A Study of the System Magnesium Oxide–Magnesium Chloride–Water and the Heat of Formation of Magnesium Oxychloride

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The precipitation of magnesium oxychlorides is discussed, and the results of solubility measurements are given. The heats of solution in HCl, $26 \cdot 61H_2O$ (2.00 N HCl at 25° C) of four compounds in the system $MgO-MgCl_2-H_2O$ were determined. From those data and other data taken from the literature, the heats of formation of the compounds at 25° C were calculated. The results are applied to the calculation of the heat of reaction of hardening of magnesium oxychloride cement.

1. Introduction

Magnesium oxychloride cement is widely used as a conductive flooring material in hospital operating rooms and other locations where an explosion hazard exists. It is also used widely as a general purpose floor in public buildings, stores, street cars, and elsewhere. Basic information concerning the stability of the components of magnesium oxychloride cement is needed to answer questions that arise from time to time in connection with its service life. The heats of formation of the compounds formed constitute part of the necessary fundamental information and are presented in this paper.

The compounds occurring in the system $MgO-MgCl_2-H_2O$ have been the subject of many investigations since the discovery in 1867 of the cementitious properties of mixtures of magnesium oxide with magnesium chloride solutions. Robinson and Waggaman [1][1], Lukens [2], Chassevent [3], Bury and Davies [4], Feitknecht [5], Feitknecht and Held [6], and others have identified the three solid phases occurring at room temperature as $Mg(OH)_2$, $5Mg(OH)_2 \cdot MgCl_2 \cdot nH_2O$, and $3Mg(OH)_2 \cdot MgCl_2 \cdot nH_2O$. Most of the investigations have been concerned with the identification of the magnesium oxychloride compounds or with the study of the setting process of magnesium oxychloride cement. Only Andre [7] has given heat-of-solution data from which heats of formation have been calculated [8].

In the light of the more recent work cited above, Andre's data appears in doubt because of the absence of identification of his material with the presently recognized compounds. This paper gives the results of new measurements of the heats of solution of the two oxychlorides and the heats of formation calculated therefrom.

2. Materials, Apparatus, and Procedure

2.1. Preparation of Compounds

The compounds were prepared by precipitation at 25° C from metastable solutions of MgO in $MgCl_2$ solutions of various concentrations. Aqueous $MgCl_2$

solutions were prepared from $MgCl_2 \cdot 6H_2O$ of analytical reagent quality and distilled water. Magnesium chloride is deliquescent, and it is difficult to weigh out an amount containing an accurately known quantity of $MgCl_2$. Because of this difficulty, the solutions were prepared in a weighed 1-liter volumetric flask, adjusting the compositions by trial and error until the desired densities were obtained. Densities for solutions of the desired concentrations were taken from density-concentration data for $MgCl_2$ solutions in the International Critical Tables [9]. In order to reduce the CO_2 concentration, the solutions were transferred to an Erlenmeyer flask and a stream of CO_2-free air was introduced into each solution while boiling gently under a reflux condenser fitted with a CO_2 absorption tube. After cooling and filtering if necessary, the solutions were stored in 1/3 liter portions in tightly stoppered plastic bottles. It is estimated that water loss during boiling increased the concentration of $MgCl_2$ in the solution by not more than 0.05 percent. Solutions were prepared containing 5, 10, 15, 22, 27, 32, 37, 42, 47, 52, 57, 62, 67, and 72 percent by weight of $MgCl_2 \cdot 6H_2O$ respectively. Three series of mixtures in the system $MgO-MgCl_2-H_2O$ were made using the separate portions of these $MgCl_2$ solutions.

The first series of mixtures consisted of metastable solutions of MgO prepared by shaking for 2 hr. a 1-g portion of freshly heated (18 hr at 400° C) MgO of analytical reagent quality with a ⅓-liter quantity of each of the 14 above mentioned magnesium chloride solutions. The mixtures were filtered several times if necessary to obtain clear solutions. Magnesium oxychloride began to precipitate after a few hours or days depending on the $MgCl_2$ contents of the solutions.

The second series of mixtures was made in an attempt to approach equilibrium from undersaturation. After from 1 to 3 weeks, about half of the magnesium oxychloride precipitated from each of the metastable solutions was removed by filtration and transferred to the second ⅓-liter portion of the solution of the same nominal $MgCl_2$ concentration as that in which the precipitate had formed. It was calculated that the change in $MgCl_2$ concentration

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[1] Figures in brackets indicate the literature references at the end of this paper.

of the original solution caused by precipitation of the oxychloride compounds varied from $+0.01$ to -0.08 percent. This change was ignored in plotting the data shown hereafter and in discussing solutions of the same nominal concentration.

The third series of mixtures, also an attempt to approach equilibrium from undersaturation, was prepared by adding 0.33 g of $Mg(OH)_2$ to the remaining $\frac{1}{3}$-liter portion of each of the $MgCl_2$ solutions. The $Mg(OH)_2$ was prepared by hydrating MgO for 72 hr in distilled water on the steam bath with subsequent drying at $110°$ C. A fourth series was prepared with new $MgCl_2$ solutions using 1 g of $Mg(OH)_2$ per $\frac{1}{3}$-liter portion of solution, in order to obtain material for heat-of-solution determination. Subsequently additional mixtures of MgO in solutions containing 34 and 36 percent of $MgCl_2 \cdot 6H_2O$, respectively, were made for the same purpose.

The mixtures were stored in a constant-temperature room at $25°$ C and shaken daily during their early history. From time to time the alkalinity of the solutions was determined by titrating a 10-ml pipetted sample of the supernatant liquid with 0.02 N HCl, using phenolphthalein as an indicator. The HCl solution was standardized against a calcium hydroxide solution, the CaO content of which had been determined gravimetrically. The alkalinity was calculated to the equivalent MgO and is referred to as the MgO content of the solution throughout this paper. No implication is intended as to the state of the MgO in solution. X-ray diffraction patterns of the precipitates were obtained at the time the second series of mixtures was prepared and later for precipitates of special interest.

