

## Research Article

# Thermal Decomposition of Hydrocalumite over a Temperature Range of 400–1500°C and Its Structure Reconstruction in Water

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The thermal decomposition process and structure memory effect of hydrocalumite were investigated systematically for the first time over a wide temperature range of 400–1500°C. The calcined hydrocalumite samples and their rehydrated products were characterized by XRD, FT-IR, and SEM-EDX. The results show that the calcination products at temperatures ranging from 500 to 900°C are basically mayenite and lime, while one of the final products obtained by calcination at and above 1000°C is probably tricalcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ). For the hydrocalumite samples calcined at temperatures below 1000°C, their lamellar structure can be completely recovered in deionized water at room temperature. However, the further increase of calcination temperature could impair the regeneration ability of hydrocalumite via contact with water. Upon calcination of hydrocalumite at 1000–1500°C followed by reaction with water, a stable compound tricalcium aluminate hexahydrate ( $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ ) was produced, which is the reason why less hydrocalumite could be regenerated.

## 1. Introduction

Hydrocalumite, also known as Friedel's salt [1] or AFm phase in cement science [2], belongs to the family of layered double hydroxides (LDHs) [3]. It is commonly synthesized by using calcium and aluminum salts. However, hydrocalumite could also be formed as the major stable hydration product of cement paste and concrete or as secondary precipitate during the hydration of fly ash, spent oil shale, and some other solid waste materials [4]. In the crystal structure of hydrocalumite, the divalent  $\text{Ca}^{2+}$  are located in the center of edge-sharing octahedra and partially substituted by trivalent  $\text{Al}^{3+}$ , which results in a net positive charge to the layers that has to be compensated by intercalation of gallery anions. In view of its unique structure and chemical characteristics, hydrocalumite has been applied in not only catalysis industry but also environmental remediation. In recent years, it was widely used for removing undesirable anions from wastewaters or contaminated natural waters, including  $\text{B}(\text{OH})_4^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{AsO}_2^-$ ,  $\text{MoO}_4^{2-}$ ,  $\text{SeO}_4^{2-}$  [4, 5] and even some organic anions (e.g., dodecyl benzene sulfate ( $\text{DBS}^-$ ) and methyl orange

(MO)) [6, 7]. The involved anion uptake mechanisms comprise surface adsorption, anion exchange, and dissolution-reprecipitation. Our group has also made use of hydrocalumite to remove a wide range of concentrations of fluoride and arsenate from water successfully via anion exchange and precipitation [8].

Since 1989 when the “structure memory effect” of layered double hydroxides was first reported [9, 10], it has been acknowledged that thermal treatment of LDHs is an effective way to enhance their anion uptake capacity [11–13], and therefore a full understanding of thermal behavior of hydrocalumite is quite important for its efficient application as a sorbent in reducing aqueous anionic contaminants. It is generally accepted that the thermal decomposition process of hydrocalumite can be divided into three steps. Lopez-Salinas et al. [14] denoted that the layered structure of hydrocalumite collapses when heated above 250°C, turns into amorphous phases at 300°C, and becomes a solid solution of calcium oxide (CaO) and mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ) at 600–700°C. Vieille et al. [15] indicated that the thermal decomposition of hydrocalumite consists of dehydration, dehydroxylation, and

anion decomposition. These processes may overlap with each other in different extents [16]. Upon cooling to room temperature in ambient atmosphere, low-temperature calcined hydrocalumite (<280°C) can recover its initial layered structure spontaneously, and the reaction rate depends on air humidity and other experimental conditions [15]. In comparison, the amorphous compounds obtained via calcination at 400°C have an ability to reconstruct the original structure of hydrocalumite when exposed to aqueous solution of KCl. In the relevant literatures, the conversion of calcined products to layered hydrocalumite was referred to as different terms, such as regeneration, reconstruction, and rehydration, while the whole process was reported as “calcination-rehydration process” or “structure memory effect” [17]. Although the thermal decomposition of hydrocalumite has been investigated at comparatively low temperature, there is so far a lack of systematic studies on the thermal behavior and structure memory effect of hydrocalumite at higher temperatures. This study focuses on the structural and compositional changes of hydrocalumite upon calcination over a much wider temperature range (400–1500°C). The rehydration process of the calcination products obtained at different temperatures in deionized water was also evaluated.

