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Studies on the basic compounds of magnesia cement: the thermal behaviour of magnesium oxychlorides *

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Abstract

The magnesium oxychlorides, $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ and $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, were prepared by dissolving active MgO in magnesium chloride solution to form a metastable system; the two crystalline oxychloride phases then form, one after the other, both with 5-form structure (S. Sorel, C.R., 65 (1867) 102; W.F. Cole and T. Demeduck, Aust. J. Chem., 8 (1955) 234). The samples of magnesium oxychlorides were studied by chemical analysis and confirmed by X-ray powder diffraction, DTA, DSC, TG, DTG, IR spectroscopy and electron microscopy. The results showed that both compounds change during heating at different temperatures but that the final products were both MgO. Their ΔH values of dehydration and decomposition were determined by DSC, and the thermochemical reactions are given.

INTRODUCTION

Magnesium oxychloride cement, also known as Sorel cement, was discovered by Sorel in 1867 [1]. This cement is formed by mixing finely divided magnesium oxide with an aqueous solution of magnesium chloride. Magnesium oxychloride cement possesses high compressive and flexural strength, high fire resistance and low thermal conductivity. It can be combined with many organic and inorganic aggregates, and looks like marble. Used primarily as flooring material by virtue of is acoustic and elastic properties, it has also been used as decorative interior plaster and exterior stucco, particularly with embedded stone aggregates. In recent years in China, it has been used for worksheds, packing material and in glass fibre tiles. The use of magnesium oxychloride cement is not as widespread as that of other cements because it has three disadvantages: a poor water resistance, a short lifetime and deformation and it causes corrosion of steels. It is important to study the thermal behaviour of the oxychlorides if Sorel cement is to be used widely.

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Four magnesium oxychloride compounds are known: $5Mg(OH)_2 \cdot MgCl_2$ $8H_2O$ (abbreviated as 5 · 1 · 8 or 5-form) and $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ (3 · 1 · 8 or 3-form) below 100 ° C, and $2Mg(OH)_2 \cdot MgCl_2 \cdot 5H_2O$ (2 · 1 · 5 or 2-form) and $9Mg(OH)_2 \cdot MgCl_2 \cdot 6H_2O$ (9 · 1 · 6 or 9-form) above 100 ° C [2]. Early investigations established [3,4] that the process of cement formation involved gel formation and crystallization of ternary oxychloride phases. Walter-Levy and co-workers [5,6] identified crystalline phases 5 · 1 · 8 and 3 · 1 · 8. The 3 · 1 · 8 phase belongs to the triclinic system, and the 5 · 1 · 8 to the monoclinic system. The crystal structure parameters of 3 · 1 · 8 are $a = 8.31$ Å, $c = 7.44$ Å, $\alpha = 102°54'$ and $\gamma = 85°39'$. The density determined by experiment is 1.859; the calculated value is 1.858. The structure parameters of 5 · 1 · 8 are $a = 9.66$ Å, $b = 3.14$ Å, $c = 8.29$ Å, $\alpha = 90°$, $\beta = 114°18'$ and $\gamma = 90°$. The density determined by experiment is 1.888; the calculated value is 1.925 [5].

The magnesium oxychlorides form structures with networks of needle-like crystals. The magnesium oxychlorides were studied by thermal analysis. It has been demonstrated that 5 · 1 · 8 and 3 · 1 · 8 dehydrate to form the pentahydrated, trihydrated and anhydrous oxychlorides during heating [7–11]. Cole and Demeduck [2] discovered that the dehydration products were the pentahydrated, tetrahydrated, trihydrated and anhydrous oxychloride compounds. Kassner [12] suggested that the dehydrated product is mixed oxychlorides at 130 ° C, the monohydrate at 200 ° C and MgO at 260 ° C. Bullin [13] studied the dehydration of 5 · 1 · 8 and 3 · 1 · 8 under different water pressures, formulated Arrhenius equations of dehydration for 3 · 1 · 8 and 5 · 1 · 8 at different temperatures, and obtained some new results by physical and chemical methods. The change in microstructure of the oxychlorides during heating was demonstrated by electron microscopy.

MATERIALS AND METHOD

Materials

Magnesium oxide was obtained by calcining basic magnesium carbonate, $Mg(OH)_2 \cdot 4MgCO_3 \cdot 5H_2O$, in an electric furnace at 600 ° C for 2–3 h. The resultant MgO was confirmed by X-ray diffraction, which also indicated traces of basic magnesium carbonate. A solution of $MgCl_2$ (specific gravity 1.2 g cm^3) was prepared by dissolving $MgCl_2 \cdot 6H_2O$ (A.R. grade reagent) in redistilled water. The other chemical reagents were analytically pure.