The precipitates were analyzed, sometimes after washing with alcohol and ether or acetone and drying for several hours at room temperature in a vacuum over $Cacl_2$, and sometimes after merely pressing out the solution on filter paper. Total magnesium was determined by heating the sample slowly to $450°$ to $500°$ C after the addition of a few drops of concentrated sulfuric acid and weighing as $MgSO_4$. Chloride was determined gravimetrically by precipitation as AgCl. From these data the equivalent $MgCl_2$ and MgO were calculated, and water was taken by difference.

To furnish material for the study of the variation of the heat of solution of $3Mg(OH)_2 \cdot MgCl_2 \cdot nH_2O$ with the change of water content, 4 liters of 58.5 percent $MgCl_2 \cdot 6H_2O$ solution was shaken with 15 g of freshly calcined MgO and filtered. At the end of 3 months, the oxychloride compound which had precipitated was recovered by filtration, washed with alcohol and acetone, and dried under vacuum. Analyses, heat-of-solution determinations, and dehydration studies were made using this material. Samples were exposed at room temperature to air of various humidities in desiccators containing water, saturated solutions of $Na_2Cr_2O_7$, $MgCl_2 \cdot 6H_2O$, KOH, or solid $Mg(ClO_4)_2$ respectively. Other samples were heated at $45°$, $110°$, and $180°$ C. The samples were weighed periodically to determine the loss or gain of water. Subsequently, their heats of solution in HCl, $26.61H_2O$ (2.00 N at $25°$ C) were determined.

2.2. Heat-of-Solution Measurements

The heats of solution of the oxychloride precipitates were determined in HCl $26.61H_2O$. The isothermal jacket calorimeter, described elsewhere [10], has been lined with platinum and is fitted with a four-blade platinum stirrer. The valve has been removed and the powdered samples are introduced by means of a funnel. Electrical calibration and calculations of the corrected temperature rise were performed by conventional methods [11].

3. Results and Discussion

3.1. Precipitation of Magnesium Oxychloride

The amount of MgO initially dissolved by $MgCl_2$ solutions varies with the time and temperature of heating of the MgO, with the concentration of the $MgCl_2$ solution, with the ratio of MgO to $MgCl_2$ solution, with the time of shaking, and, perhaps, with other factors. Using MgO from a single source, Lukens [2] has shown this variation in considerable detail for one particular concentration of $MgCl_2$ solution. In the present work, only sufficient MgO was used to give metastable solutions containing 3 g/liter or less of MgO, since solutions containing substantially more than this amount thickened to a gel upon precipitation of the oxychloride compounds. Under the conditions chosen, 3 g of solid MgO per liter of solution and 2 hr of shaking before filtration, solutions containing 27 percent or more of $MgCl_2 \cdot 6H_2O$ dissolved nearly all of the MgO. There were some variations in MgO content of the clear solutions, indicating perhaps that 2 hr was not the optimum shaking time, but all of these solutions after filtration contained from 20 to 40 times the concentration reached subsequently upon standing for 7 months. The solutions containing 22, 15, 10 percent of $MgCl_2 \cdot 6H_2O$ dissolved substantially less MgO, but even these after filtering contained 10 or more times the final concentration. The solution containing 5 percent of $MgCl_2 \cdot 6H_2O$ dissolved very little MgO.

The equivalent MgO content of magnesium chloride solutions shaken with $Mg(OH)_2$ depended on the relative amounts of $Mg(OH)_2$ and solution and upon the time of contact, as well as upon the concentration of $MgCl_2$. Many of the solutions of the series shaken with 1 g of $Mg(OH)_2$ per liter of solution dissolved it slowly, reaching maximum MgO concentration in about 2 weeks. These solutions were metastable, and subsequently with the precipitation of magnesium oxychloride the concentration of MgO fell, approaching the final value reached by the other solutions of the same $MgCl_2$ content. This behavior was characteristic of the solutions containing 37 percent or more of $MgCl_2 \cdot 6H_2O$. The solutions of less $MgCl_2$ content did not become greatly supersaturated, but slowly approached a final MgO concentration depending on the amount of $MgCl_2$ in solution. The magnesium chloride solutions shaken with 3 g of $Mg(OH)_2$ per liter behaved similarly,

except that the maximum MgO concentrations were generally higher and more quickly attained.

The changes of the MgO concentration of the solutions containing 47 percent MgCl$_2$·6H$_2$O are plotted in figure 1 as a function of time. The changes occurring in these solutions are typical of those found with the other solutions of such MgCl$_2$ concentration that oxychloride compounds were formed. The original supersaturated clear solution contained 3.02 g MgO per liter. In 13 days, precipitation of magnesium oxychloride reduced the concentration to 0.073 g MgO per liter, where it remained for more than 6 months. At 16 days about half of the precipitate formed was transferred to a fresh solution of the same MgCl$_2$ concentration. The MgO concentration of this solution, which, at 1 day, was 0.135 g/liter, was reduced in 5 days to 0.107 and in 9 days to 0.068 g/liter where it remained within experimental error. The possible significance of the 1-day value will be discussed later.

One-third gram of solid magnesium hydroxide suspended in ⅓ liter of 47-percent MgCl$_2$·6H$_2$O solution gave an MgO concentration of 0.132 g/liter in 1 day, and 1 g under the same conditions gave a concentration of 0.386 g MgO per liter. In the first solution, additional Mg(OH)$_2$ dissolved, raising the MgO concentration to 0.233 g/liter in 15 days. Thereafter precipitation of magnesium oxychloride reduced the concentration to 0.080 g/liter at 51 days and 0.063 g/liter at 219 days. In the second solution, the MgO concentration remained near the 1-day value for about a week, and then decreased to 0.109 g/liter at 21 days and to 0.078 g/liter at 43 days. It remained essentially constant thereafter until the precipitate was removed for analysis at 156 days.

In figure 2 are plotted the concentrations of MgO in the MgCl$_2$ solutions when the experiments were terminated at about 7 months. This figure represents the 25° C isotherm of the system MgO-MgCl$_2$·6H$_2$O–H$_2$O with the MgO scale greatly expanded. A vertical line T—T is drawn through the concentration of MgCl$_2$·6H$_2$O (10.89% of MgCl$_2$) given by Bury

and Davies [4a] as the triple point at which magnesium chloride solution, Mg(OH)$_2$, and 3 Mg(OH)$_2$·MgCl$_2$·8H$_2$O coexist. The data of Robinson and Waggaman [1] are represented by the open squares, and the solubility of Mg(OH)$_2$ in pure water at 30° C [15] is also shown. Chassevent's value of 0.030 g/liter for the solubility of magnesium oxide in magnesium chloride solution [3] is plotted in figure 2 as an open triangle.