## 2. Experimental

**2.1. Synthesis of Hydrocalumite.** Hydrocalumite was prepared by the coprecipitation method that has been described elsewhere [18]. Typically, the synthesis was carried out at 65°C under vigorous magnetic stirring. A mixed solution of 0.66 M  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and 0.33 M  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  was added dropwise to a beaker filled with a mixture consisting of water and ethanol in a 2:3 volumetric ratio. The pH was kept constant at 11.5 by the simultaneous addition of 2 M NaOH. The suspension was aged at 65°C for 24 h after the addition of metallic salts had been complete. The solid products were separated by centrifugation and washed several times with deionized water until pH 7-8. The synthesized hydrocalumite sample was subjected to an elemental analysis, based on which its approximate chemical formula was estimated to be  $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{Cl}_{1.71}(\text{OH})_{0.29} \cdot 3.43\text{H}_2\text{O}$  (MM = 543.5 g/mol), very close to the theoretical formula ( $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ ).

**2.2. Calcination and Regeneration Procedure.** The synthesized hydrocalumite was calcined for 2 h in a muffle furnace under ambient atmosphere at the temperatures ranging from 400 to 1500°C with an increasing step of 100°C. The calcination products were cooled to room temperature in a container previously filled with allochromic silica gel as desiccant. The mass of the samples was measured before and after calcination. The regeneration procedure for the calcined hydrocalumite was performed by reacting with deionized water in polyethylene bottles at a constant temperature of 25°C for 24 hours.

**2.3. Characterization Techniques.** The solid samples dried in oven of 50°C were characterized by an X'Pert PRO DY2198 diffractometer with Cu K $\alpha$  radiation, and the XRD patterns

TABLE 1: Mass loss of hydrocalumite samples calcined at different temperatures.

$T$ (°C)	Mass loss (%)
400	26.6
500	27.7
600	31.8
700	31.9
800	34.9
900	31.4
1000	39.1
1100	38.0
1200	40.7
1300	41.6
1400	35.8
1500	40.8

were recorded in the  $\theta$ - $2\theta$  mode between 5° and 65° with a  $2\theta$  step of 0.033°. Their Fourier transform infrared spectra (FT-IR) were obtained using a FTIR Equinox 55 Bruker spectrometer with a scan range of 400–4000  $\text{cm}^{-1}$  and a resolution of 4  $\text{cm}^{-1}$ . The KBr pellet technique was used to prepare the sample that was introduced into the FT-IR cell. The calcined hydrocalumite samples together with those undergoing regeneration procedures were also analyzed with a FEI Quanta200 Scanning Electron Microscope (SEM) equipped with an Energy Dispersive X-Ray (EDX) analytical capability for morphology, crystallinity, and elemental composition. Both SEM and EDX analyses were taken at 20 kV excitation.

## 3. Results and Discussion

**3.1. Mass Loss of Calcined Products.** In general, the mass loss of calcined product increases as the calcination temperature rises, except for three samples heated at 900, 1100, and 1400°C showing anomalously low mass losses. The possible reason is the rehydration of these samples during their cooling to room temperature. The mass loss of hydrocalumite upon calcination at 400°C is 26.6% (Table 1), very close to 23.3%, a theoretical value corresponding to the calcination process during which all interlayer water molecules, including  $\text{OH}^-$  and  $\text{Cl}^-$ , break away from the hydrocalumite structure as other investigators had noticed [14, 15]. In this case, the calcined product could spontaneously reconstruct its original structure with water molecules upon exposure to atmosphere. The calcination products obtained at temperatures higher than 500°C, however, can only regenerate the layered hydrocalumite structure by incorporating anions in aqueous solution. At temperatures higher than 1000°C, the mass loss of hydrocalumite upon thermal decomposition is approaching 40.0%, a value indicating that it broke up into mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ) and lime (CaO) [15]. The formation of these

