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HYPOTHETICAL TRANSFORMATION OF $Ca(OH)_2$ INTO $CaCO_3$ IN SOLID-STATE REACTIONS OF PORTLAND CEMENT

Ewa T. Stepkowska[*]

Institute of Hydro-Engineering PAS, 80-953 Gdańsk, Poland

Previous study of the hydration and ageing products of two cement pastes created the basis for the postulate of the course of solid-state reactions between the portlandite $Ca(OH)_2$ and the CO_2 from air in the hydrated and air dry cement.

XRD basal spacing *d*(001) of portlandite exceeded the nominal value and increased with ageing, with the wetting and drying procedure and with carbonate content of the paste, indicating that a part of OH^- ions was gradually substituted by CO_3^{2-} ions, which are about twice bigger. IR spectroscopy showed a considerable content of portlandite, of CO_3^{2-}, of water and silicates. Also HCO_3^-, H_2O and CO_2 in cavities between hexagonal rings and hexagonal hydrates were indicated. By MS (mass spectrometry) in vacuum the evaporation of sorbed water was detected at 100–120°C, of gel water at 350°C of portlandite water at 400°C and of high temperature water between 500 and 700°C, simultaneously with CO_2 escape. Slightly higher peak temperatures were found by the TG test either in air or in argon.

From these results and from geometric considerations it is postulated that the solid-state reactions take place on ageing of the cement paste and on its heating:

hexagonal portlandite→calcium carbonate hydroxy hydrate→calcium carbonate hydrate→
hexagonal vaterite and/or orthorhombic aragonite→rhombohedral calcite

The analysis of the standard files of the calcium carbonate hydroxy hydrates supports this postulate and indicates a gradual transformation.

Keywords: *aragonite, calcium carbonate, calcium carbonate hydroxide, calcium carbonate hydroxide hydrate, carbonation of portlandite, cement hydration, vaterite*

Introduction

Cement hydration results in two main products, i.e. C–S–H gel (kCaO·mSiO$_2$·nH$_2$O, amorphous) and portlandite (P, $Ca(OH)_2$). On a prolonged storage in air of the hydrated paste, the OH^- ions may be substituted by CO_3^{2-} ($\leftarrow CO_2+2OH^- - H_2O$) and also CaO, if present, may be transformed into $CaCO_3$. This was found in the study of the aged pastes; it occurs in form of stable calcite, C, and/or metastable aragonite (A) and vaterite (V). All of them were detected by XRD.

The study of the hydrated and aged paste by XRD, DTA/DTG/TG, IR and MS (mass spectroscopy) gave inconsistent results, which were published elsewhere [1–5]. Indication was obtained on the possible course of this reaction, which is presented hypothetically below, and will be checked in the future study.

Experimental

Materials and method

Two cement pastes from India of different strength and different specific surface (C-33<C-43), were hydrated for 1 month at $w/c=0.4$. As freshly hydrated they were studied by static heating (SH) at 110, 220, 400, 600 and 800°C. After ageing for 1 year they were tested by XRD, SEM and HRTEM [1, 2] and after 5–6 years [3–5]:

- by XRD (Philips X-pert-Pro with high *T* chamber Anton Parr, HTK 1200, X'celerator, copper tube and θ–θ goniometer),
- by DTA/DTG/TG (Seiko TG/DTA 6300, 1 K min^{-1}, up to 1000°C, in argon or in air)
- by IR spectroscopy in KBr discs after heating at various temperature (Nicolete, FT-IR 510),
- by mass spectrometry (MS) of H_2O and CO_2, measured by Balzers Quadstar quadrupole QMS200 mass spectrometer and by the CI electronic microbalance, up to 800°C at the heating rate 5 K min^{-1}, in vacuum

Hypothetical interpretation of joint results is indicated below.