A second vertical line X—X is drawn in figure 2 separating the diagram in two regions. To the right of this line the final precipitates were, with two exceptions, 3Mg(OH)$_2$·MgCl$_2$·8H$_2$O, and to the left, with three exceptions, they were Mg(OH)$_2$. The exceptions are indicated in the figure by the letters A, B, and M attached to the various points and indicating the presence of 3Mg(OH)$_2$·MgCl$_2$·8H$_2$O, 5 Mg(OH)$_2$·MgCl$_2$·8H$_2$O, and Mg(OH)$_2$ respectively. The line X—X makes the same separation for the results of Robinson and Waggaman and thus indicates the approximate location of the triple point Mg(OH)$_2$-3Mg(OH)$_2$·MgCl$_2$·8H$_2$O solution for their work as well as for the author's.

In the present work it was planned to approach equilibrium from both directions. Because Mg(OH)$_2$, contrary to statements in the literature, formed supersaturated solutions, the approach from undersaturation was not accomplished with certainty when Mg(OH)$_2$ was added to MgCl$_2$ solutions. In every case the concentration of MgO in these solutions passed through a maximum within a few days after the Mg(OH)$_2$ had been added. With solutions containing 27 percent or less of MgCl$_2$·6H$_2$O, the final concentrations of MgO were equal to or
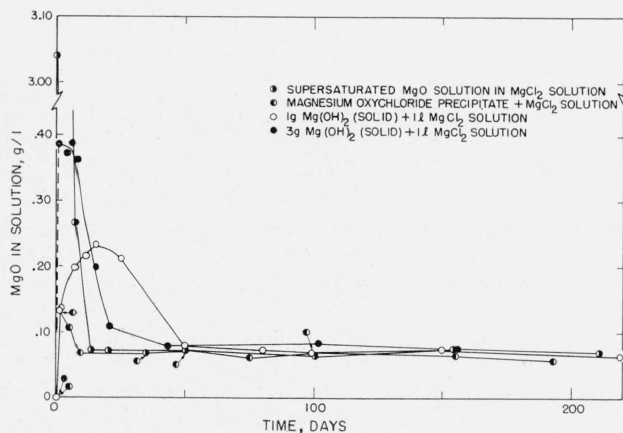

FIGURE 1. *Concentration-time relationship of MgO in MgCl$_2$ solution.*

Concentration of MgCl$_2$ solution, 47 percent of MgCl$_2$·6H$_2$O. (22% of MgCl$_2$, equivalent to 23.6° B.)
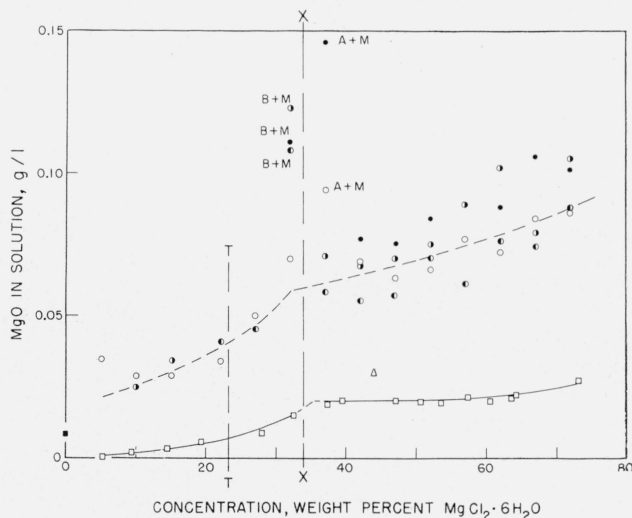

FIGURE 2. *Equivalent concentration of MgO in MgCl$_2$ solutions at 25° C.*

(◗, Precipitated from metastable solution of MgO in MgCl$_2$ solution; ◖, precipitate from metastable solution added to fresh MgCl$_2$ solution; ◯, 1 g/1 of solid Mg(OH)$_2$ suspended in MgCl$_2$ solution; ●, 3 g/l of solid Mg(OH)$_2$ suspended in MgCl$_2$ solution; □, Robinson and Waggaman solubility data [1]; ■, solubility of Mg(OH)$_2$ in pure water [15]; △, Chassevent solubility data [3]; A, solid phase 3Mg(OH)$_2$·MgCl$_2$·8H$_2$O; B, solid phase 5Mg(OH)$_2$·MgCl$_2$·8H$_2$O; C, solid phase Mg(OH)$_2$.

greater than the early maxima. Thus, over the range 10 to 27 percent $MgCl_2 \cdot 6H_2O$ apparent equilibrium was approached from both directions. At higher concentrations, however, it was not approached from undersaturation even in solutions to which precipitated magnesium oxychloride had been added. For these solutions the same sort of early maximum was found in the curves of concentration versus time as for the solutions to which $Mg(OH)_2$ had been added. The final concentration was greater than the early maximum only for the solution containing 57 percent of $MgCl_2 \cdot 6H_2O$. In this solution the final concentration was approached both from under- and from supersaturation, the usual criterion for equilibrium. In spite of this approach, the final concentration was substantially higher than that reported by Robinson and Waggaman.

Both Bury and Davies and Robinson and Waggaman shook their mixtures continuously whereas in the present work the mixtures were shaken only occasionally. The former authors attribute the higher concentration found for the triple point by Robinson and Waggaman to the formation of metastable substances but state that this formation is less likely to occur in the absence of shaking. In a subsequent paper on the system MgO-CaO-$MgCl_2$-H_2O [4b] Bury and Davies state that continuous shaking is necessary to attain equilibrium in that system. The author can make no comment on the differing concentrations indicated for the triple point but considers that the scatter of the points and the generally higher solubilities obtained in the present work indicate that equilibrium was not attained in the absence of continuous shaking in spite of the duration and manner of approach.