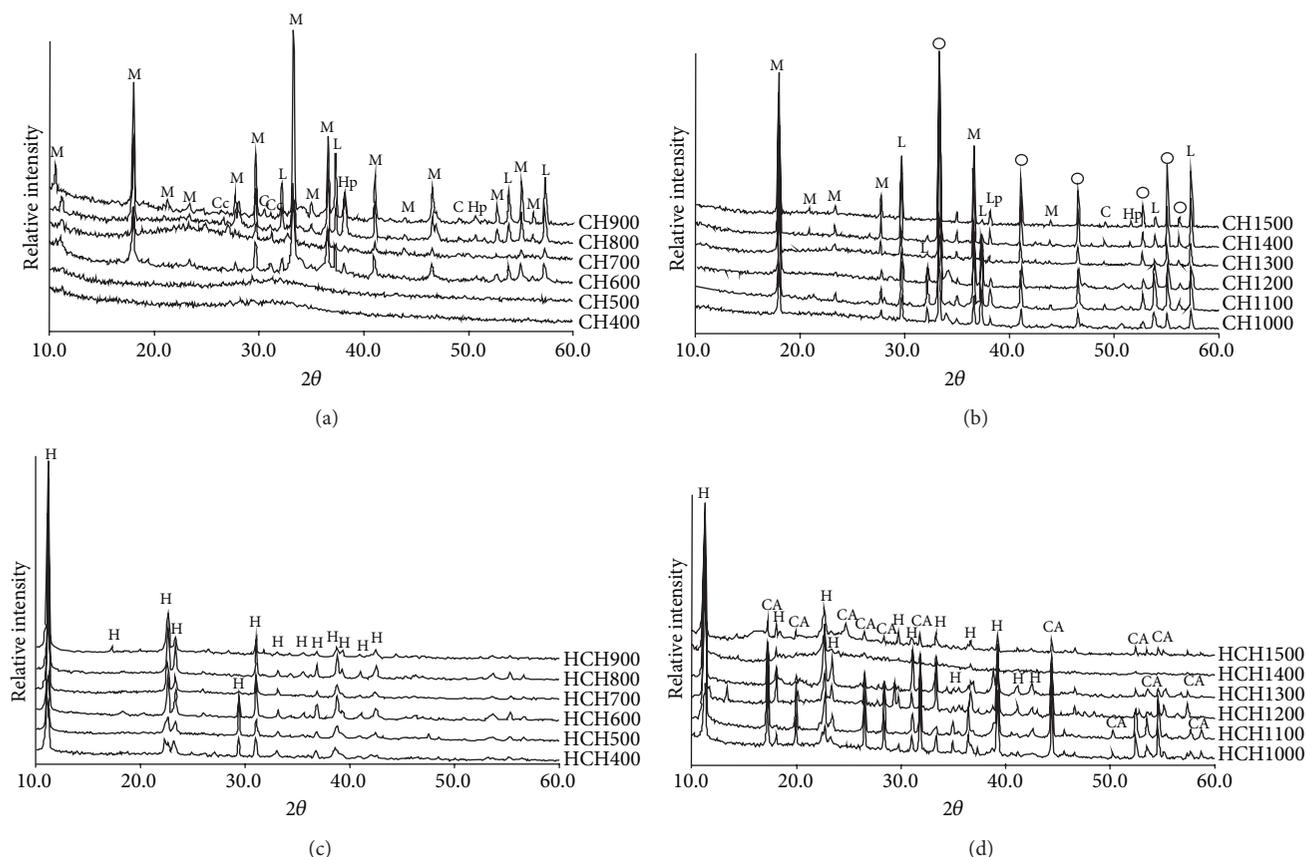
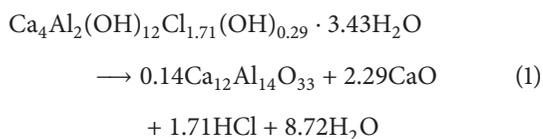


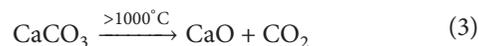
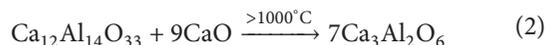
FIGURE 1: XRD patterns of hydrocalumite samples calcined over a temperature range of 400–1500°C and their rehydrated products. (a) Hydrocalumite samples calcined at temperatures ranging from 400 to 900°C; (b) hydrocalumite samples calcined at temperatures ranging from 1000 to 1500°C; (c) rehydrated samples corresponding to those in Figure 1(a); (d) rehydrated samples corresponding to those in Figure 1(b). C: calcite; CA: tricalcium aluminate hexahydrate; Cc: calcium chloride hydroxide; H: hydrocalumite; Hp: hydrophilite; L: lime; M: mayenite; O: tricalcium aluminate.