Preparation of specimens

Magnesium oxide (29) was dissolved in 500 ml of 2.5 M $MgCl_2$ aqueous solution at 50 ° C and stirred for 2–3 h. The solution was filtered and kept at room temperature for different periods of time. The 5 · 1 · 8 compound

TABLE 1

The analysis of the oxychlorides

No.	Mg^{2+}(%)	Cl^-(%)	OH^-(%)	$Mg(OH)_2:MgCl_2:H_2O$
1	27.18	13.42	32.07	4.98 : 1 : 8.01
2	27.45	13.36	32.07	5.00 : 1 : 8.00
3	23.47	17.11	24.03	3.00 : 1 : 8.00

crystallized out first; the solid phase was separated by centrifuging and was washed thoroughly with alcohol [14,15]. It was dried under an IR lamp and stored in a desiccator over saturated $Na_2Cr_2O_4$ solution [16]. The composition of the samples was determined by chemical analysis and verified by X-ray powder diffraction. The 3 · 1 · 8 compound crystallized out later and was treated similarly.

The specimens were analysed as follows: the amount of Hg^{2+} was determined by titration against ethylenediaminetetraacetic acid, volumetric (EDTA) solution, Cl^- by $Hg(NO_3)$ [17], OH^- by titration against acid and water was determined by difference. The compositions of 3 · 1 · 8 and 5 · 1 · 8 are shown in Table 1.

Experimental method

The DTA curves were recorded using a DRC-1 thermal analyser, made in China, and the enthalphies of dehydration and decomposition were measured on a Perkin–Elmer DSC-2 differential scanning calorimeter. The TG and DTG data were determined on a Perkin–Elmer TGS-2 thermograph analyser. The temperature was calibrated using percalloy. The samples (3–5 mg) were heated from room temperature up to 700 °C at a heating rate of 10 °C min^{-1} in flowing nitrogen.

The IR spectra were recorded (KBr disk method) using a Hitachi EP-1 and a Perkin–Elmer 683 spectrophotometer.

An X-ray diffractometer, model D/MAX-111-B, made in Japan, was used: the experimental conditions were Cu $K\alpha$, 40 kV, 50 mA, and a scan rate of 10° min^{-1} with intervals of 0.01°. The electron microscope was a Hitachi H600 (700 kV).

The samples were heated isothermally to constant weight in a thermostatted muffle furnace in air. Samples were obtained at every stage and were investigated by X-ray diffractometry, thermoanalysis, IR spectroscopy and electron microscopy.

RESULTS AND DISCUSSION

The results shown in Table 1 indicate that the 3 · 1 · 8 and 5 · 1 · 8 forms have eight molecules of water; this was confirmed by X-ray diffractometry, with the results shown in Table 2.

TABLE 2

Data from X-ray powder patterns of magnesium oxychlorides

$3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$				$5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$			
Experimental data		JCPDS [a] data		Experimental data		JCPDS [b] data	
d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
8.130	100	8.066	100	7.661	55	7.576	50
7.092	20	7.075	92	7.505	92	7.407	100
5.952	30	5.933	21	4.171	100	4.132	75
4.065	35	4.048	47	3.732	18	7.704	14
3.876	70	3.854	62	3.287	5	3.257	14
3.559	25	3.550	21				
3.058	16	3.039	8	2.987	4	2.959	16
2.717	25	2.706	32			2.899	18
2.611	10	2.605	11	2.732	19	2.717	25
2.532	3	2.560	5	2.651	4	2.639	55
2.457	50	2.445	57			2.558	14
2.410	18	2.406	15	2.432	14	2.421	90
2.522	8					2.392	55
1.567	14			1.975	9	1.972	45
1.980	10					1.927	14
1.862	10	1.857	12	1.845	5	1.842	14
1.490	8	1.490	6			1.572	30
1.319	8					1.541	30
						1.451	16

[a] X-ray powder diffraction in D/Max 3B No. 70412.

[b] X-ray powder diffraction in D/Max 3B No. 70426.

DTA, TG, DTG and DSC peaks

Five endothermic peaks appear on the DTA curve of 3 · 1 · 8 during heating: the peak temperatures are 94, 149, 189, 216 and 446 ° C respectively. The DSC curve has one more endothermic peak at 388 ° C. The enthalpy values determined by DSC dehydration and decomposition (Fig. 1) are $\Delta H_{1a} = 78.36$ kJ mol^{-1}, $\Delta H_{2a} = 286.9$ kJ mol^{-1} and $\Delta H_{3a} = 666.35$ kJ mol^{-1}. On the DTA curve of the 5 · 1 · 8 form, there are six endothermic peaks at 90, 140, 202, 250, 390 and 430 ° C respectively.

The enthalpy values determined by DSC during dehydration (Fig. 2) are $\Delta H_{1b} = 76.58$ kJ mol^{-1} and $\Delta H_{2b} = 353.36$ kJ mol^{-1}, and that of decomposition is $\Delta H_{3b} = 607.0$ kJ mol^{-1}.

The DTG and TG curves of 5 · 1 · 8 and 3 · 1 · 8 are also given in Figs. 1 and 2.

The high temperature DTA curves of magnesium oxychlorides from 500 to 1300 ° C are flat, with no phase transition. The results of the isothermal analysis are shown in Table 3.