The results of X-ray examination of the precipitates are given in table 1. Except in three instances, the final precipitates were $Mg(OH)_2$ or $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$. The compound $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ was the first formed in a number of solutions and appeared as an intermediate phase in several instances when $Mg(OH)_2$ was placed in contact with $MgCl_2$ solution. The rate of conversion to $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ appears to increase with increase in the concentration of magnesium chloride in solution. The 5:1 oxychloride was not present (according to the X-ray patterns) at 1 day in the more concentrated $MgCl_2$ solutions and remained at 7 months in the most dilute in which it was formed. Lukens [2] found that in 71-percent $MgCl_2 \cdot 6H_2O$ solutions the 5:1 compound formed first, and Feitknecht and Held [6] found it was that precipitated first and subsequently converted to the 3:1 compound at all concentrations above about 27.8 percent of $MgCl_2 \cdot 6H_2O$. In the present work when the oxychloride precipitates were transferred to fresh solutions containing no MgO, these solutions became supersaturated (in terms of MgO) with respect to their final concentrations. This initial supersaturation may be an indication that $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ was still present at the time of transfer even in the precipitates from the three most concentrated magnesium chloride solutions where the X-ray pat-

terns did not indicate its occurrence. There appears, however, to be no concentration range in which the 5:1 oxychloride is the stable compound in equilibrium with magnesium chloride solution.

3.2. Heats of Dilution of $MgCl_2$ Solutions

In order to obtain data for correcting the observed heats of solution of samples containing magnesium chloride solution, heat-of-dilution experiments were performed. Magnesium chloride solutions of various strengths were added in small quantities to 600 g of

TABLE 1. *X-ray identification of solid phases found in contact with magnesium chloride solutions*

$MgCl_2 \cdot 6H_2O$ concentration (%)	Preparation[a]	Age in days and X-ray pattern[b]	$MgCl_2 \cdot 6H_2O$ concentration (%)	Preparation[a]	Age in days and X-ray pattern[b]
74.3	1	12-A	47		0-M
		14-A			6-M+A
72	1	1-A		2	53-A
		3-A			100-A
		6-A			166-A
		99-A			196-A
		0-M		3	0-A
	2	6-A+B	42	1	13-B
		203-A			21-B
		267-A			100-A
	3	0-A		2	0-M
		197-A			21-M+A
67	1	1-A			46-A
		2-A			65-A
		6-A		3	0-B
		203-A			78-A
	2	0-M	37	1	14-B
		6-A			21-B
		162-A			92-A
		203-A			100-A
	3	0-A			150-A
		197-A			0-M
64	1	1-A		2	6-M
	1	2-A			46-M
		6-A			100-M
62	2	0-M			155-M+A
		6-A+B			165-M+A
		162-A		3	0-B
		214-A			100-A+B
	3	0-A			212-A
58.5	1	134-A	36	1	7-B
		3-A+B			38-B
57	1	7-A	32	1	21-B
		160-A			100-B
	2	0-M			225-B+M
		225-A		2	0-M
	3	0-A			7-M
55	1	2-A			46-M
52.5	1	1-A			50-M
		15-A		2	155-M
		21-A			162-A
		2-B		3	0-B
52	1	6-A+B			92-B+M
		11-A			15-M
		17-A	27	1	103-M
		0-M			(c)
	2	6-A+B		2	0-M
		53-A			(c)
		100-A		3	0-M
		162-A			50-M
		196-A			100-M
	3	0-A+B	22	1	11-M
		1-B			(c)
47	1	2-B		2	0-M
		8-A			(c)
		16-A		3	0-M
		30-A			(c)

[a] Preparation 1, made by shaking 1 g of freshly calcined MgO with ⅓ liter of $MgCl_2$ solution; 2, made by adding 0.3 g of $Mg(OH)_2$ to ⅓ liter of $MgCl_2$ solution and 3, made by transferring about half of the precipitate from companion preparation 1 to a MgO-free solution.

[b] The number preceding the dash indicates the age of the preparation at the time the X-ray sample was taken. The letter following the dash represents the compound indicated by the X-ray pattern. A = $3\,Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, B = $5\,Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, M = $Mg(OH)_2$.

[c] At the end of the experiments these precipitates were judged by inspection to contain only $Mg(OH)_2$ because of the difference between their appearance and that of the bulky slow-settling magnesium oxychlorides. X-ray patterns and heats of solution were not obtained.

HCl, 26.61H$_2$O to which had previously been added 1 g of MgO (equivalent to 0.02 moles MgO per mole HCl). The data are summarized in table 2. The precision of the data was not adequate to establish the variation of the heat of dilution with variation in the quantity of MgCl$_2$ solution used. Therefore, only the average values are given in the table.

TABLE 2. *Heat of dilution*

These data represent the heat effect of adding MgCl$_2$ solutions of various strengths to HCl, 26.61 H$_2$O to which 0.02 mol MgO per mol of HCl had previously been added.

Composition of MgCl$_2$ solution		Range of dilution ratio, R	Heat of dilution, $-\Delta H298°C$
Percent MgCl$_2$	mol H$_2$O per mol MgCl$_2$	mol MgCl$_2$ per mol HCl	kcal/mol MgCl$_2$
35.1	9.77	0.012 to 0.060	2.33
24.1	16.64	.008 to .037	0.79
20.7	20.25	.006 to .032	.56
16.6	25.56	.005 to .024	.22

Measurements were made in duplicate at each of three dilution ratios for each solution. The standard deviation of a single determination was 0.07 kcal/mol MgCl$_2$, calculated by the formula

$$S = \sqrt{\frac{\Sigma(\Delta H_1 - \Delta H_2)^2}{24}}$$

where ΔH_1 and ΔH_2 are the duplicate measurements. No significant values of $d(-\Delta H)/dR$ could be calculated from these data. Therefore, only the average value for each concentration is given.

3.3. Heats of Solution

a. 3Mg(OH)$_2$·MgCl$_2$·nH$_2$O

Magnesium oxychloride having the ratio three Mg(OH)$_2$ to one MgCl$_2$ is the stable form in equilibrium with solutions in which an oxychloride is formed. This material could be filtered from the solution and washed with alcohol and ether without change in the X-ray pattern. Consequently most of the analyses and heat-of-solution measurements were performed on samples so treated. A few samples were prepared without washing, however, by removing as much MgCl$_2$ solution as possible by pressing. The results of the analyses and the heats of solution are given in table 3. The unwashed samples are indicated by the letter P and contain excess MgCl$_2$ solution as shown by the analyses.