mixed metal oxides can be expressed as the following reaction:



**3.2. X-Ray Diffraction.** The X-ray diffraction patterns of the calcined hydrocalumite samples obtained at different temperatures as well as their rehydrated products were presented in Figure 1. When calcined over a temperature range of 400–500°C, hydrocalumite was transformed into an amorphous phase and its crystalline structure totally collapsed as demonstrated by the very broad and indistinct XRD peaks (Figure 1(a)). As the calcination temperature increases from 600 to 900°C, hydrocalumite was converted to mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ) and lime (CaO). Several small peaks of calcite ( $\text{CaCO}_3$ ) were also observed. The formation of calcite ( $\text{CaCO}_3$ ) is due to the fact that mixed  $\text{CaO}/\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  solid can act as an effective  $\text{CO}_2$  adsorbent at temperatures of 700–1000°C. Mayenite, as an inert binder, prevented the sintering of CaO during the calcination process and strengthened the

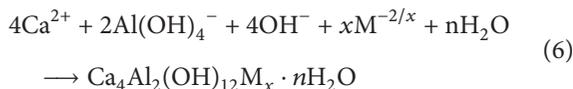
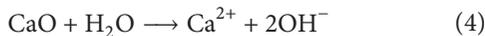
incorporation of CaO with atmospheric  $\text{CO}_2$  [19]. When the calcination temperature was not less than 1000°C, the  $\text{CO}_2$  capture reactivity of calcined products declined evidently as revealed by the decrease in mass ratio of calcite, which is attributed to the conversion of CaO to tricalcium aluminate ( $\text{Ca}_3\text{Al}_2\text{O}_6$ ) at higher temperatures [20]. In Figure 1, the XRD peaks marked with “O” are very close to the standard peaks of both mayenite and tricalcium aluminate, but they were considered to be the latter in view of the positive correlation between their intensity and calcination temperature. The above-mentioned processes were described below:



Moreover, a trace of hydrophilite ( $\text{CaCl}_2$ ) and calcium chloride hydroxide ( $\text{Ca}(\text{OH})\text{Cl}$ ) were identified from the calcination products as well, suggesting that not all interlayer chloride ions escaped during the dehydroxylation process and some of them were combined with calcium in the original hydrocalumite structure to form hydrophilite or calcium chloride hydroxide. Vieille et al. [15] denoted that, after the

release of structural water molecules of chloride-intercalated hydrocalumite driven by calcination, the interlayer chloride anions are closer to the calcium atoms on the layers, improving the possibility of their incorporation. It is also worth noting that all the XRD peaks of minerals in the calcined samples generally become sharper with increasing calcination temperature, reflecting that better crystallinity of calcined products could be acquired at higher temperatures.

Upon mixing with deionized water, the calcined hydrocalumite could totally or partially recover its original layered structure as reflected by the XRD evidence. Hydration is the driving force for the structural reconstruction of hydrocalumite, just like other types of LDHs, for example, hydrotalcite and meixnerite [21]. In Figure 1(c) where the XRD patterns of the rehydrated hydrocalumite samples that were previously calcined at temperatures below 900 °C were presented, only typical peaks for hydrocalumite can be recognized. It implies that the original structure of hydrocalumite was sufficiently recovered as expressed by the following reactions:



where the  $\text{M}^{-2/x}$  could be  $\text{OH}^-$ ,  $\text{Cl}^-$ , and  $\text{CO}_3^{2-}$  with  $\text{OH}^-$  being dominant in this experimental study. In contrast, Figure 1(d) shows the characteristic peaks for both hydrocalumite and tricalcium aluminate, indicating that the hydrocalumite samples calcined at temperatures not less than 1000 °C could be only partially rehydrated. Furthermore, the intensities of the XRD peaks for the reconstructed hydrocalumite decrease with the increase in calcination temperature, suggesting that the structural regeneration ability of hydrocalumite can be impaired significantly by calcination at very high temperatures. The reason is that  $\text{Ca}_3\text{Al}_2\text{O}_6$  in the calcination products could be immediately converted to a stable compound upon exposure to water over 35 °C: tricalcium aluminate hexahydrate ( $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ ) [20]. In this study, the rehydrated solid samples were dried at 50 °C, which offered an enough environmental temperature for the formation of  $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ .