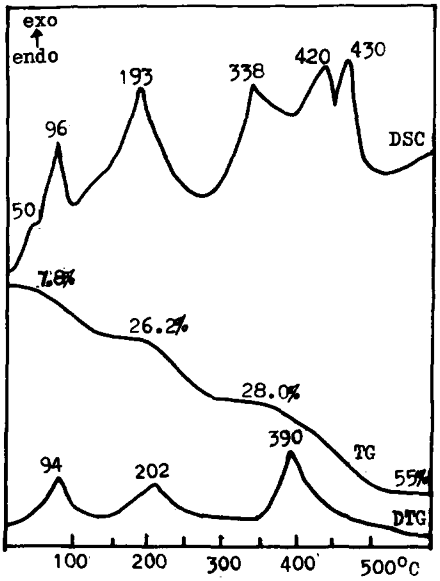


Fig. 1. TG, DTG and DSC curves of 5·1·8.

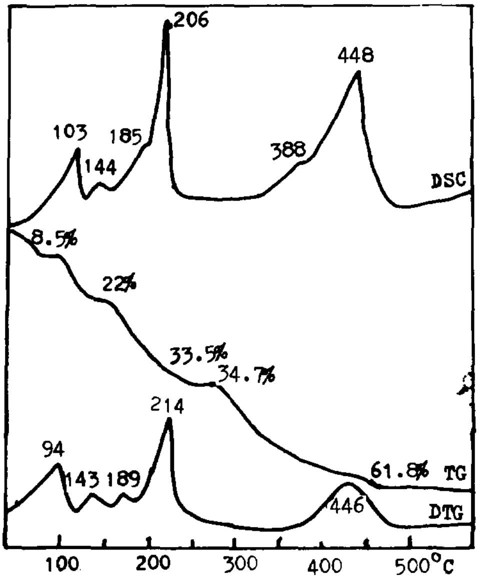


Fig. 2. TG, DTG and DSC curves of 3·1·8.

TABLE 3

Thermal–analytical results of the magnesium oxychlorides

No.	DSC (°C)	ΔH (kJ mol^{-1})	DTA (°C)	TG (wt.%)	Products
$3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$					
1	03	78.36	94	8.5	$3Mg(OH)_2 \cdot MgCl_2 \cdot 6H_2O$
2	144		149	19.0	$3Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$
3	185		189	22.0	$3Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$ $+ 3Mg(OH)_2 \cdot MgCl_2$
4	206	286.9	216	33.5	$3Mg(OH)_2 \cdot MgCl_2$
5			250	34.7	$3Mg(OH)_2 \cdot MgCl_2$
6	388				$3Mg(OH)_2 \cdot MgCl_2 + MgO$
7	448	666.4	446	61.8	MgO
$5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$					
1	96	76.58	90	7.8	$5Mg(OH)_2 \cdot MgCl_2 \cdot 6H_2O$
2	145		140	13.5	$5Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$
3	193	363.4	202	26.4	$5Mg(OH)_2 \cdot MgCl_2$
4			250	27.0	$5Mg(OH)_2 \cdot MgCl_2$
5	378		390	44.0	$5Mg(OH)_2 \cdot MgCl_2 + MgO$
6	420	607.0	430	54.5	MgO

The products of dehydration and decomposition at different temperatures were studied by IR spectroscopy, X-ray powder diffraction, thermal analysis and electron microscopy.

TABLE 4

The analyses of the products from the heating of component 3·1·8

No.	Heating (°C)	DSC peak (°C)	XRD			IR peaks[a] (cm^{-1})	Electron microscopy
			d	I/I_0	Phase		
1	40	218	8.073	50		3660 s	Crystals
		455	7.075	25		3400 ms	
		455	4.046	24	3·1·8	3526 wsh	
			3.879	12		3440 mb	
			3.879	12		3440 mb	
			3.858	21	$Mg_2(OH)_2$	3120 mb	
			3.553	22	Cl·	1620 vs	
			2.705	25	$4H_2O$	1120 mb	
			2.611	11		700 wsh	
			2.442	100		71 mb	
			2.435	22		668 mb	
2	62	220	7.406	7		3660 msh	Crystals
		460	6.835	31	3·1·6	3600 vs	
			4.285	7		3480 mb	
			4.133	16		1630 ms	
			2.713	21		1140 mw	
			2.618	11		760 mb	
			2.458	100		700 mb	
			2.408	18		650 mb	
			1.906	8		578 sb	
3	130	215	7.213	11		3650 vs	Crystals
		456	6.379	26		3600 vs	
			6.137	45		3490 msh	
			5.865	10		3330 sb	
			5.611	13	3·1·4	1620 sb	
			5.541	10		1140 vb	
			4.433	30		750 vs	
			4.320	13		680 sh	
			3.618	10		664 sb	
			3.070	13		570 sb	
			2.716	22			
			2.626	11			
			2.478	100			
4	200	460	5.552	100		3700 w	
			2.500	17	$Mg_2(OH)$	3600 sh	
			1.987	4	·Cl	3640 ms	
			1.978	5		1630 m	
			1.814	4		620 sb	