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[*] est@ibwpan.gda.pl

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Results

XRD of the aged pastes

The values of basal spacings, as observed in the aged paste, are presented in Table 1 [5]. They are generally exceeding the nominal ones and also they increase with ageing time and with wetting–drying procedure, whereas they are lowered after acetone pretreatment. Also the stronger paste (C-43), containing less carbonates in the aged state, indicated generally lower basal spacings, and they did not change with ageing time exceeding 1 year, what was the case of the weaker one C-33.

The main XRD peak of portlandite, *d*(001), was at room temperature the highest. In the stronger paste C-43, it was relatively higher than in C-33, where it was almost equal the calcite peak (6-year old paste). In both cases it disappeared above 400°C. The value of *d*(001) exceeded the nominal one, i.e. 4.895 Å (72-156) and it increased with ageing : in paste C-33 it was 4.925 and 4.936 Å, in paste C-43 it was 4.916 and 4.916 Å, after 1 and 6 years, respectively (Table 1). It increased with *T* showing a high thermal expansion coefficient [5], compared to [6]. The high *d*(001) basal spacing may be due to substitution of some part of OH^- ions by the bigger CO_3^{2-} ions resulting in (*i*) the increased basal spacing, (*ii*) increased thermal expansion coefficient, (*iii*) simultaneous escape of H_2O and CO_2 observed by MS between 500 and 650°C, (*iv*) a complex mass loss between 500 and 700°C observed by TG (see below). The net ionic lattice energy is lowered.

The carbonation of portlandite by the CO_2 from air is especially important at the temperature of its decomposition. This may also involve the adsorbed CO_2, which could be present in C-33 (IR).

The main calcite peak (3.04 Å) was low and broad at room temperature, indicating its limited content or poor crystallinity. It was slightly lowered at 220°C, increased above 400°C after decomposition of portlandite, and after transformation of aragonite, and vaterite, into calcite (at 450°C according to Lucas *et al.* [6]) and this peak disappeared above 700°C. Calcite peaks were relatively higher in C-33, than in C-43. These peaks became the highest after the disappearance of portlandite peak and after transformation of aragonite and vaterite into calcite. These compounds were found as nanocrystals by HRTEM, aragonite indicating a better crystallinity than vatertite [2]. Thus the change in peak intensity of calcite on heating may be due to various reasons.

In case of small crystallites of low crystallinity the peaks are low and broad; calcite may be present in form of nanocrystals (found by HRTEM) and amorphous material. Transformation of other components (A and V) into calcite increases its peak intensity. The decomposition of portlandite and disappearance of its peaks results in the increase in the relative intensity of calcite peak formed by carbonation of $Ca(OH)_2$.

In analogy with portlandite the CO_3^{2-} ions in carbonates may be partly substituted by OH^- ions, which remain from the original P, lowering the regularity of the crystal lattice. In some cases the *d*(*hkl*) spacings of vaterite were smaller than the nominal ones (Table 1). Thus there may be some vacancies causing a decrease in the ionic lattice energy and the thermal expansion coefficient becomes higher [5].

IR spectroscopy

IR at room temperature showed a considerable content of portlandite (3644 cm^{-1}), of CO_3^{2-} (1488–1411 and 875 cm^{-1}), of water (3447 cm^{-1}) and silicates (1048–971 cm^{-1}). Also HCO_3^-, coinciding with other compounds, H_2O and CO_2 in cavities between hexagonal rings and hexagonal hydrates were possible, as indicated by very small peaks at 3690–3674 and 2346 cm^{-1}, respectively [4]. Figures 1a and b presents the IR spectra of pastes pretreated in acetone, at room temperature and heated at 400°C.

Portlandite content was found higher in C-43 and it was still present at 400°C, whereas it disappeared in C-33.