Since the amount of material was limited, generally only one heat-of-solution determination was made on each sample. However, replicate determinations were made in a number of instances with a precision (standard deviation of a single test) of ±1.15 cal/g (1 cal=4.1840 abs j).

The heat of solution of magnesium oxychloride was calculated from the data in table 3. It was assumed that Mg(OH)$_2$ was present in excess in samples having a ratio Mg(OH)$_2$/MgCl$_2$ greater than three and that MgCl$_2$·6H$_2$O was present in samples having a smaller ratio. The first condition would be caused by the removal of MgCl$_2$ from the precipitated oxychloride by too vigorous washing.

TABLE 3. *Heats of solution of 3Mg(OH)$_2$·MgCl$_2$·H$_2$O preparations in HCl, 26.61H$_2$O*

Sample	Composition			Molar ratio		Heat of solution in HCl, 26.61H$_2$O
	MgO	MgCl$_2$	H$_2$O	Mg(OH)$_2$/ MgCl$_2$	H$_2$O/ MgCl$_2$ [a]	
	%	%	%			cal/g
74.3A[b]	28.85	23.31	47.84	2.923	7.926	165.8
74.3A						166.8
72 P	9.42	30.42	60.16	0.731	9.723	59.1
72 P	8.11	30.71	61.18	0.624	9.907	77.3
72 A	29.84	23.34	46.82	3.020	7.584	177.1
72 B	29.41	22.63	47.96	3.070	8.133	169.5
72 C	29.58	23.92	46.50	2.921	7.355	172.4
67 P	8.07	30.12	61.81	0.633	10.22	51.7
67 A	29.84	24.12	46.04	2.922	7.168	178.3
67 B	29.86	23.09	47.05	3.055	7.716	170.6
67 C	29.94	23.85	46.21	2.965	7.277	177.7
62 P	8.01	28.00	63.99	0.676	11.40	51.7
62 A	30.65	24.17	45.18	2.995	6.886	186.7
62 B	29.59	23.14	47.27	3.020	7.778	170.1
62 C	30.36	23.92	45.72	2.998	7.106	184.6
58.5 P	24.01[c]	24.50[c]	51.49[c]	2.315	8.794	139.6
58.5 P						139.8
58.5 A	29.83	23.11	47.06	3.049	7.715	175.5
58.5 A	29.89	23.18	46.93	3.046	7.656	174.4
58.5 A	29.88	23.11	47.01	3.054	7.699	173.6
58.5 A	29.88	23.11	47.01	3.054	7.699	176.1
58.5 AD	33.80	26.19	40.01	3.048	5.027	219.6
58.5 AD	44.68	34.61	20.71	3.049	0.114	377.5
58.5 AD	35.67	27.63	36.70	3.049	3.972	242.2
58.5 AD	35.49	27.50	37.01	3.048	4.066	239.7
58.5 AD	44.66	34.60	20.74	3.049	0.120	377.0
58.5 AD	44.41	34.40	21.19	3.049	0.207	378.6
58.5 AD	39.69	30.75	29.56	3.049	2.032	303.5
58.5 AH	29.50	22.85	47.65	3.049	7.974	169.4
58.5 AH						170.7
57 P	9.43	25.53	65.04	0.872	12.60	56.2
57 C	31.20	24.15	44.65	3.052	6.722	190.2
55 A	30.80	23.93	45.27	3.040	6.960	189.1
55 A	31.17	23.93	44.90	3.077	6.841	187.7
55 A	30.64	23.57	45.79	3.070	7.199	175.5
55 AD	33.83	26.03	40.14	3.070	5.082	223.2
55 AD	35.36	27.20	37.44	3.070	4.206	238.8
55 AD	43.87	33.75	22.38	3.070	0.435	370.3
52.5 A	29.66	23.90	46.44	2.931	7.340	171.2
52.5 A						174.5
52.5 A	29.76	23.22	47.02	3.027	7.677	175.1
52.5 A	29.68	22.94	47.38	3.056	7.862	169.9
52.5 AD	32.57	26.12	41.31	3.056	5.054	215.0
52.5 AD	35.32	27.30	37.38	3.056	4.181	234.0
52 P	7.49	24.86	67.65	0.712	13.67	44.5
52 A	30.44	24.12	45.44	2.981	6.978	183.2
52 B	29.97	23.42	46.61	3.023	7.497	175.2
52 C	31.43	23.97	44.60	3.097	6.739	189.6
47 P	8.64	22.45	68.91	.909	15.32	52.3
47 P	11.41	21.57	67.02	1.249	15.18	67.7
47 A	30.37	23.50	46.13	3.052	7.325	174.6
47 B	29.63	23.26	47.11	3.009	7.697	172.2
47 C	30.34	23.94	45.72	2.993	7.102	183.1
42 A	30.12	23.52	46.36	3.025	7.394	177.3
42 B	29.74	22.71	47.55	3.093	7.975	169.9
42 C	30.07	23.47	46.46	3.026	7.438	176.8
37 C	31.00	24.05	44.95	3.045	6.835	186.6

[a] Corrected for water equivalent to MgO to form Mg(OH)$_2$.
[b] 74.3, etc., equals original percent of MgCl$_2$·6H$_2$O by weight in the solution from which the sample was obtained. A, Precipitated from clear metastable solution of MgO in MgCl$_2$ solution. Washed with alcohol and ether. B, Reaction product of Mg(OH)$_2$ and MgCl$_2$ solution. Washed with alcohol and ether. C, Precipitate A placed in fresh MgCl$_2$ solution containing no dissolved MgO. Washed with alcohol and ether. P, Precipitated as in A. MgCl$_2$ solution removed by pressure. Precipitate not washed. D, Partially dehydrated. H, Equilibrated over saturated solution of Na$_2$Cr$_2$O$_7$.
[c] Average of four determinations. Standard deviation of individual test for MgO=±0.027 percent, for MgCl$_2$=±0.032 percent.

