Pseudomorphic Conversion of Mineral SrSO₄ to SrCrO₄ under Hydrothermal Conditions

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Abstract

The conversion of SrSO₄ ions to SrCrO₄ in natural strontium sulfate (Celestite) single crystals was investigated under alkaline hydrothermal conditions. Hydrothermal treatments were conducted using a stainless steel Teflon lined vessel, and the experiments were carried out at different temperatures from 175 to 250°C for various reaction intervals between 1 and 96 h with a molar ratio of $CrO_4^{2^2}/SO_4^{2^2} = 1$, 3 and 5. The crystal structure of the partially converted samples was characterized by X-ray powder diffraction technique. SEM was used to observe some aspects related with the morphology and dimensions of the reacted specimens. Experimental results showed that the pseudomorphic conversion partially proceeds on the raw Celestite crystals. The partially reacted crystals showed the formation of a thin reaction product layer, which matched the inorganic compound SrCrO₄ with monoclinic structure. The growth of this layer was controlled by the reaction temperature and the CrO₄²⁻ /SO4²⁻ molar ratio. In accordance with the EDX line analyses, it was found that the SrCrO4 layer was formed on the surface of the crystals by the mechanism of dissolution-precipitation. This layer has not a peculiar microstructure since it is continuous and includes only some microcracks. Details regarding the pseudomorphic conversion mechanism are discussed in the present work.

Introduction

The reaction of ion replacement in mineral species has been the subject of many research work, because mineral species are no longer in equilibrium with the surrounding fluids; furthermore, most of these mineral replacement reactions take place by a mechanism of dissolution-recrystallization [1,2]. Hitherto, it has been found that in alkaline hydrothermal fluids, the topotaxial replacement of ions in mineral species, such as mineral apatite, is enhanced by the formation of a peculiar texture, which consists of tiny tunnels randomly distributed in the converted mineral. Yanagisawa et al. [3] reported that this texture is preferentially formed during the particular conversion of chlorapatite single crystals to hydroxyapatite single crystals; the presence of tiny tunnels might compensate the dimensional change resulting from the structural conversion. This type of process occurs mainly when large ions are exchanged with small ones in the parent mineral. However, an anisotropic dissolution process can also led to a replacement reaction, but this process strongly depends on the reactivity of the parent mineral with the hydrothermal fluid. This ion replacement process was revealed during the conversion of chlorapatite to fluorapatite, after the treatment the replaced fluorapatite crystals had a microstructure consisting in very large holes produced by a marked dissolution of solute in the hydrothermal media [4]. In addition, an important observation made on the ion exchange of CI ions with OH ions was that a chlorapatite single crystal was converted to a hydroxyapatite single crystal. Under alkaline hydrothermal conditions, the topotaxial ion exchange process is achieved by a mechanism of dissolution and precipitation of clusters which are much larger than the ionic species. The

uptake of OH⁻ ions and the release of Cl⁻ take place at the surface of the clusters, which are then reassembled to form the new single crystal [3].

On the other hand, for the mineral specie of Celestite, only the anion exchange reaction of SO_4^{2-} ions of Celestite with CO_3^{2-} has been the subject of many research works since last century, because Celestite is the mineral raw source for producing strontium inorganic compounds [5-7]. Recently, the leaching of Celestite particles and crystal plate (10 x 10 x 10 mm³) was found to proceed in sodium carbonate solutions at very low temperatures under atmospheric pressure [8]. Iwai et al [8] studied the leaching from a thermodynamic and kinetic point of view, and reported that the exchange of $SO_4^{2^2}$ ions with $CO_3^{2^2}$ in large bulk crystal plates is achieved by two mechanisms. An initial reaction involves a surface reaction. The second mechanism proposed is related to SO_4^2 ions diffusion through a dense strontium carbonate layer, which is produced during earlier stages of the conversion process [8]. In addition, other investigations reported that the leaching reaction in Celestite particles, which lead to their conversion to Strontianite; is achieved by a topo-chemical ion exchange mechanism [9,10]. However, the above cited references did not report details on the effect of the crystallographic structural changes associated with the conversion of Celestite to Strontianite. In contrast, Yoshino et al. [11] reported the first evidence that the conversion of Celestite to Strontianite proceeds under hydrothermal conditions and the ion exchange is achieved by a solid state ion exchange mechanism. The ion exchange in the solid state is faster under hydrothermal conditions at pressures between 1-100 MPa, and the interface of the reaction in the Celestite crystal remains smooth, bearing a SO₄² concentration gradient [12]. In recent work conducted by the present authors [13], it was found that in high concentrated carbonate solutions. Na₂CO₃ and K_2 CO₃, the conversion of Celestite parent into Strontianite, proceeded in large Celestite single crystals at low temperatures, less than 250 °C; under hydrothermal conditions. Chemical and microstructural analyses conducted on partially and completely converted crystals, showed that conversion is lead by a pseudomorphic ionic replacement process, similar to that described by Putins [1]. Therefore, in accordance wit the former information, we expect that the ion exchange of SO_4^{2-} ions with CrO₄² ions is likely to occur in mineral Celestite single crystals under alkaline hydrothermal conditions bearing a high concentrated chromate ion exchange media. Initial attempts were made to determine the stability of the mineral SrSO₄ specie in hydrothermal media bearing CrO_4^{2-} ions, as well as to evaluate aspects related with the replacement mechanism.

