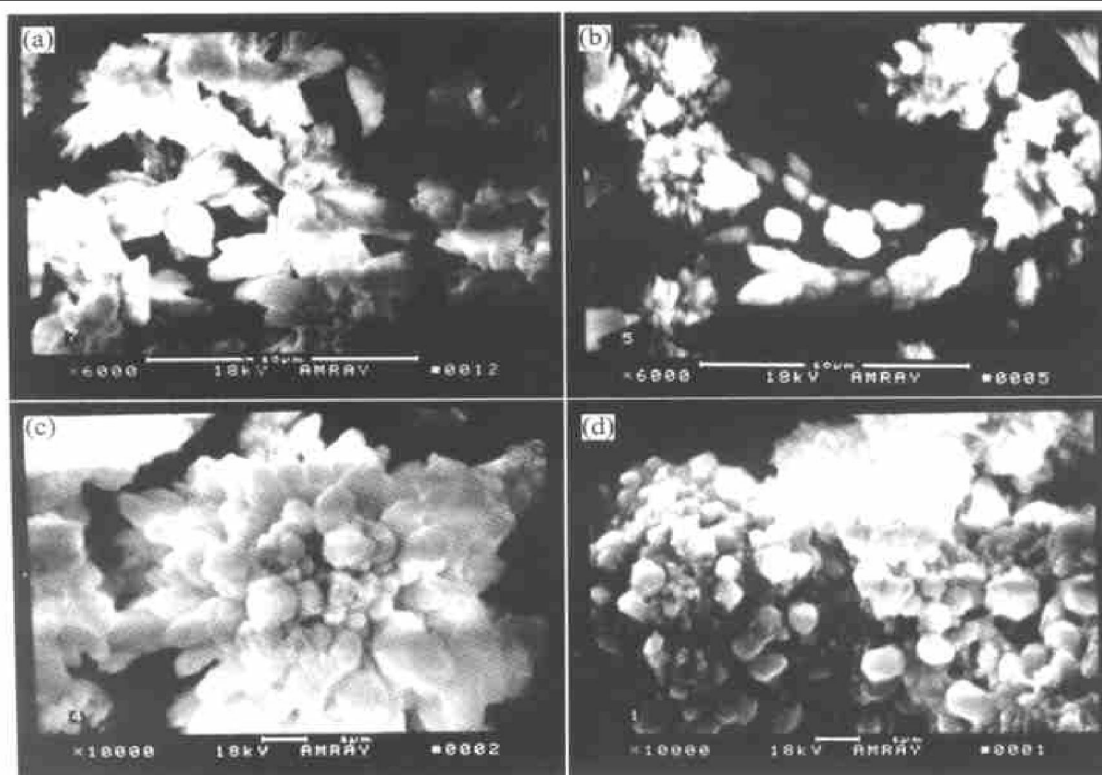


Fig. 7 SEM images of $SrCO_3$ prepared by $Sr(OH)_2 (0.5 \text{ mol} \cdot \text{L}^{-1})$ under different flow rates of CO_2 (a) 500 mL/min ; (b) 1000 mL/min ; (c) 1500 mL/min ; (d) 2000 mL/min

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