Finally, it is interesting to compare the interlayer spacing values of the regenerated hydrocalumites with that of the original one. It is obvious that the intercalation of  $\text{OH}^-$  resulted in the decrease in  $d$ -spacing of the primary XRD peak (003) of the hydrocalumites recovered from the solid samples calcined at 500, 1000, and 1500 °C (Figure 2), since  $\text{OH}^-$  has a smaller crystallographic radius (0.137 nm) than  $\text{Cl}^-$  (0.168 nm). The hydrocalumite obtained via 500 °C calcination followed by rehydration shows less reduction of interlayer spacing, probably as a result of the incorporation of a trace of carbonate ions with much larger radius (0.189 nm) [22].

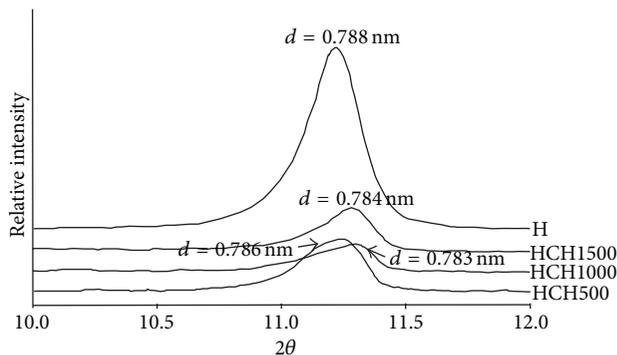


FIGURE 2:  $d$ -spacing of the primary XRD peaks (003) of original hydrocalumite and those regenerated from the samples calcined at 500, 1000, and 1500 °C.

**3.3. Infrared Spectroscopy (FT-IR).** The FT-IR spectra of the original hydrocalumite, the calcined products obtained at different temperatures, and the rehydrated samples are shown in Figure 3. For the original hydrocalumite, the absorption band at  $3639\text{ cm}^{-1}$  represents the stretching vibrations of lattice water together with surface-adsorbed water, while the strong band at  $3477\text{ cm}^{-1}$  is related to the OH stretching vibrations in the portlandite-like layers of hydrocalumite. The band at  $1621\text{ cm}^{-1}$  is assigned to the H–O–H bending vibrations of the interlayer water molecules, and that at  $1433\text{ cm}^{-1}$  can be designated to electrostatically adsorbed  $\text{CO}_2$  on the surface of hydrocalumite micrograins or interlayer carbonate anions, indicating that the as-prepared hydrocalumite is not totally carbonate free. Moreover, the absorption bands at  $789\text{ cm}^{-1}$ ,  $535\text{ cm}^{-1}$ , and  $425\text{ cm}^{-1}$  indicative of metal hydroxides were also detected. The stretching and deformation vibrations of Al–OH are reflected by the band at  $789\text{ cm}^{-1}$ , whereas those of Ca–OH, Ca–O–Ca, and O–Ca–O bonds are reflected by the broad bands at  $535\text{ cm}^{-1}$  and  $425\text{ cm}^{-1}$  [7]. The FT-IR spectra of uncalcined hydrocalumite clearly demonstrate its layered structure composed mainly of  $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ , which match well with the XRD results.

Upon calcination at different temperatures, the FT-IR spectra of hydrocalumite were changed evidently. The band at  $3639\text{ cm}^{-1}$  disappeared from the spectra of all calcined hydrocalumite samples, indicating a total loss of interlayer water molecules. However, the absorption bands representative of other functional groups were still present even after hydrocalumite had been calcined at 1500 °C (Figure 3(b)) but show a decrease in intensity and a shift in wavenumber. It is in agreement with the fact that the expected escape of interlayer anions (e.g., chloride) during calcination was actually prevented by the formation of new minerals as indicated by the XRD analyses. In the low-wavenumber region of the FT-IR spectra, the shifts in the absorption bands generally increase as the calcination temperature rises, implying a progressive collapse of the layered structure of hydrocalumite [15]. However, it is noted that, for the sample obtained at 500 °C, a strong band at  $1418\text{ cm}^{-1}$  is presented in its FT-IR spectra, indicating the formation of certain