Experimental procedure

Materials

Single crystals of mineral Celestite were obtained from typical mineral ores in a mining area of Coahuila, Mexico. Raw mineral single crystals were cut parallel to the cleavage plane (001) direction with a diamond disk, in order to obtain square plates with the dimensions of 10 mm wide and 3 mm thick. These plates were washed with deionized water and cleaned using an ultrasonic equipment. X-ray analyses (Fig. 1) revealed that the Celestite single crystals belong to the orthorhombic system with the space group *Pnma* with unit cell parameters of $a = 8.3628 \pm 0.0004$ Å, $b = 5.3511 \pm 0.0004$ Å and $c = 6.8675 \pm 0.0004$ Å. The chemical composition of the Celestite crystals was determined by wet chemistry analyses, which show that the major constituents are: Sr= 44.93 wt%, Ba= 3.83 wt% CO₃= 1.22 wt% and SO₄= 49.98 wt %, those correspond to SrSO₄ 90.0 wt %, SrCO₃ 3 wt % and BaSO₄ 6.5 wt %, respectively. The mineralizer fluid selected as ion-exchange media was prepared from reagent grade K₂CrO₄ (Aldrich).

Hydrothermal Treatments

A Celestite (SrSO₄) crystal plate (approximately 0.5 g) was placed at the bottom of Teflonlined stainless steel vessel with inner volume of 27 ml, and then the mineralizer, K_2CrO_4 , was added to get three different CrO_4^{2-}/SO_4^{2-} ratios (1, 5 and 10). Additionally, three different volumes of deionized water were poured in the autoclave to obtain volume filling ratios of 40%, 55% or 70%, respectively. The conventional hydrothermal treatments were conducted at a predetermined temperature ($150 - 250^{\circ}$ C) by heating the vessel at a rate of 10 °C/min. The vessel was held at each temperature for several reaction intervals (1 - 96 h). The cooling stage was conducted using an electric fan. After the hydrothermal treatments, the reaction products were washed with deionized water using an ultrasonic equipment.

Characterization

Powder X-ray diffraction analyses were carried out to determine the crystalline phases and the lattice constants of the treated crystals by an X-ray diffractometer (Rigaku, Rotaflex) with graphite-monochromatized CuK α radiation at 40 kV and 100 mA. Diffraction patterns were taken in the 20 range from 10 to 80 ° at a scanning speed of 4 °/min. The morphology of the products was observed by scanning electron microscopy (Philips XL30 ESEM). To determine the reaction process, compositional analyses of sulfur were conducted, using an energy dispersive X-ray device. The samples were selected from the early and the intermediate stages; the crystals were then mounted in epoxy resin and polished to a mirror-like surface. The surfaces observed were perpendicular to the cleavage plane (001).



Figure 1 X-ray diffraction pattern of the raw mineral Celestite crystals obtained from the Northwest part of Mexico. Solid line= main diffraction peaks of pure Celestite; dotted line= Barite diffraction peaks.