TABLE 4 (continued)

No.	Heating (°C)	DSC peak (°C)	XRD			IR peaks [a] (cm^{-1})	Electron microscopy
			d	I/I_0	Phase		
5	340	457	5.748	12		3620 s	Partial break-up
			5.600	28	$Mg_2(OH)_2$	3560 s	of crystals
			2.433	10	·Cl	3420 sb	
			2.107	100	+MgO	1640 sb	
			1.489	43		620 sb	
			1.217	8		510 sb	
6	600		2.433	9		610 wb	Total break-up
			2.107	100		550 sb	of crystals
			1.491	4	MgO		
			1.269	4			
			1.216	10			

[a] s, small; m, medium; sh, shoulder; b, broad; w, weak; vs, very small.

IR spectra

In the IR spectra of the 5 · 1 · 8 form and its products during dehydration, there are three small absorption peaks at 3693, 3652 and 3612 cm^{-1}, but in those of the 3 · 1 · 8 form and its products there are only two small peaks at 3659 and 3643 cm^{-1}. The small peaks in the 3700 cm^{-1} region may be due to the bending vibration of Mg–OH, depending on their structure groups. From the IR spectra of hydrated salts, the absorption bands at 1620–1640 cm^{-1} are due to the bending vibrations of the OH in the water of crystallization, and the absorption bands at 3300–3400 cm^{-1} are due to the bond vibrations of the OH in the water of crystallization. The broad bands at 400–600 cm^{-1} are due to the bond vibrations of Mg–OH. The weak bonding vibration spectra of Cl–O, seen as $Cl–O_2$ in $KClO_2$ at 1156–1162 cm^{-1}, are listed in Tables 4 and 5.

When the temperature reaches 200 °C, both magnesium oxychlorides are anhydrous; absorption peaks appear at 3600–3700 cm^{-1} in the IR spectra. At 600 °C, the bands situated at 3600–3700, 3340–3400 and 1630–1640 cm^{-1} disappear. The IR spectra of 5 · 1 · 8 and 3 · 1 · 8 and their products formed during heating, are shown in Figs. 3 and 4.

X-ray diffraction

Each product obtained from the 5 · 1 · 8 and 3 · 1 · 8 forms heated to different temperatures, was examined by X-ray powder diffraction; the results are shown in Tables 4 and 5. For dehydration temperatures up to 200 °C, they have almost the same strong diffraction peaks at $d = 5.541$–

TABLE 5

The analyses of the products from the heating of 5·1·8

No.	Heating (°C)	DSC peak (°C)	XRD			IR peaks [a] (cm^{-1})	Electron microscopy
			d	I/I_0	Phase		
1	80	207	8.523	19		3700 s	Crystals
		345	7.387	16	5·1·8	3644 ms	
		427	6.573	100		3600 vs	
			4.283	39		3410 sb	
			3.260	8		3300 ms	
			2.621	20			
			2.357	68		1640 s	
			1.009	9			
			1.973	13	5·1·6	1180 mb	
			1.848	15		623 wb	
			1.567	9		540 mb	
2	200	345	5.541	100		3700 msh	Crystals
		426	2.410	19		3660 msh	
			1.588	15		3604 m	
						1640 mb	
						550 sb	
3	300	433	5.862	81		3640 s	Partial break-up of crystals
			2.774	4		3420 sb	
			2.552	14		1635 s	
			2.405	22		540 mb	
			2.107	100		540	
			1.489	41	MgO		
			1.484	22			
			1.261	11			
			1.214	9			
4	600		2.108	100		3420 sb	Total break-up of crystals
			1.269	5	MgO	610 wb	
			1.489	41		1640 mb	
			1.218	10		535 sb	

[a] s, small; m, medium; sh, shoulder; b, broad; w, weak; vs, very small.

5.552 and $d = 2.41$–2.51. At temperatures up to 600 °C, both forms become MgO, the X-ray diffraction peaks becoming weaker.

Thermal analysis

The products of the 5 · 1 · 8 and 3 · 1 · 8 forms were heated to different temperatures and determined by DTA (see Figs. 5 and 6). There were no dehydration peaks above 200 °C, and decomposition peaks appeared at about 440 °C.

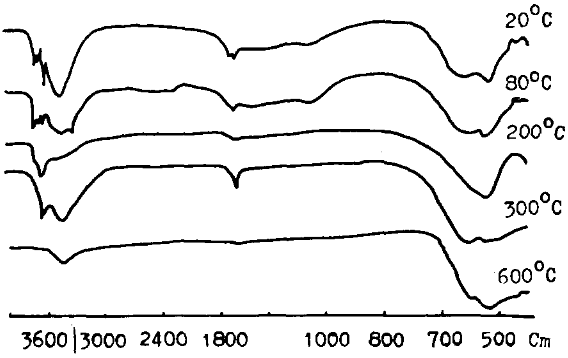


Fig. 3. IR spectra of the products of 5·1·8 formed during heating.