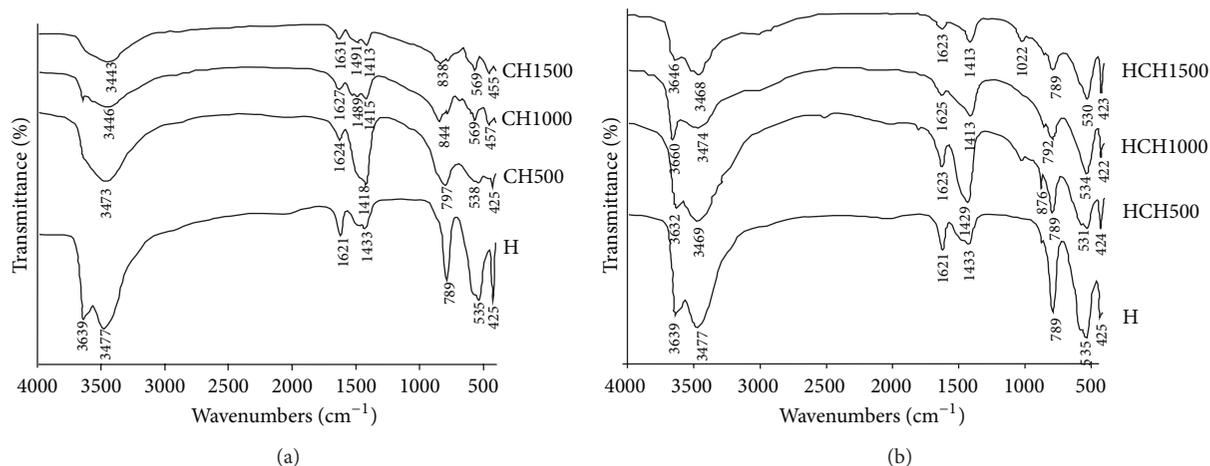


FIGURE 3: IR spectra of hydrocalumite samples calcined at 500, 1000, and 1500°C (a) and their rehydrated products (b). The IR spectra of an original hydrocalumite sample were presented in the figures for comparison.

carbonate-bearing mineral (very likely to be calcite taking account of the XRD evidence). The existence of a weak band at around  $1415\text{ cm}^{-1}$  for the samples calcined at 1000 and 1500°C is indicative of possible  $\text{CO}_2$  capture by CaO during the cooling of calcined products to room temperature.

After contact with deionized water, the band corresponding to lattice water molecules (at around  $3632\text{ cm}^{-1}$ ) reappeared, suggesting different extents of reconstruction of the hydrocalumite structure. Nevertheless, the FT-IR spectra of the rehydrated hydrocalumite samples that had been previously calcined at 1000 and 1500°C showed less similarity to the original hydrocalumite as compared to that calcined at 500°C, demonstrating that the hydrocalumite structure cannot be totally regenerated after being calcined at temperatures over 1000°C. This is in agreement with the XRD results as well. It is worth noting that the FT-IR vibrations indicative of carbonate still existed in the rehydrated samples, although there are no peaks for any carbonate mineral in the XRD patterns of these samples.

**3.4. Scanning Electron Microscope and Energy Dispersive X-Ray (SEM-EDX) Analysis.** The selected samples were also subjected to SEM-EDX analysis for a better understanding of the effects of calcination-regeneration process on the surface morphology and elemental composition of hydrocalumite. As shown in the SEM image, the original hydrocalumite sample presents a hexagonal platy structure (Figures 4(a) and 4(b)). After a treatment of calcination at 400°C and subsequent rehydration, the hexagonal lamellar structure of hydrocalumite was totally reconstructed (Figure 4(c)). More importantly, the regenerated sample shows more complete and larger crystals as compared to the original hydrocalumite (Figure 4(b)). As for the sample calcined at 1000°C and rehydrated in deionized water, less hexagonal hydrocalumite can be identified (Figure 4(d)), implying that only parts of the sample could recover its original structure. In comparison, the sample regenerated from the calcination product at

TABLE 2: Results of EDX analysis for elemental composition of original hydrocalumite and regenerated samples (in atomic percent). The locations where the EDX analyses were made are shown in Figure 4 (points 1, 2, 3, and 4).