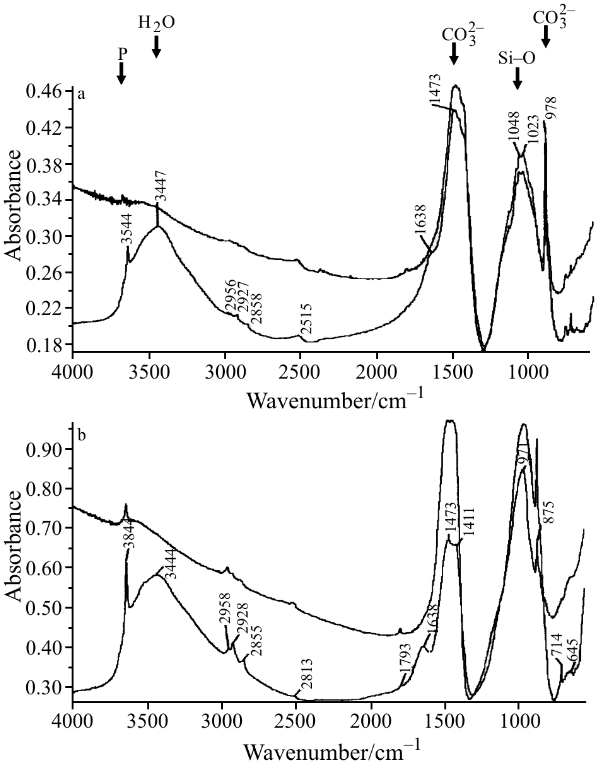

Fig. 1 IR spectra of the acetone pretreated pastes, at room temperature and heated at 400°C: a – C-33-ac and b – C-43-ac

Table 1a Basal spacings (Å) measured by XRD in the paste C-33 after ageing for 1 and 6 years and also after acetone pretreatment (ac) and after wetting and drying (wet–dry)

Compound	C-33 1 year		C-33 1 year (ac)		C-33 6 years		nominal d		
		(wet–dry)		(wet–dry)		(ac)			
a	b		c		d		f		
		5.612							
portlandite	4.925	4.937	4.902	4.912	4.936	4.931	4.985	P	001
	4.247	4.395		4.685		4.000			
	3.839	3.889		4.386		3.908			
				3.860					
	3.578	3.585		3.587	3.584				
aragonite	3.403	3.394			3.405	3.400	3.397	A	111
vaterite	3.318	3.296	3.318	3.289	3.296	3.295	3.294	V	112
							3.274	A	021
portlandite	3.113		3.103	3.110	3.114	3.118	3.105	P	100
calcite	3.038	3.038	3.026	3.035	3.046	3.043	3.035	C	104
		2.978			2.978				
	2.880	2.880	2.871	2.871	2.889	2.881			
	2.783	2.785	2.776	2.779	2.786	2.783	2.783	b,a	–121
vaterite	2.742	2.742	2.737	2.743	2.746	2.750	2.730	V(b,a)	114
portlandite	2.631	2.633	2.622	2.625	2.635	2.633	2.622	P	101
		2.612		2.492		2.392	2.610	b	301
	2.500	2.567		2.460		2.337			
	2.449	2.498	2.448		2.490	2.311	2.373	A	112
	2.410	2.412	2.282	2.282	2.289	2.283	2.285	C	113
	2.284	2.287	2.182	2.191	2.196	2.187			
vaterite	2.189	2.192			2.099	2.095	2.113	V	008
	2.093	2.099		2.088		2.022			
vaterite	2.063	2.062			2.064		2.063	V	300
	1.982	1.982	1.982	1.978	1.980	1.985	1.977	A	221
portlandite	1.928		1.925	1.926	1.930	1.927	1.922	P	102
		1.913	1.874	1.876	1.880	1.918			
		1.877							
vaterite	1.824	1.822	1.826	1.822	1.824		1.820	V	118
	1.796		1.793	1.795	1.799		1.793	P	110
	1.764	1.740	1.759						
	1.687		1.686	1.686	1.690		1.683	P	111
	1.632			1.658					
	1.483		1.481	1.484	1.485		1.480	P	201
			1.448				1.444	P	103
					2.701				
					2.025				

The carbonate content was higher in C-33 and it increased at 400°C, more in C-43 than in C-33. In both cases the doublet peak of CO_2^{2-} was found at 1473–1411 cm^{-1}, the lower value indicating calcite (1435–10 [7], 1440 and 1407 cm^{-1} [8]), the higher one corresponding to aragonite (1493–70 [7], 1490 cm^{-1} [8]) and vaterite (1450–20 [7], 1490 and 1420 cm^{-1} [8]), or to calcite of imperfect lattice, thus of a lowered vibration energy (higher wave number).