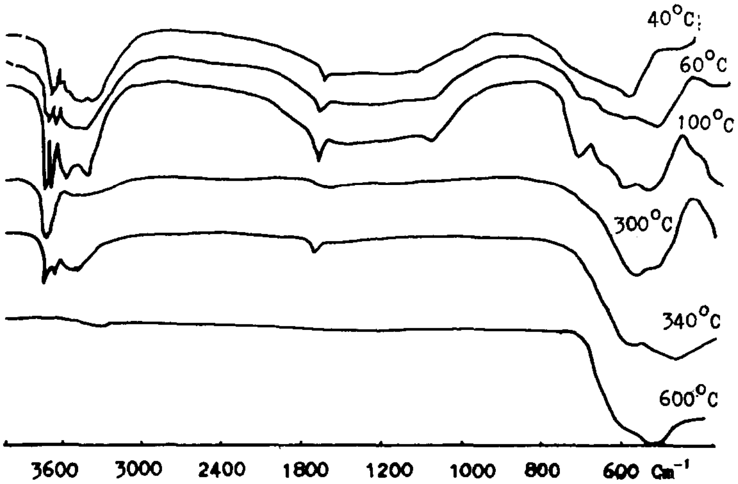


Fig. 4. IR spectra of the products of 3·1·8 formed during heating.

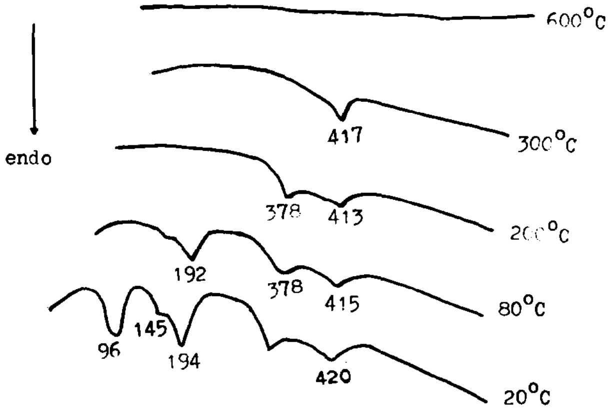


Fig. 5. DTA of the products of 5·1·8 formed during heating.

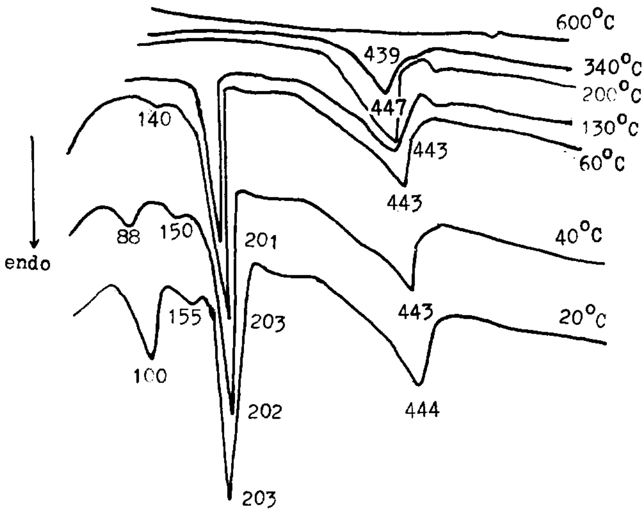


Fig. 6. DTA of the products of 3·1·8 formed during heating.

Micrograph results

The electron micrographs of the products of 5 · 1 · 8 and 3 · 1 · 8 heated to 200 ° C reveal that the needle-like crystals remain. Above 300 ° C, the crystals begin to break down MgO. Up to 600 ° C, the MgO products are hexagonal crystals. These results can be seen in Figs. 7 and 8.

Chemical analysis

The Mg^{2+}, OH^-, Cl^- and H_2O contents of the products of the 5 · 1 · 8 and 3 · 1 · 8 forms heated to different temperatures were determined. The molar ratios of Mg : OH : Cl : H_2O are shown in Table 6; they agree with the chemical formulae. The following compounds were indicated: $3Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$, $3Mg(OH)_2 \cdot MgCl_2 \cdot 7H_2O$, $3Mg(OH)_2 \cdot MgCl_2 \cdot 5.5H_2O$ and $3Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$, and $5Mg(OH)_2 \cdot MgCl_2 \cdot 5H_2O$ and $5Mg(OH)_2 \cdot MgCl_2$. Because of dehydration at low temperatures, it is difficult to obtain the pure hexahydrate. They were hydrate mixtures.

Thermochemical analysis

The thermal reactions of dehydration and decomposition were deduced from the IR spectra and the X-ray powder diffraction results. From TG and DTG, the isothermal losses can give information on the different reactions indicated by the various DTA peaks. The DSC thermographs show that dehydration and decomposition are accompanied by endothermal effects.