Element	Point 1	Point 2	Point 3	Point 4
Ca	13.16	22.34	5.27	24.53
Al	8.49	16.47	3.83	20.37
O	71.70	47.04	62.93	55.09
Cl	6.65	14.16	2.02	—

1500°C is characterized by much more rhombic dodecahedron crystals (Figure 4(e)). These crystals have an elemental composition very close to that of tricalcium aluminate hexahydrate ( $\text{Ca}_3\text{Al}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$ ), as shown in Table 2 (point 4). The results of the SEM-EDX analyses are generally in accordance with the XRD results, suggesting that, with the increase of calcination temperature, the mass ratio of hydrocalumite decreased while that of tricalcium aluminate hexahydrate increased after the calcination-regeneration treatment.

**3.5. Summarization of Calcination-Regeneration Process of Hydrocalumite and Its Comparison with Hydrotalcite.** This is the first systematic study on the rehydration of hydrocalumite calcined over a wide temperature range (400–1500°C). The results of this study show that hydrocalumite heated at temperatures below 500°C can be rehydrated since its positive charged structure ( $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$ ) remained after calcination, while those calcined at and above 600°C can be totally or partially regenerated in water as a result of dissolution of mayenite and lime as well as subsequent reprecipitation of hydrocalumite. To the best of our knowledge, only the mechanism for structural reconstruction of hydrocalumite calcined over a low-temperature range (80–400°C) was clarified in published literatures. Another new point worth being addressed here is that calcite, a secondary calcination product of hydrocalumite, was detected in this experimental