The second condition would be caused (under the conditions of drying) by inadequate washing so that the sample retained magnesium chloride solution. The observed heats of solution were corrected using 26.88 kcal/mole [12] for the heat of solution of excess Mg(OH)$_2$ and 1.65 kcal/mole (determined in this work) for the heat of solution of MgCl$_2$·6H$_2$O. The total water was corrected for that in the MgCl$_2$·6H$_2$O or Mg(OH)$_2$ and the corrected value taken as n in

the formula $3Mg(OH)_2 \cdot MgCl_2 \cdot nH_2O$ for the oxychloride.

The calculated heats of solution for the oxychloride samples are shown in figure 3 where they are plotted in kilocalories per mole of $MgCl_2$ (equivalent to per mole of $3Mg(OH)_2 \cdot MgCl_2 \cdot nH_2O$) against the value of n. The standard deviations of the individual tests calculated from the relatively few replicate measurements are ± 0.48 kcal/mole for the heat of solution and ± 0.026 for the value of n.

The straight lines in figure 3 were calculated by the method of least squares from the data in the range of values of n from 0 to 4 for one line and from 4 to 8 for the other. Values near $n = 4$ were used for both lines. The data as a whole could be represented by a single curved line. However, the grouping shown would be explained if the samples were composed of three oxychlorides containing 8, 4, and 0 moles of water respectively per mole of $MgCl_2$. In the dehydration experiments there was evidence of a hydrate containing four molecules of water, since the material heated at 110° C tended to reach and remain at that composition, as did material heated at 45° C. A washed sample of magnesium oxychloride kept over saturated solution of $MgCl_2$ (relative humidity 33 percent [9]) attained the composition $3Mg(OH)_2 \cdot MgCl_2 \cdot 7.859H_2O$. When the sample was transferred to a desiccator containing a saturated solution of $Na_2Cr_2O_7$ (relative humidity 52% [13]) the composition became $3Mg(OH)_2 \cdot MgCl_2 \cdot 7.974H_2O$.

It should be pointed out that the dehydration of certain samples was arbitrarily stopped when the composition reached approximately 5 and 2 molecules of water per mole of $3Mg(OH)_2 \cdot MgCl_2$ in order to secure the heats of solution of samples containing those amounts of water. On the other hand, the composition at 4 molecules of water was reached in 1 day by samples heated at 110° C whereas further heating at that temperature for several days resulted in very little further loss of water. The dehydration of $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ over KOH and magnesium perchlorate did not show with certainty the existence of other hydrates.
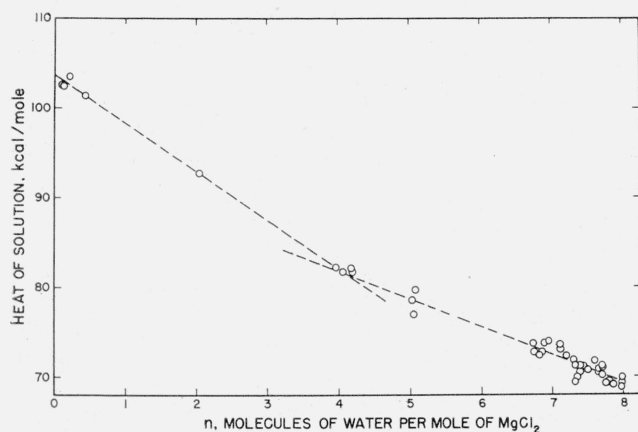
The author believes that the oxychloride as precipitated contains 8 molecules of water in agreement with the composition $2MgO \cdot HCl \cdot 5H_2O$ (equivalent to $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$) given by Robinson and Waggaman [1] from analyses of unwashed precipitates and of the solutions in which they formed. (Their reported composition $3MgO \cdot MgCl_2 \cdot 10H_2O$ seems to be erroneously converted from their determined composition of $2.02MgO \cdot HCl \cdot 5.04H_2O$.) Part of this water is removed when the precipitated material is prepared for analysis, and samples are obtained containing from 7 to 8 molecules of water as given in table 3. Feitknecht and Held [6] prepared materials containing 7, 5.14, 3.4, or 0.15 molecules of water per mole of $3Mg(OH)_2 \cdot MgCl_2$ by drying the precipitated oxychloride. Wehner [14], who also concluded that the precipitated form contained 8 molecules of water, found that an air-dried sample originally containing 10 molecules of water contained 7 after drying for 30 min at 80° C, 4.7 after drying at 120° C for 1 hr, and 3.1 molecules after 5 hrs at 120° C. After drying for 5 hrs at 200° C, the material was anhydrous. The differential thermal analysis [19] obtained in the present work and shown in figure 4 indicates the loss of water in three steps A, B, and C at 140°, 165°, and 210° C, respectively. The other deflections in this curve at higher temperatures represent the further stepwise decompositions of $3Mg(OH)_2 \cdot MgCl_2$ to the final solid product of MgO. If hydrates other than that containing four molecules of water were formed during the dehydration of the precipitated oxychloride, however, the heat-of-solution measurements shown in figure 3 were not precise enough to reveal their presence.

From the equations for the straight lines in figure 3, the following heats of solution in HCl, $26.61H_2O$ were calculated:

$3Mg(OH)_2 \cdot MgCl_2$,   103.96 kcal/mole;
$3Mg(OH)_2 \cdot MgCl_2 \cdot 4H_2O$,   81.43 kcal/mole;
$3Mg(OH)_2 \cdot MgCl_2 \cdot 7H_2O$,   72.54 kcal/mole;
$3Mg(OH)_2 \cdot MgCl_2 \cdot H_2O$,   69.61 kcal/mole.