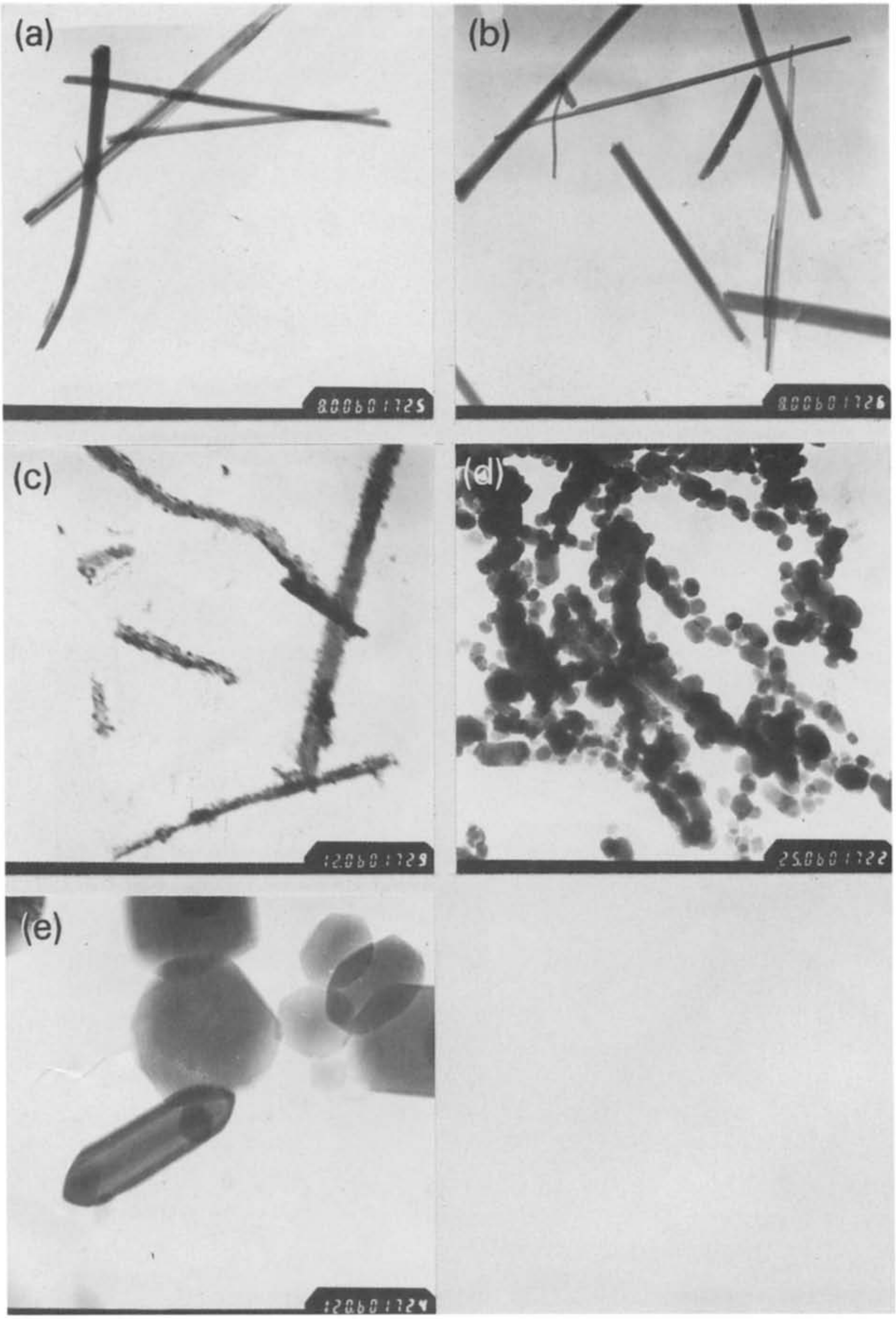


Fig. 7. Electron micrographs of the products of heating 5·1·8 to various temperatures (the original magnification is given in parentheses): (a) 80 °C (8.0×10^3); (b) 200 °C (8.0×10^3); (c) 300 °C (1.2×10^4); (d) 600 °C (2.5×10^4); (e) 600 °C (1.2×10^5).