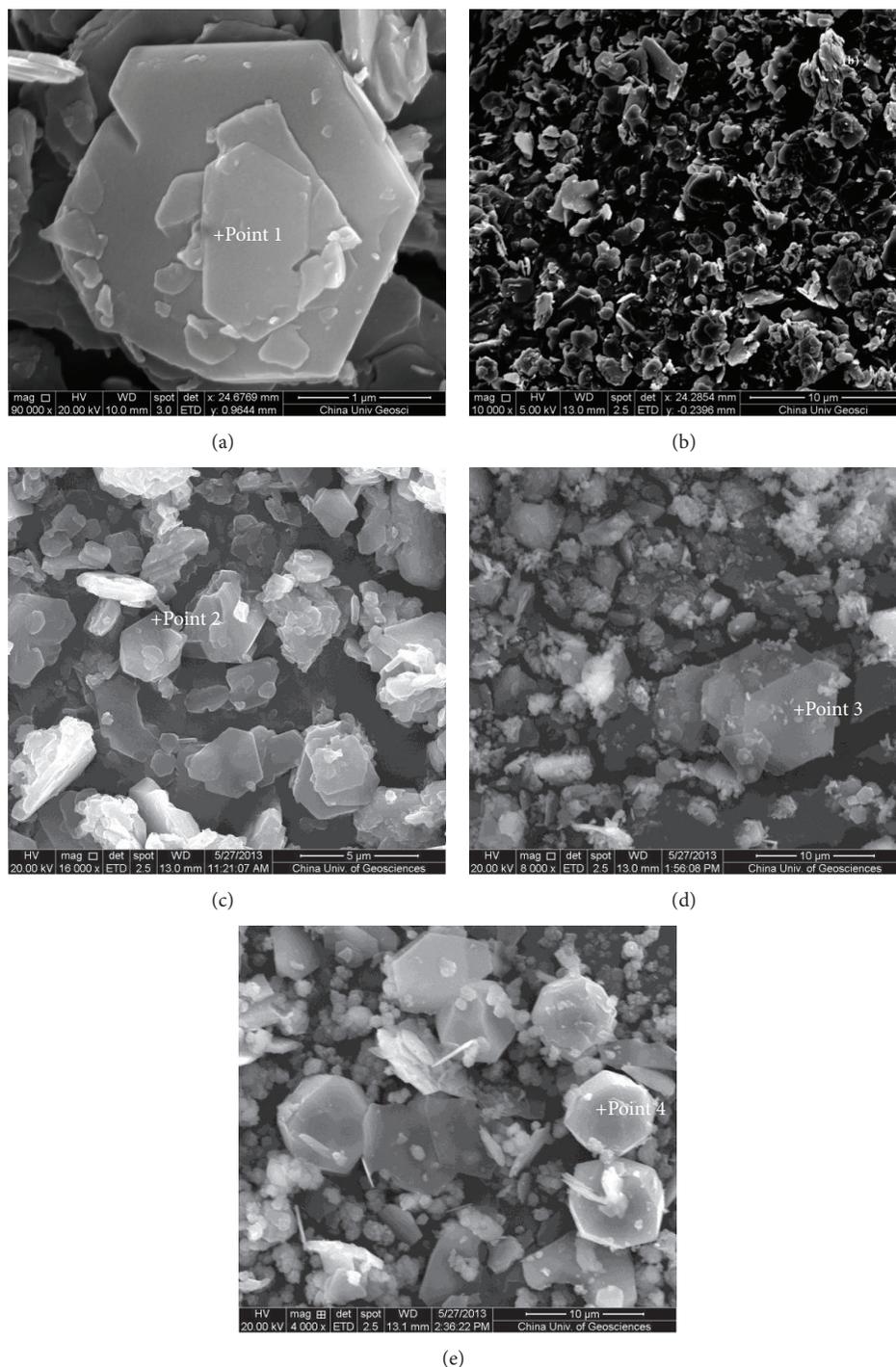


FIGURE 4: SEM images of original hydrocalumite at two different magnifications (a and b) and the rehydrated products of calcined hydrocalumite at 400°C (c), 1000°C (d), and 1500°C (e).

study. It was formed through an effective sorption of  $\text{CO}_2$  by mayenite-bound lime above 600°C.

It is interesting that other types of layered double hydroxides, typically hydrotalcite [23, 24], can reconstruct their destroyed structure by calcination in solution via dissolution-reprecipitation as well. However, as compared to calcined hydrocalumite that can be rehydrated immediately upon

exposure to water and restore its original structure within 24 hours, the calcination product of hydrotalcite shows much slower kinetics in structural restoration. It was reported by Rocha et al. [25] that hydrotalcite previously calcined at 650 and 750°C could be recovered completely after 72 hours of rehydration. The distinctly different reconstruction rates of calcined hydrocalumite and hydrotalcite are probably due to

the much higher solubility of  $\text{Ca}(\text{OH})_2$  (1.59 g/L at 25°C) as compared to  $\text{Mg}(\text{OH})_2$  (0.02 g/L at 25°C) [26]. Furthermore, the calcination-regeneration process of hydrocalumite can be divided into three stages in terms of calcination temperature, whereas only two different stages can be identified for hydrotalcite as confirmed by previous studies. Miyata et al. [27] suggested that the calcination of hydrotalcite at temperatures ranging from 350 to 800°C causes the formation of periclase-like Mg–Al oxide solid solution capable of recovering its layered structure via being treated with pure water or aqueous solutions. In contrast, it has been proved [17, 28, 29] that the heating of hydrotalcite at higher temperatures produces spinel ( $\text{MgAl}_2\text{O}_4$ ), resulting in a partial regeneration of calcined hydrotalcite upon contact with water. It means that hydrotalcite would recover its original structure totally only if calcined at temperatures not higher than 800°C, while this critical calcination temperature for hydrocalumite is 900°C.

#### 4. Conclusions

The results obtained in this study demonstrate that the thermal decomposition behavior of hydrocalumite varies at different temperatures. The extents of structural regeneration of calcination products in deionized water are also different. The hydrocalumite samples calcined over a temperature range of 400–900°C could totally recover their layered structure upon contact with deionized water. However, for those calcined at temperatures not less than 1000°C and reacting with deionized water later, both tricalcium aluminate hexahydrate and hydrocalumite were identified in the rehydrated samples. That is, only parts of the samples heated over 1000°C can be converted to hydrocalumite through reaction with water. Finally it is noted that all the rehydration experiments in this study were conducted using deionized water. Research into appraising the rehydration process of calcined hydrocalumite in aqueous solution containing different types of harmful anions (e.g.,  $\text{B}(\text{OH})_4^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{AsO}_2^-$ ,  $\text{MoO}_4^{2-}$ , and  $\text{SeO}_4^{2-}$ ) is urgently needed for determining optimal temperatures at which hydrocalumite can be calcined and used to remove these anions from solution most efficiently.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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