FIGURE 3. *The heat of solution of* $3Mg(OH)_2 \cdot MgCl_2 \cdot nH_2O$ *in HCl. 26.61H_2O at 25° C.*
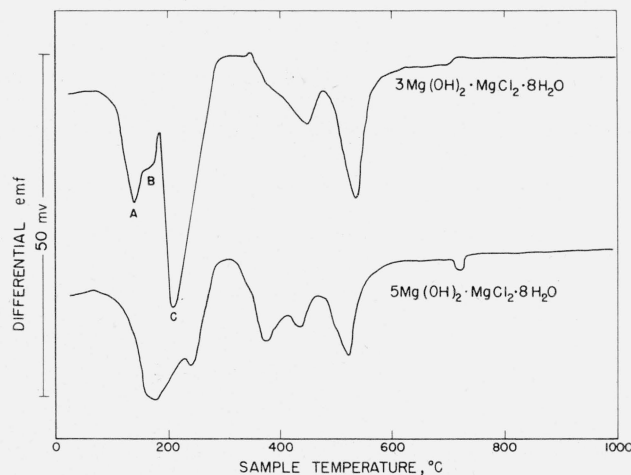

FIGURE 4. *Differential thermal analysis of magnesium oxychlorides.*

The heats of solution of the pressed samples, the crystals of which presumably were $3Mg(OH)_2\cdot MgCl_2\cdot 8H_2O$, agreed reasonably well with the value taken from figure 3. Corrected for the heat of dilution of the appropriate quantity of the $MgCl_2$ solution from which the precipitates were taken, heats of solution of 69.29, (72.96), 70.74, (72.96), 69.94, 70.04, 69.31, 69.07, 69.88, and 70.97 kcal/mole were obtained. Omitting those in parentheses which differed from the average of the others by more than four times their individual standard deviation, the average value is 69.90 kcal/mole.

b. $5Mg(OH)_2\cdot MgCl_2\cdot nH_2O$

The compound $5Mg(OH)_2\cdot MgCl_2\cdot nH_2O$ is metastable at $25°$ C in $MgCl_2$ solutions of all concentrations. It was obtained in the present work as the first precipitate from solutions containing 34 or 36 percent of $MgCl_2\cdot 6H_2O$ respectively, and supersaturated with MgO. Most of the samples were obtained by pressing out the solution without washing, but some were obtained by washing the material with alcohol and acetone. The analyses and the heats of solution are given in table 4. The heats of solution were corrected for the heat of dilution of the $MgCl_2$ solution, or the heats of solution of $Mg(OH)_2$ or $MgCl_2\cdot 6H_2O$, as indicated by the analysis and are given in the last column of the table, expressed as kilocalories per mole of the 5:1 compound. The value of n for the 7 samples of washed material varied only over the range 7.798 to 7.955. Over this short range, correlation was found between the heat of solution and the value of n. The heat of solution thus found for $n=8$ was 124.14 kcal/mole of $5Mg(OH)_2\cdot MgCl_2\cdot 8H_2O$. However, since in some cases differences were found in the X-ray patterns of samples before and after washing, the average value of the heats of solution of both the washed and the pressed samples was taken

as the heat of solution in HCl, $26.61H_2O$ of the 5:1 compound. The value found was 125.94 kcal/mole. The standard deviation of the average was 0.30 kcal/mole. The associated value of n is considered to be 8 in the material as precipitated. Feitknecht and Held [6] found n to be for their preparation after washing and drying, but this value was not approached with the 5:1 compound in the present work

3.4. Heats of Formation

The heats of formation of the four magnesium oxychlorides were calculated from their heats of solution and the heats of solution of $MgCl_2.6H_2O(c)$ and $Mg(OH)_2$. The samples were small (0.5 to 2.0 g) in comparison with the 600 g of HCl, $26.61H_2O$ used in the calorimeter. Heats of dilution and differences in final composition of the calorimeter solution from sample to sample were therefore in general neglected. The precision of the measurements did not warrant the labor of determination or calculation of the small corrections generated, for example, by the small deviations in the final concentrations caused by the use of differing small quantities of the various oxychloride preparations. The heats of reaction between $Mg(OH)_2(c)$ (brucite), $MgCl_2\cdot 6H_2O$ (c) and H_2O (1) to form the oxychlorides were calculated from the observed heats of solution and applied with the heats of formation of those reactants [8] to calculate the heats of formation of the oxychlorides. Pertinent data and the calculated results are included in table 5.

These heats of formation differ from those calculated [8] from the results of Andre's work [7]. He identified the compound obtained from 20.8 percent $MgCl_2$ solution (44.4 percent of $MgCl_2\cdot 6H_2O$) as $MgO\cdot MgCl_2\cdot 16H_2O$, a compound not reported elsewhere. The proportions given by the average of his

TABLE 4. *Heat of solution of $5Mg(OH)_2\cdot MgCl_2\cdot 8H_2O$ preparations in HCl, $26.61H_2O$*

Sample	Composition			Molar ratio		Heat of solution of sample	Calculated heat of solution of $5Mg(HO)_2\cdot MgCl_2\cdot 8H_2O$
	MgO	MgCl$_2$	H$_2$O	Mg(OH)$_2$/MgCl$_2$	aH$_2$O/MgCl$_2$		
	%	%	%			cal/g	kcal/mole
34P1 [b]	13.88	17.27	68.85	1.898	19.18	87.9	127.4
34P1						88.2	127.9
34P2	14.31	16.91	68.78	1.999	19.50	89.5	125.8
34P3	10.03	16.89	73.08	1.403	21.47	64.0	128.2
34P4	12.95	16.83	70.22	1.817	20.24	80.7	125.4
34P5	17.97	17.58	64.45	2.414	16.96	111.7	125.2
34P6	16.98	17.54	65.48	2.287	17.45	104.4	123.7
34P7	12.92	16.91	70.17	1.805	20.13	81.7	127.2
34P8	13.10	18.38	68.52	1.683	18.02	82.6	126.8
36P1	13.88	17.50	68.62	1.873	18.86	88.6	128.4
36P2	12.50	17.67	69.83	1.671	19.22	77.0	123.8
36P3	15.62	18.76	65.62	1.967	16.52	97.1	125.0
36P4	11.07	17.06	71.87	1.533	20.74	69.2	125.5
36P5	14.16	17.73	68.11	1.886	18.42	86.8	123.6
36A1	37.85	18.06	44.09	4.950	7.955	234.3	124.8
36A2	38.30	17.93	43.77	5.045	7.859	238.4	125.4
36A3	39.16	17.51	43.33	5.282	7.799	247.0	126.8
36A4	37.95	18.18	43.97	4.931	7.825	237.4	126.1
36A5	38.70	17.78	43.52	5.141	7.798	242.6	126.2
36A6	38.07	18.09	43.84	4.971	7.839	238.0	125.9
36A7	38.33	17.93	43.74	5.049	7.846	239.0	125.6

a Corrected for water equivalent to MgO to form $Mg(OH)_2$.
b 34 and 36, Original percent of $MgCl_2.6H_2O$ by weight in the solution from which the sample was precipitated. A, Precipitated from clear solution of MgO in $MgCl_2$ solution. Washed with alcohol and acetone. P, Precipitated as in A. $MgCl_2$ solution removed by pressure. Precipitate not washed. 1, 2, etc., Preparation number.