Table 1b Basal spacings (Å) measured by XRD in the paste C-43 after ageing for 1 and for 6 years and also after acetone pretreatment (ac) and wetting and drying (wet–dry)

Compound	C-43 1 year		C-43 1 year		C-43 6 years (ac)		C-43 800→32°C		nominal d		
		(wet–dry)	(ac)	(wet–dry)							
a	b		c		d		e		f		
	5.587	5.622		5.625							
portlandite	4.916	4.927	4.914	4.927	4.916	4.916			4.895	P	001
	4.678	4.407									
	3.872	3.872					3.881	C_3S			
	3.578	3.582		3.864	3.870	3.856	3.841	C_2S			
					3.580	3.580	3.489				
aragonite	3.404	3.396	3.395	3.403	3.394	3.394	3.392	C_2S	3.397	A	111
vaterite	3.295	3.289	3.283	3.295	3.291	3.291	3.186	C_2S	3.294	V	112
portlandite	3.108		3.114	3.109	3.112	3.111	3.154		3.105	P	100
calcite	3.032	3.036	3.036	3.037	3.035	3.035	3.049	C_3S	3.035	C	104
					2.781	2.781	2.887	C_2S			
	2.777	2.775	2.779	2.778			2.784	CaO			
	2.739	2.742	2.737	2.724	2.743	2.743	2.764	C_3S			
portlandite	2.627	~2.63	2.631	2.629	2.630	2.630	2.709	C_3S	2.622	P	101
	2.606	2.605					2.651				
	2.493	2.486		2.500	2.492	2.492	2.555	C_2S			
	2.369						2.455	C_2S	2.373	A	112
	2.285	2.285	2.284	2.290	2.285	2.285	2.411	CaO	2.285	C	113
	2.185	2.197	2.186	2.192			2.382	$C_{2.3}S$			
	2.105	2.115	2.109	2.109	2.107	2.107	2.289	C_2S			
vaterite	2.061	2.066	2.057	2.053	2.060	2.060	2.246		2.063	V	300
	1.975	1.976	1.985		1.984	1.984	2.199	$C_{2.3}S$	1.977	A	221
	1.927	1.912	1.927	1.927	1.928	1.928	2.144		1.922	P	102
	1.877			1.878	1.877	1.880	2.108	C_2S	1.815	A	132
vaterite	1.822	1.821	1.826	1.829	1.820	1.815	2.088	C_3S	1.820	V	118
	1.795		1.797	1.796	1.796	1.796	2.048	C_2S	1.793	P	110
	1.740	1.743					1.977	C_3S			
	1.688		1.687	1.686	1.688	1.688	1.947	C_3S	1.683	P	111
	1.626						1.925				
	1.489	1.488	1.484	1.485			1.829	C_3S	1.480	P	201
	1.449						1.797	C_2S	1.444	P	103
							1.764	C_3S			
							1.742				
					3.182	3.185	1.738	C_2S			
							1.703	CaO			

Mass spectrometry, MS

MS spectra (in vacuum) were different depending on the paste quality and preparation. In Fig. 2 these spectra are compared to paste C-33, C-43 [4] and to paste C-43-I with a lower density and hydrated in distilled water [3].