Results and discussion

Stability of Celestite in chromate hydrothermal solutions

Initial experiments were directed towards the determination of the stability of the parent raw mineral Celestite (SrSO₄) in hydrothermal fluids which bear a high concentration of $CrO_4^{2^-}$ ions, at different conditions of reaction time, temperature and ion exchange media filling ratio. In Table 1 are summarized the experiments conducted in this study, the phases determined by Xray diffraction on the reaction products are also included. These results showed that the stability of the inorganic SrSO₄ crystalline phase is high even at temperatures below 175 °C, because during the treatments conducted at 150 °C for a long reaction interval, 96 h, only traces of the SrCrO₄ compound were determined.

Figure 2a shows typical X-ray diffraction patterns of the crystals partially converted during the hydrothermal treatments for long reaction intervals in a K_2CrO_4 solution with a molar ratio of $CrO_4^{2^-}/SO_4^{2^-}=1$. These results revealed that the exchange of $SO_4^{2^-}$ ions with $CrO_4^{2^-}$ ions in Celestite crystals proceeds very slowly, because one can clearly observe a slight increase in

the content of the new phase by increasing the reaction time up to 96 h. The formation of strontium chromate compound with monoclinic structure (space group P2₁/n, JCPDS card 35-0743), was observed to occur after the treatment for a long interval, 72 h. One point that deserves emphasis is that the conversion of SrSO₄ into SrCrO₄ proceeded in a single reaction step, because the formation of intermediate solid solutions on the system SrSO₄-SrCrO₄ was not determined during the hydrothermal conversion reaction, in contrast to that recently determined in some mineral species such as Celestite [13] or Apatite [3,4,14], i.e. SrSO₄-SrCO₃ or CaClAP-CaOHAP, where was found that the pseudomorphic conversion under hydrothermal conditions proceeds with the formation of solid solutions, respectively.

Sample	CrO^{2-}/SO^{2-}	Solution	Temperature	Fill	Duration	Determined
ID	ratio		(°C)	Ratio	(h)	Phases
	Tatio			(vol. %)		
M1	1	K_2CrO_4	250	40	48	SrSO ₄ + SrCrO ₄
M2	1	K_2CrO_4	250	40	72	SrSO ₄ + SrCrO ₄
M3	1	K_2CrO_4	250	40	96	SrSO ₄ + SrCrO ₄
M4	5	K_2CrO_4	250	50	72	$SrSO_4 + K_2CrO_4$
M5	1	K_2CrO_4	250	70	96	SrSO ₄ + SrCrO ₄
M6	1	K_2CrO_4	200	40	24	SrSO ₄ + SrCrO ₄
M7	1	K_2CrO_4	200	40	48	SrSO ₄ + SrCrO ₄
M8	1	K_2CrO_4	200	40	72	SrSO ₄ + SrCrO ₄
M9	1	K_2CrO_4	200	40	96	$SrSO_4 + SrCrO_4$
M10	1	K_2CrO_4	200	55	96	SrSO ₄ + SrCrO ₄
M1 1	3	K_2CrO_4	200	70	2	SrSO ₄
M12	1	K_2CrO_4	200	70	24	SrSO ₄ + SrCrO ₄
M1 3	1	K_2CrO_4	200	70	48	SrSO ₄ + SrCrO ₄
M14	1	K_2CrO_4	200	70	72	SrSO ₄ + SrCrO ₄
M15	1	K_2CrO_4	200	70	96	SrSO ₄ + SrCrO ₄
M16	1	K_2CrO_4	175	40	48	$SrSO_4 + SrCrO_4$
M17	1	K_2CrO_4	175	40	72	$SrSO_4 + SrCrO_4$
M1 8	1	K_2CrO_4	175	40	96	SrSO ₄ + SrCrO ₄
M1 9	1	K_2CrO_4	175	40	24	SrSO ₄ + SrCrO ₄
M20	1	K_2CrO_4	150	40	96	SrSO ₄ + traces
						SrCrO ₄

Table 1 Summary of the hydrothermal treatments carried out for the determination of the stability aspects of the mineral parent Celestite single crystals in K₂CrO₄ solutions.