Table 5. *Heats of solution and formation of magnesium oxychlorides*

Compound	ΔH_{298}	
	Heat of solution in $HCl26.6!H_2O$	Heat of formation
	kcal/mole	*kcal/mole*
MgO (c)		−143.84[8]
MgO (c) finely divided		−142.95[8]
Mg(OH)$_2$ (c) brucite	−25.64[12]	−221.00[8]
Mg(OH)$_2$ (c) finely divided	−26.88[12]	
MgCl$_2$ (c)		−153.40[8]
MgCl$_2$·6H$_2$O (c)	−1.65	−597.42[8]
MgCl$_2$·20.69H$_2$O (soln.) ^{a}	−0.42	−188.12[8]
MgCl$_2$·43.25H$_2$O (soln.) ^{b}		−189.03[8]
H$_2$O (l)	−0.017[16]	−68.317[8]
3Mg(OH)$_2$·MgCl$_2$·8H$_2$O (c)	−69.61	−1409.05
3Mg(OH)$_2$·MgCl$_2$·4H$_2$O (c)	−81.43	−1123.90
3Mg(OH)$_2$·MgCl$_2$ (c)	−103.96	−828.04
5Mg(OH)$_2$·MgCl$_2$·8H$_2$O (c)	−125.94	−1848.00

^{a} 22° B solution.
^{b} Solution containing 10.69 percent of MgCl$_2$.

analyses are 0.94:1.00:15.8. Since his material was dried on paper it contained magnesium chloride solution in unknown amount, and because of his method of preparing the supersaturated solution of MgO in MgCl$_2$, of unknown concentration. Andre's description of his method of preparation is incomplete, because he did not give times of heating, but attempts were made to duplicate his procedure. When successful, these resulted in products which the X-ray patterns indicated were mixtures of the 5:1 and the 3:1 oxychlorides. The proportions varied with the time of standing before filtration, the 5:1 oxychloride predominating at short times. The heats of solution of these preparations were not determined.

3.5 Heat of Hardening of Magnesium Oxychloride Cement

The potential heat of hardening of magnesium oxychloride cement can be calculated from the heats of formation of the oxychlorides. As Rodt [17] and others have pointed out, the reaction of MgO and MgCl$_2$ solution is incomplete in a paste of a usable consistency because insufficient MgCl$_2$ solution is present. If the assumption is made that the concentration of the MgCl$_2$ solution does not fall below that given by Bury and Davies [4] as necessary to maintain the stability of the 3:1 oxychloride, 10.89 percent, the extent of the reaction can be calculated. Such a calculation was made for a paste made of 40 percent of MgO and 60 percent of 22° B MgCl$_2$ solution, a composition approximating those used in actual practice. The X-ray pattern of such a paste showed that at 254 days it consisted of the 5:1 oxychloride and Mg(OH)$_2$. The observed heat of hardening [18] was 235 cal/g MgO at 60 days. The potential heat of hardening calculated, based on the formation of Mg(OH)$_2$, the 5:1 oxychloride, and 10.89 percent MgCl$_2$ solution, was 265 cal/g of MgO. Only about one half of the MgO would be converted to the 5:1 compound under the conditions assumed, the rest would be present as Mg(OH)$_2$. Details of the calculation are shown in the appendix. As indicated

there, by far the greater part of the heat evolved is due to the hydration of the magnesia to magnesium hydroxide.

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4. References

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5. Appendix

Calculation of the composition and potential heat of hardening of a paste consisting of 40 g MgO and 60 g of 22° B MgCl$_2$ solution (MgCl$_2$,20.69H$_2$O).
Products: 5Mg(OH)$_2$·MgCl$_2$·8H$_2$O, Mg(OH)$_2$, and 10.89 percent MgCl$_2$ solution (MgCl$_2$,43.254H$_2$O).
Basis: 100 g of paste
0.9921 MgO+0.1282 (MgCl$_2$,20.69H$_2$O)
  =X Mg(OH)$_2$+Y(5Mg(OH)$_2$·MgCl$_2$·8H$_2$O)+ Z(MgCl$_2$,43.254H$_2$O)
MgO=0.9921=X+5Y,
MgCl$_2$=0.1282=Y+Z,
H$_2$O=2.65246=X+13Y+43.254Z.
Solving; X=0.4411, Y=0.1102, Z=0.01801
Therefore the desired equation is:
0.9921MgO(c)+0.1282(MgCl$_2$,20.69H$_2$O)(soln.)
  =0.4411 Mg(OH)$_2$(c)+0.1102 (5Mg(OH)$_2$·MgCl$_2$·8H$_2$O)(c)
  +0.01801(MgCl$_2$,43.254H$_2$O)(soln.)+ΔH. (A)

This equation is the sum of the following equations:

$0.9921MgO$(c, finely divided)$+0.9921H_2O$(1)
$=0.9921Mg(OH)_2$(c), $\Delta H_1 = -9.656$ kcal

$0.5510Mg(OH)_2$(c)$+0.1102(MgCl_2 \cdot 6H_2O)(c)+$
$0.2204H_2O$(l)$=0.1102(5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O)$(c),
$\Delta H_2 = -0.986$ kcal

$0.1102MgCl_2$(c)$+0.6612H_2O$(l)$=0.1102(MgCl_2 \cdot 6H_2O$.
(c), $\Delta H_3 = -3.760$ kcal

$0.1102(MgCl_2 \cdot 20.69H_2O)$(soln.)
$=0.1102MgCl_2$(c)$+2.2800H_2O$(l), $\Delta H_4 =$
$+3.826$ kcal.

$0.01801(MgCl_2 \cdot 20.69H_2O)$(soln.)
$+0.4063H_2O=01801(MgCl_2 \cdot 43.25H_2O)$(soln.),
$\Delta H_5 = -0.016$ kcal.

The ΔH of eq (A) is the sum of the five ΔH's shown. These have been calculated in the usual manner [20] from the data in table 5.

The ΔH of eq (A) is found to be -10.59 kcal or 265 cal/g MgO.

WASHINGTON, November 5, 1954.