In the first case, C-33 (Fig. 2a) the sorbed water escaped at 120°C, which peak was connected by a plateau with the bump at about 350°C (C–S–H gel water) on the peak with maximum at 400°C (portlandite water), followed by a rapid drop and the escape of residual water between 500 and 700°C. In the second case (Fig. 2b) sorbed water escape started at 100°C, it proceeded up to the peak at 400°C and the residual water evaporated between 500 and 700°C. In the third case

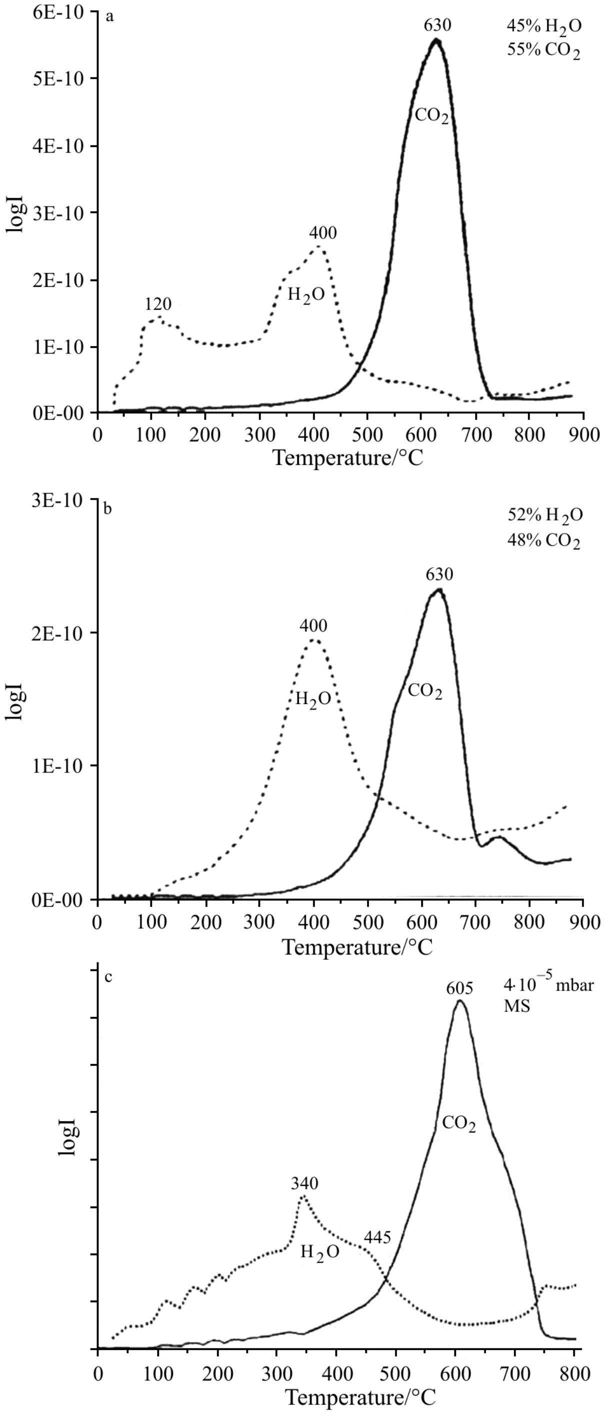

Fig. 2 Mass spectrometry curves of the aged pastes (5–6 years), a – C-33, b – C-43 [4] and c – C-43-I [3]

(Fig. 2c) the most important peak was observed at 340°C, followed by a bump at 445°C and after the escape of residual water at 500–600°C a small peak was found at 750°C, which was smaller in Fig. 2b.

CO_2 evolution started at about 300°C (Figs 2a–c) and showed a bump at about 550, a peak at 630°C (Figs 2a and b) or at 605°C (Fig. 2c). In Fig. 2b another peak is observed about 750°C. This indicates the presence of three carbonates, decomposing at respective temperature. TG showed a complex mass loss between 500 and 700°C, corresponding to a simultaneous escape of H_2O and CO_2.

Thermal analysis

The TG results in aged pastes were estimated from the straight linear sections of the TG curves, determined graphically. In SH the temperature ranges were determined from experiment.