Figure 2b shows X-ray diffraction patterns of those crystals remained after the hydrothermal treatments at different temperatures for 96 h in a K_2CrO_4 solution with a molar ratio of $CrO_4^{2^-}/SO_4^{2^-}$ =1. These results revealed that the exchange of $SO_4^{2^-}$ ions with $CrO_4^{2^-}$ ions in Celestite crystals proceeds at temperatures as low as 175°C (Table 1). After the treatments at low temperatures below 200°C, two phases were observed in the reaction products. One of these phases was the original Celestite, and the new phase corresponded to the inorganic compound SrCrO_4. In contrast, when the Celestite crystal plate was treated at 250°C, the amount of the new reaction product, SrCrO_4, was slightly increased. The effect of the molar ratio ($CrO_4^{2^-}/SO_4^{2^-}$) value in the ion exchange media on the XRD patterns of hydrothermally treated crystals are shown in Fig. 2c. Although from the reaction products it can be inferred that a complete conversion occurred, because only a single phase corresponding to the SrCrO_4 compound was detected on the diffraction pattern. However, only a partial conversion of Celestite occurred when the crystal was treated in a K_2CrO_4 solution at a low value of the molar ratio ($CrO_4^{2^-}/SO_4^{2^-} = 1$). The increase of the molar ratio value to 5 resulted in a minimum increase in the transformation of Celestite to SrCrO_4.



Figure 2 X-ray diffraction patterns of the reaction products obtained from the Celestite crystals after hydrothermal treatments (a) 250 °C for various reaction intervals, (b) for 96 h at different temperatures, these treatments were conducted with a filling ratio of 40% and a molar ratio $CrO_4^{2^-}/SO_4^{2^-}=1$, respectively; and (c) at 200 °C for 96 h with a filling ratio of 55%. Solid line= Celestite; dotted line= $SrCrO_4$.

Microstructural and compositional aspects of the hydrothermally treated crystals

In general, the hydrothermal treatments in a concentrated K₂CrO₄ solution resulted in reduced transparency of the original crystals as well as in the formation of a yellow reaction layer on the surface of the partially converted crystal. This new layer was homogeneously formed on the surface of the crystal that was surrounded with the ion exchange fluid; therefore, the partially converted crystals did not exhibit severe changes on their original shape and dimensions. It is well known that conventional hydrothermal treatments, especially with a temperature gradient, produced new crystals from the original ones by means of dissolution and precipitation process [3]. In our investigation, no extra crystals were produced during the hydrothermal treatments. A typical microstructure of the remaining product is shown in Fig. 3. The SEM image was taken on a polished cross section parallel to the cleavage plane (001) of the crystal. Although the aspect of crystals remained unchanged after the conversion process, some original holes randomly distributed inside the raw crystals remained at the same position after the conversion reaction (Fig. 3a). Furthermore, he crystal exhibited the formation of a new phase without peculiar texture, since it is continuous and solid. Energy dispersive area scan microanalyses taken on either phase showed that the

phase remaining inside the crystal contains the original Sr and S elements (Fig. 3b), while the major elements determined in the outer new phase were Sr and Cr. Hence, these results show clear evidences that the reaction of the parent $SrSO_4$ to $SrCrO_4$ proceeds in a single step by a pseudomorphic conversion process.



Figure 3 (a) SEM micrograph of the partially reacted crystals at 200 °C for 96 h in a hydrothermal media with a molar ratio $CrO_4^{2^2}/SO_4^{2^2}=1$. Energy dispersive spectra of the inner (b) and outer (c) phases revealed inside the partially converted $SrSO_4$ crystals.

Effect of the structural changes on the pseudomorphic conversion of SrSO₄ to SrCrO₄

Additional microstructural aspects determined on the partially converted SrSO₄ are shown in Figure 4. This Figure shows the variation on the thickness of the outer SCrO₄ layer, for that crystals treated under hydrothermal conditions at 200 °C with a molar ratio of $CrO_4^{2^\circ}/SO_4^{2^\circ}=1$ for intermediate and long reaction intervals (Fig. 4a). When the Celestite crystals were treated for 24 h, the formation of a solid layer on the surface of the crystal was observed, which maintains the same surface flatness of the original crystal, but the reaction boundary is very irregular. A minimum thickness of the longest period of reaction, 72 h (Fig. 4b) and 96 h (Fig. 4c). Under these hydrothermal conditions, the conversion of the parent SrSO₄ to SrCrO₄ was further limited during long reaction intervals (> 72 h); from these results we suggest that the maximum thickness of the layer that can be obtained by the hydrothermal conversion process is about 45 μ m. Furthermore, the formation of some microcracks was revealed on the new SrCrO₄ layer for the specimens treated for 72 and 96 h. This fact might be related to structural differences associated with the conversion of SrSO₄ to SrCrO₄.