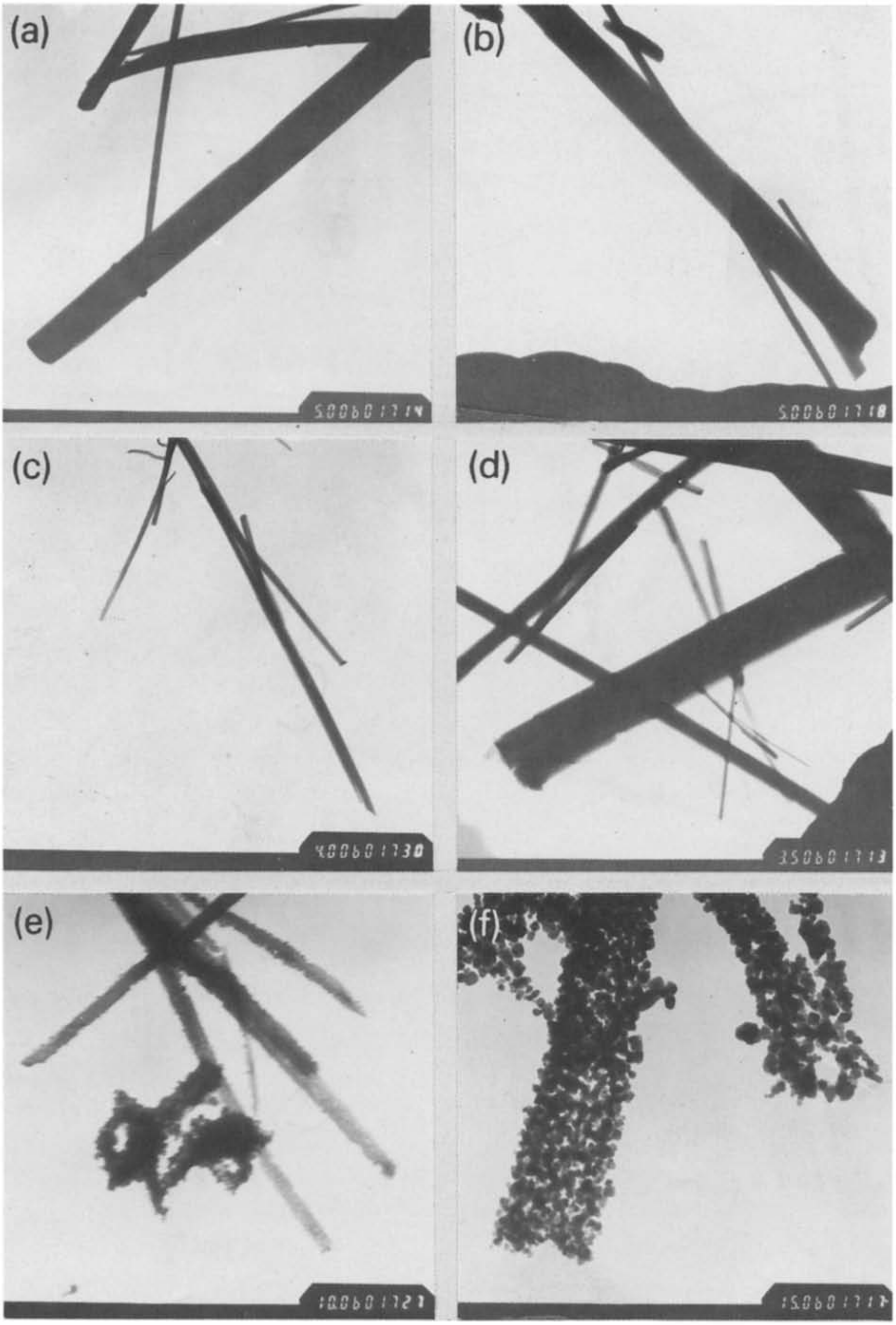


Fig. 8. Electron micrographs of the products of heating 3·1·8 to various temperatures (the original magnification is given in parentheses): (a) 40 °C (5.0 × 10^3); (b) 62 °C (5.0 × 10^3); (c) 130 °C (4.0 × 10^3); (d) 200 °C (3.5 × 10^3); (e) 340 °C (1.0 × 10^4); (f) 600 °C (1.5 × 10^3).

TABLE 6

Chemical analysis of the products of heating

No.	*t* (°C)	Mg:OH:Cl:H_2O	Chemical formula
$3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$			
1	44	2.00:3.00:1.00:3.54	$3Mg(OH)_2 \cdot MgCl_2 \cdot 7H_2O$
2	62	2.00:3.00:1.00:2.75	$3Mg(OH)_2 \cdot MgCl_2 \cdot 5.5H_2O$
3	130	2.00:1.00:1.02:2.02	$3Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$
4	200	2.00:2.99:1.00:0	$3Mg(OH)_2 \cdot MgCl_2$
5	340	3.85: *X* :1.00:0	$3Mg(OH)_2 \cdot MgCl_2 + MgO$
		Mg:0	
6	600	1.00:1.00	MgO
$5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$			
1	80	2.99:4.99:1.00:2.51	$5Mg(OH)_2 \cdot MgCl_2 \cdot 5H_2O$
2	200	2.99:4.99:1.00:0	$5Mg(OH)_2 \cdot MgCl_2$
3	300	3.64: *X* :1.00:0	$5Mg(OH)_2 \cdot MgCl_2 + MgO$
		Mg:0	
4	600	1.00:1.00	MgO

In the thermographs of 3 · 1 · 8 and 5 · 1 · 8, there are five and six processes of dehydration and decomposition respectively. From the above comprehensive data, the following reaction mechanisms can be deduced.