Both C–S–H gel water (220 to 400°C) and portlandite water content (400 to 600°C), measured by static heating in fresh pastes, were higher in C-43 than in C-33 (6.7 and 6.4% in C–S–H gel; 5.6 and 3.1% in P, respectively [4]). It changed to 8.7 and 5.7% in C–S–H gel+hydrates; 3.2 and 2.6% in P, respectively in 5-year old pastes (TG). A part of the sorbed water (13.2 and 10.3% in freshly hydrated, 7.6–7.5% after 5 years) was more strongly bound on ageing and escaped partly as hydrate and gel water (160–450°C) and partly between 500 and 700°C together with CO_2 (2.6 and 5.2%, respectively, compare MS), which was especially high after acetone pretreatment of C-43 (11.1%) [5], Fig. 3.

The quantity of calcite determined from the mass loss in air between 685 and 760°C was similar in both aged pastes (7.8–7.9% after 5 years), indicating a similar sensitivity to carbonation. In the freshly hydrated ones it was higher in the weaker paste C-33 than in C-43 (5.7 and 3.3%, respectively).

The peaks in DTG were observed at temperature depending on environment: the highest temperature was found in air (470 and 720–740°C), lower in argon (450 and 680–710°C) and the lowest in vacuum (MS, 400 and 630°C for portlandite and calcite, respectively, lower in C-43 than in C-33). The nominal temperature of their decomposition is 580 and 898.6°C, respectively.

Interpretation

These observations are interpreted hypothetically as follows: on the prolonged contact with CO_2 from air, the carbonate ions (CO_3^{2-} and $HCO_3^- \leftarrow CO_2 + OH^-$) are substituting gradually the OH^- ions in the hexagonal lattice of portlandite and causing an increase in the *d*(001) spacing, as they are about twice bigger. This causes a decrease in ionic lattice energy and in temperature of portlandite decomposition. Also water may be present in the cavities between hexagonal rings (IR).

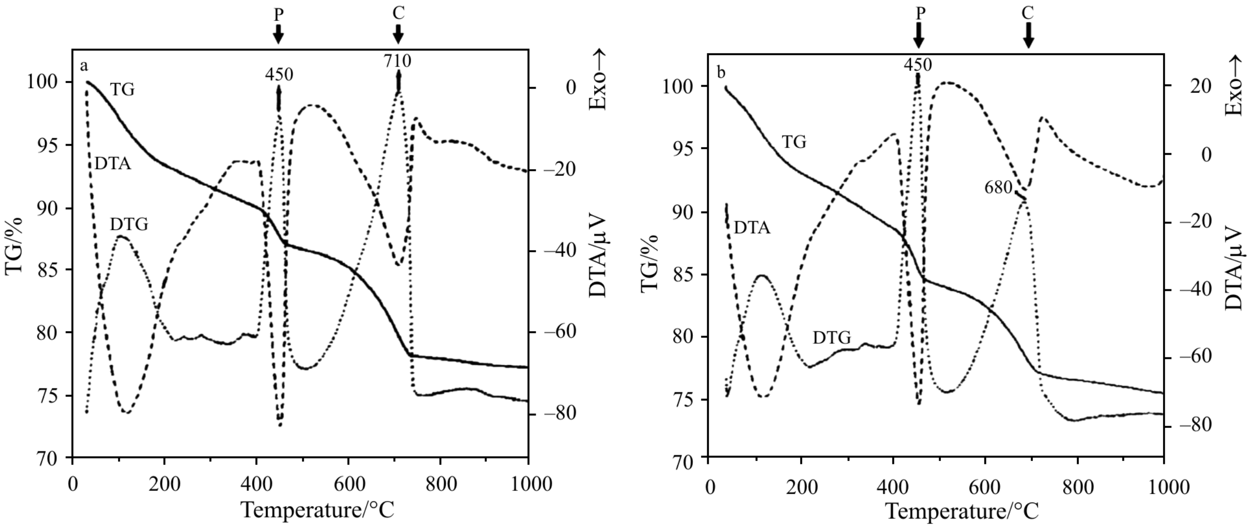

Fig. 3 Thermoanalytical curves of paste a – C-33 and b – C-43, both heated in argon [4]

Standard basal spacings

Four standard files of synthetic portlandite were found in JCPDS-ICDD and the lowest one 4.895 Å was selected as reference.

