



Experimental study of formation and relationship between double hydroxide minerals of calcium

Експериментално изследване на образуването и съотношенията на минерали, двойни хидроксиди на калция

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The crystal chemical features of the Ca^{2+} ion lead to greater variety and specific character of the structures of the single calcium – carbonate, sulfate etc. minerals in comparison to those of the other bi-valent cations like Mg, Sr, Ba, Ni и Zn. In the current study the structure characteristics, structure relationships and the chemical stability of three different complex calcium minerals: hydrocalumite – $\text{Ca}_4\text{Al}_2(\text{OH})_{12}(\text{Cl},\text{OH})_2 \cdot 5\text{H}_2\text{O}$, kuzelite – $\text{Ca}_4\text{Al}_2(\text{OH})_{12,8}\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and ettringite – $\text{Ca}_6\text{Al}_2(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ were analyzed. These minerals are rarely observed in nature. That is why in the current study the synthetic samples obtained by standard methodologies were used. Hydrocalumite has been synthesized by co-precipitation of mixed acid solution (CaCl_2 and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) and alkaline solution of NaOH (Miyata, 1980). The ettringite has been obtained by a reaction of CaO with a water solution of $\text{Al}_2(\text{SO}_4)_3$ (Pöllmann, 1989). The kuzelite has been obtained by a hydro thermal treatment (130 °C for 6 hours) of ettringite (Kuzel, 1965).

The three minerals have similar chemical composition but have different structures: the hydrocalumite is a layered double hydroxide (LDH) with a monoclinic

symmetry (SG P 2₁), the kuzelite is also a layered double hydroxide, but with a trigonal symmetry (SG R 3), while ettringite has a chain structure with a hexagonal symmetry (SG P 6₃/mmc). The study of the structural relationships showed that in the presence of sulfate ions the three minerals can have mutual structural transformations. For example from hydrocalumite can be obtain the 2 other structures: the hydrocalumite in a solution of K_2SO_4 crystallizes in ettringite in a 24 hour time interval and room temperature, but crystallizes into kuzelite at temperature of 130 °C for 2 hours. **On the other hand the ettringite structure transforms into kuzelite one after hydrothermal treatment (Fig. 1).** The SEM observations showed that these mineral phase transitions go trough the dissolution of the initial mineral and a subsequent crystallization of new mineral structure.

The chemical stability of the three structures has been tested and it has been determined their place in the previously published (Zaneva et al., 2006) row of the stability of the minerals layered double hydroxides. The test conditions and the obtained results are shown in Table 1.

The experiments showed that all three minerals are destroyed in the environment of chloride solutions of Mg^{2+} , Ni^{2+} и Zn^{2+} , and as a result the hydrotalcite-type layered double hydroxides of the corresponding bi-valent cations are formed. These results imply the place of investigated Ca-Al minerals in the row of stability of the minerals layered double hydroxides as follows: Mg-Al-LDH (hydrotalcite) > Zn-Al-LDH (zakanaite) > Ni-Al-LDH (takovite) >> Ca-Al LDH (kuzelite) ≥ Ca-Al (ettringite) > Ca-Al LDH (hydrocalumite). In the minerals layered double hydroxides with a hydrotalcite-type structure the charge balancing anion is mostly carbonate one. In the studied Ca-Al double hydroxides the carbonate does not practically exist. The study of the behavior of the Ca-Al minerals in car-

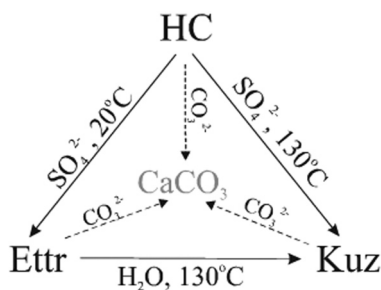


Fig. 1. Mutual relationship of calcium aluminates and inter-relationship with calcium carbonate

Table 1. Chemical stability of double hydroxide minerals of calcium

№	Experimental Environment					Results	
	Min.	Solution	min.H ₂ O, g	T, °C	Time, h	Phase composition	d, nm
1	HC	0.01 M MgCl ₂	1:600	90	24	Mg-Al LDH, Gb, Bay	7.60
		0.01 M NiCl ₂	1:660	90	24	Ni-Al LDH	7.53
		0.01 M ZnCl ₂	1:660	90	24	Zn-Al LDH	7.56
2	Ett	1 M MgCl ₂	1:100	100	0.5	Mg-Al LDH	7.75
		1 M NiCl ₂	1:25	20	24	Ni-Al LDH	7.78
		1 M ZnCl ₂	1:50	20	24	Zn-Al LDH	8.03
3	Kuz	0.01 M MgCl ₂	1:600	90	15	Mg-Al LDH	7.75
1	HC	H ₂ CO ₃	1:100	20	3	Cal, HC, Gb	7.60
		0.1 M Na ₂ CO ₃	1:100	20	2	Cal, Ar, Gb	–
2	Ett	H ₂ CO ₃	1:100	20	3	Cal, Ett	9.80
		0.1 M Na ₂ CO ₃	1:100	20	2	Cal	–

Determined phases: Ar – aragonite, Bay – bayerite, Cal – calcite, Ett – ettringite, Gb – gibbsite, HC – hydrocalumite, LDH – layered double hydroxide with hydrocalcite-like structure

bonate solutions (Table 1) showed that these calcium minerals are unstable in an environment rich in CO₂ regardless of the fact if it is an acid or alkaline one. In both cases, partial or total destruction of Ca-Al min-

erals and the formation of the calcium carbonate(s) and/or aluminum hydroxide are observed (Fig. 1). This result is relevant to the solubility of the simple hydroxides and carbonates of calcium.

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