The thermal chemical reactions of 3 · 1 · 8 are complex. The loss of water molecules was detected at several stages.

$$3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O \xrightarrow[\Delta H_{1a} = 75.36 \text{ kJ mol}^{-1}]{75\text{–}120\,°C} 3Mg(OH)_2 \cdot MgCl_2 \cdot 6H_2O + 2H_2O \quad (1)$$

$$3Mg(OH)_2 \cdot MgCl_2 \cdot 6H_2O \xrightarrow[\Delta H_{2a} = 14.48 \text{ kJ mol}^{-1}]{120\text{–}160\,°C} 3Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O + 2H_2O \quad (2)$$

$$3Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O \xrightarrow[\Delta H_{3a} = 275.91 \text{ kJ mol}^{-1}]{180\text{–}230\,°C} 3Mg(OH)_2 \cdot MgCl_2 + 4H_2O \quad (3)$$

$$3Mg(OH)_2 \cdot MgCl_2 \xrightarrow{300\text{–}400\,°C} MgCl_2 \cdot H_2O + 2H_2O + 3MgO \quad (4)$$

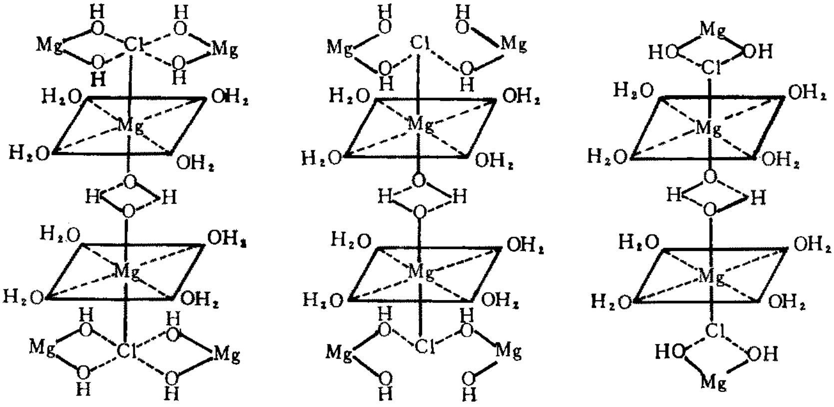
$$MgCl_2 \cdot H_2O \xrightarrow{400\text{–}600\,°C} MgO + 2HCl \quad (5)$$

for eqns. (4) and (5), total $\Delta H_{4a} = 666.35$ kJ mol^{-1}.

The thermal chemical reactions of 5 · 1 · 8 are

$$5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O \xrightarrow{72\,°C} 5Mg(OH)_2 \cdot MgCl_2 \cdot 6H_2O + 2H_2O \quad (6)$$

$$5Mg(OH)_2 \cdot MgCl_2 \cdot 6H_2O \xrightarrow[\Delta H_{1b} = 76.58 \text{ kJ mol}^{-1}]{72\text{–}130\,°C} 5Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$$



5-form(1) 5-form(2) 3-form

Fig. 9. The structures of the magnesium oxychlorides.

$$+ 2H_2O \qquad (7)$$

$$5Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O \xrightarrow[\Delta H_{2b} = 353.4\ \mathrm{kJ\ mol^{-1}}]{140\text{–}200\,^\circ\mathrm{C}} 5Mg(OH)_2 \cdot MgCl_2 + 4H_2O \qquad (8)$$

$$5Mg(OH)_2 \cdot MgCl_2 \xrightarrow{300\text{–}350\,^\circ\mathrm{C}} MgCl_2 \cdot H_2O + 4H_2O + 5MgO \qquad (9)$$

$$MgCl_2 \cdot H_2O \xrightarrow{350\text{–}500\,^\circ\mathrm{C}} MgO + 2H_2O \qquad (10)$$

For eqns. (9) and (10), total $H_{3b} = 607$ kJ mol^{-1}.

These results can be interpreted from the structures. The ternary oxychlorides consist of Mg^{2+}, OH^-, Cl^- and H_2O. The Mg^{2+} has six coordination ligands. The $Mg(OH)_2$ are hydrogen bonded with Cl–O; their structures are shown in Fig. 9. During heating, when the oxychlorides lose part of the coordinated water, the bond vibration of the hydrate peaks in the IR spectra appear like those of $MgCl_2 \cdot 8H_2O$ and $MgCl_2 \cdot 2H_2O$ [18]. The transformation of these phases is sharp. Bands at 3300–3400 and 1630–1640 cm^{-1} are absent in the IR spectra of the anhydrous compounds. The IR bands at 3600–3700 cm^{-1} due to the Mg–OH bond remain but the Cl–O bonding characteristics have disappeared. Thus the anhydrous phase contains $Mg(OH)_2$ in the crystals. At higher temperatures (300 °C), the anhydrous phase decomposes in two stages: first, it decomposes to $MgCl_2$, H_2O and MgO, the $MgCl_2$ hydrate appearing in the IR spectra; then it decomposes to MgO and H_2O with loss of HCl. In the IR spectra and the DTA curves there are no peaks, and the X-ray diffraction results show that the residue is MgO.

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