We have found that the conversion of Celestite to SrCrO₄ proceeds at low temperatures (200 °C) in relatively alkaline hydrothermal conditions (K₂CrO₄ solution), with the formation of

a peculiar phase on the surface of the partially converted crystals. The factor that have a marked influence in limiting the ion exchange of SO4²⁻ ions by CrO4²⁻ ions in the SrSO4 crystals may be explained as follows. The dissolution of mineral species in hydrothermal fluids normally proceeds anisotropically, producing a peculiar texture with holes inside the recrystallized mineral specie [3.4]. The holes might not be inherited from etch pits produced during the dissolution process, because they did not penetrate the crystals. The peculiar microstructure consisting on a continuous solid phase can be attributed to changes in the Celestite structure by the replacement of small ions (SO_4^2) by large ions (CrO_4^2) . This fact is suggested from the structural change of the orthorhombic to monoclinic structure, which might occur during the conversion. In terms of the global unit cell volume, an expansion processes might be involved, therefore, in accordance with the differences on the unit cell volume between that for Celestite (312.37 Å³) and that of SrCrO₄ (354.11 Å³), a volume increase of 41.74 Å³ must occur in the converted new layer of SrCrO₄. Hence, the global volumetric unit cell expansion must be compensated by the formation of a continuous solid phase and the formation of some microcracks in this new phase [12]. This solid phase might reduce the transfer of fresh ion exchange media, because under hydrothermal conditions the absence of a texture (small porosity) in the converted phase avoids the penetration of the hydrothermal fluid [15], resulting in a decrease in the conversion kinetic.



Figure 4 Morphological aspects of the SrCrO₄ layers obtained on Celestite crystals treated under hydrothermal conditions at 200 °C with a filling ratio of 40% and a molar $CrO_4^{2^-}/SO_4^{2^-}$ ratio equal to 1, for reaction intervals of (a) 24, (b) 72 and (c) 96 h.

Effect of the experimental parameters on the growth of the converted SrCrO₄ layer

The Figure 5 shows the variation in thickness of the converted layer of $SrCrO_4$ obtained on the partially converted Celestite crystals, as a function of experimental parameters such as reaction interval, temperature and solution filling ratio. These factors have a marked influence in accelerating the thickness of the $SrCrO_4$ phase. The value of the $SrCrO_4$ layer corresponds to an average of 30 measurements conducted on this layer on the transversal area of the partially converted crystal. A significant thickening of the new converted layer of $SrCrO_4$ was observed to occur up to 24 h at a temperature of 200 °C, above this reaction interval the growth of the new layer proceeded slowly. Below 48 h, the growth of the reacted layer under hydrothermal conditions was further limited, because the thickness of the layer was nearly the same for the specimens treated at 72 and 96 h (Fig. 5a). Thought a similar layer grown behavior to that determined for the crystals treated at 200 °C against the reaction interval, was observed on the specimens treated at 250 °C, however, the thickness of the layers obtained for intermediate and long reaction intervals were approximately 20 μ m smaller, in comparison with those obtained at a lower temperature (200 °C). This trend was also observed when the specimens where treated with different filling ratios and a peculiar decrease of the layer thickness was detected on the specimen treated at 250 °C with 70% of ion exchange media filling ratio.

These results suggest that the marked difference on the thickness of the converted layer determined on the specimens treated at different temperatures can be attributed to the dissolution of the formed $SrCrO_4$ layer; the dissolution of this layer might depend on the chemical stability of the $SrCrO_4$ compound, which is reduced by increasing the temperature an the concentration of the hydrothermal fluid. In fact, this inference agrees well with the results reported in previous studies [15], where it was found that during the pseudomorphic conversion of Ca-apatite into Sr-apatite, the outer cation-exchanged Sr-apatite layer which had no peculiar texture, was continuously dissolved in the alkaline hydrothermal media of $Sr(OH)_2$. This process caused a reduction in the original dimensions of the original Ca-apatite crystals and retarded the complete conversion of the parent Ca-apatite.