	72-156	4-733	87-673	44-1481
d(001)=	4.895	4.900	4.911	4.922 Å

Each $CaCO_3$ species was represented by a single file

C – 5-586 A – 41-1475 V – 33-268

and the values of *d*(*hkl*) were similar (generally only slightly higher) as those measured in the hydrated pastes, Table 1.

It is postulated that only the lowest basal spacing (*d*(001)=4.895 Å, 72-156) represents a pure or almost pure portlandite, otherwise it contains some CO_3^{2-} ions.

Solid-state reactions

It is postulated here that on ageing of cement pastes, containing (IR, Fig. 1) portlandite, OH^-, H_2O, CO_2, HCO_3^-, CO_3^{2-}, vaterite, aragonite, calcite (CSH gel, sil-

Table 2 Crystallographic parameters of calcium carbonate hydrates

Compound	System	*a*/Å	*b*/Å	*c*/Å	File number
ikaite	monoclinic	8.792	8.310	11.021	75-1733
$CaCO_3·6H_2O$		8.870	8.230	11.020	37-416
$CaCO_3(H_2O)_6$		8.870	8.230	11.020	72-670
monohydrocalcite	hexagonal	6.092		7.534	22-0147
$CaCO_3·AH_2O$		10.566		7.573	29-306
$CaCO_3·H_2O$		6.093		7.545	84-49
$CaCO_3·H_2O$		10.554		7.545	83-1923
$CaCO_3·H_2O$		6.093		7.545	83-1922
calcium carbonate hydroxide $Ca_3(CO_3)_2(OH)_2$	?	d_{max}=2.94	*d*=7.75	*d*=2.68 *d*=2.72	23-0106
calcium carbonate hydroxide hydrate $Ca_3(CO_3)_2$ $(OH)_2A\ 1.5H_2O$	?	d_{max}=2.73	*d*=3.28	*d*=3.06	23-0107
defernite $Ca_6(CO_{2.65})_2$ $(OH_{.66})_7(H_2O)_2$	orthorhombic	17.860	22.78	3.658	78-1540

22-0147: The sample is described in: Marschner, Science, 165 (1969) 1119 ; 83-1922 and 83-1923: H. Effenberger, Monatsh. Chem. V., 112 (1981) 899; 29-306: G. Taylor, South Australia. Am. Mineral. V., 60 (1975) 690; 84-49: H. Effenberger and K. Lueger-Ging, European Crystallographic Meeting, 8 (1980) 107; 23-106: Sample from: J. Schaefer, Kalkwerke 6252 Diez/Lahn Germany. Powder data also from Phys. Blatter, 5, 213-16 (1970). Mwt: 274.27; 23-107: Sample from: J. Schaefer, Kalkwerke 6252 Diez/Lahn Germany. Powder data also from Phys. Blatter, 5, 213-16 (1970). Mwt: 301.30; 78-1540: B. W. Liebich and H. Szarp, Schweiz. Mineral. Petrogr. Mitt., 65 (1985) 153.

icates etc. are not discussed here), the solid-state reactions may occur, as mentioned below:

hexagonal P→calcium carbonate hydroxy hydrate→
calcium carbonate hydrate→
hexagonal V and/or orthorhombic A→
rhombohedral C

The calcium carbonate hydroxy hydrates, etc. may not be detected by XRD as their content may be small, their crystallinity low and their stoichiometric composition variable. Those described in standard files and listed in Table 2. Analyzing the data in Table 2 it is postulated that between pure portlandite $Ca(OH)_2$ and pure $CaCO_3$ there may exist the whole series of transitional compounds, as mentioned above, not all of them being present in the standard files.

Acknowledgements

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