Figure 5 Variation on the thickness of the converted $SrCrO_4$ layer as a function of the experimental parameters. These thickness values correspond to specimens treated (a) for various intervals with a filling ratio of 40%; and (b) employing different filling ratios. In both cases, the treatments were carried out with a molar ratio $CrO_4^{2^-}/SO_4^{2^-}=1$ at two temperatures of (\blacksquare) 200 and (\blacklozenge) 250 °C, respectively.

Characteristics of the SrCrO₄ conversion mechanism under hydrothermal conditions

The details of the ion exchange mechanism were investigated by observing the cross section of the partially ion exchanged crystals obtained by hydrothermal treatment at 200 °C for 96 h with a molar ratio $CrO_4^{2^-}/SO_4^{2^-} = 1$. Figure 6 shows a SEM image taken on the cross section of the crystals normal to the cleavage plane (001). In the SEM photograph, it is easy to identify two continuous phases. These phases are separated by a sharp textured boundary. From these observations, it is clear that the pseudomorphic conversion process begins at the surfaces of the crystal that were in contact with the reaction fluid. Hitherto, a mechanism for the ion exchange of $SO_4^{2^-}$ with $CO_3^{2^-}$ between Celestite crystals and Whiterite (BaCO₃) powder [11] was proposed to proceed in solid state conditions even under hydrothermal conditions at 500 °C for 168 hrs at high pressure (100 MPa). It was found that an atomic diffusion mechanism was responsible for the anion motion through the crystalline structure and the structural defects play an important role in achieving ion motion,

because the motion of ions may be accelerated by the interaction between vacancies and ions [3,14]. The conversion investigated in the present work, however, cannot be associated with a solid state ion exchange, because it proceeded at lower temperatures than that necessary to achieve atomic diffusion in the solid state [11].

The above mentioned inference is supported by the sulfur compositional X-ray line profiles, which were conducted across the conversion front (distance between the arrows in Fig. 6a), direction in which the conversion process proceeds. The profile (Fig. 6b) reveals that a sharp boundary in sulfur composition was formed at the reaction interface. From this result, we consider that the pseudomorphic conversion of $SrSO_4$ to $SrCrO_4$ is achieved by a mechanism of bulk dissolution-recrystallization process [16]. The bulk dissolution is different to the cluster dissolution process that also allows converting $SrSO_4$ to $SrCrO_3$ even under hydrothermal conditions [15]. Consequently, the recrystallization of the new converted phase ($SrCrO_4$) must occur at the fluid-crystal interface. However, the pseudomorphic conversion is then retarded, because the solid converted $SrCrO_4$ blocks the transference of the saturated K_2CrO_4 solution.



Figure 6 (a) SEM image of the reaction interface and (b) sulfur concentration in a partially converted celestite crystal obtained by hydrothermal treatment in a K_2CrO_4 solution with a molar $CrO_4^{2^-}/SO_4^{2^-}$ ratio equal to 1, and a filling ratio of 55%, at 200 °C for 96 h.

Conclusions

Mineral Celestite single crystals (SrSO₄, square plates 10 mm wide and 3 mm thick) were partially transformed to SrCrO₄ under alkaline hydrothermal conditions by a typical pseudomorphic conversion process. The pseudomorphic conversion of SrSO₄ to SrCrO₄ rapidly proceeds at a temperature of 200 °C, in a relatively saturated fluid (CrO₄²⁻/SO₄²⁻=1). The increase in temperature (250 °C), molar ratio (CrO₄²⁻/SO₄²⁻) and filling ratio, resulted in a further dissolution of the SrCrO₄ converted layer. The dissolution process was caused by two factors; the first one was related to decrease in the chemical stability of SrCrO₄ and the second one to the microstructural conditions of the reacted layer. Thus, the expansion of the lattice cell volume associated with the conversion process resulted in the formation of a continuous SrCrO₄ phase which blocks the transfer of fresh fluid to the reacted layer took place. The present result showed that the conversion of mineral Celestite to SrCrO₄ proceeds by a mechanism of bulk dissolution-recrystallization, rather than by a cluster dissolution-precipitation, because in our case the conversion proceeds without the formation of solid solutions on the system SrSO₄-SrCrO₄.

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