

[CONTRIBUTION FROM THE TOWNE SCIENTIFIC SCHOOL OF THE UNIVERSITY OF PENNSYLVANIA]

THE COMPOSITION OF MAGNESIUM OXYCHLORIDE

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The composition of magnesium oxychloride has been the subject of a number of reported investigations.¹

The more recent investigations indicate uncertainty as to the existence of definite compounds of MgO and MgCl₂. It was the purpose of this investigation to endeavor to establish the existence or absence of such definite combinations.

The Reaction between Magnesium Oxide and Magnesium Chloride Solutions.—The solubility of magnesium oxide in solutions of magnesium chloride with the subsequent formation of a precipitate in the filtered solutions was first reported by G. André.²

The product of this reaction was subsequently investigated by W. Feitknecht,¹ who showed that the products resulting from the interaction of magnesium oxide and magnesium chloride bear a definite relation to the source of the magnesium oxide, *i. e.*, whether obtained by the ignition of the carbonate or oxalate.

The present investigation had, as an initial objective, the investigation of the reaction between magnesium chloride solutions and magnesium oxide obtained by the ignition of magnesium hydroxide.

Experimental

For the purpose of these experiments, magnesium oxide of the following analysis was used:

¹ Sorel, *Compt. rend.*, **65**, 102 (1867); Bender, *Ber.*, **3**, 932 (1871); *Liebig's Ann.*, **159**, 341 (1871); Davis, *Chem. News*, **25**, 258 (1872); Krause, *Liebig's Ann.*, **165**, 38 (1873); André, *Compt. rend.*, **94**, 444 (1882); Andre, *Ann. chim. phys.*, [VI] **3**, 79 (1884); Moldenhauer, *Z. anorg. Chem.*, **51**, 369 (1906); Hof, *Chem.-Ztg.*, **32**, 993 (1908); *ibid.*, **33**, 693 (1909); Kallauner, *ibid.*, **33**, 871 (1909); Robinson and Waggaman, *J. Phys. Chem.*, **13**, 673 (1909); Krieger, *Chem.-Ztg.*, **34**, 246 (1910); Lahrman, *Tonind.-Ztg.*, **35**, 265 (1911); Kallauner, *Chem.-Ztg.*, **37**, 1045 (1913); Krieger, *ibid.*, **37**, 1274 (1913); Kallauner, *ibid.*, **37**, 1275 (1913); Edwards, *Concrete Cement Age*, [1] **4**, 184 (1912); Ralston, Pike and Dushak, *Bur. Mines Bull.*, 236 (1925); Maeda, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, [5] **76**, 141-154 (1926); Maeda and Yamane, *ibid.*, [4] **50**, 85 (1926); Maeda, *ibid.*, [5] **73**, 95 (1926); Feitknecht, *Helv. Chim. Acta*, **9**, 1018 (1926); **10**, 140 (1927); **13**, 1380 (1930); Maeda, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, [5] **75**, 133 (1926); Maeda and Yamane, *Bull. Inst. Phys. Chem. Research (Tokyo)*, **7**, 340 (1928); Kurnakov, Zhemchuzhnuui, and Agieva, *Zhur. Prikladnoi Khim.*, **2**, 651 (1929).

² André, *Compt. rend.*, **94**, 444 (1882).

Maximum Impurities, %			
Water-soluble substances	0.7500	Nitrates (N_2O_5)	0.0064
Insoluble in HCl	.0000	Barium (Ba)	.0200
Sulfates (SO_3)	.0250	Calcium (Ca)	.0200
Chlorides (Cl)	.0100	Iron (Fe)	.0250
Carbonates	Trace	Other heavy metals	.0000

The material was digested with an excess of distilled water for twenty-four hours at a temperature of 100° . It was then dried on a steam-bath and heated to constant weight at a temperature of 110° . A sample ignited to constant weight at 1000° showed a loss of 30.86% as contrasted with a calcd. loss of 30.88%.

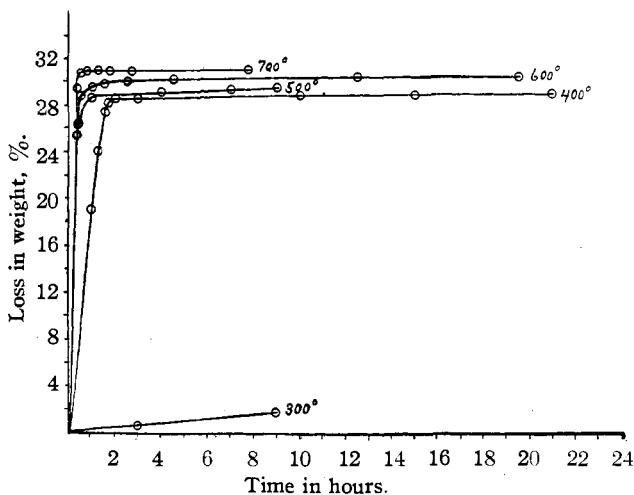


Fig. 1.—Effect of temperature on magnesium hydroxide; $Mg(OH)_2 \rightarrow MgO + H_2O$ —loss = 30.88%. Reaction at 800° , complete in 30 min.; reaction at 900° , complete in 15 min.; reaction at 1000° , complete in 10 min.

Lacking data regarding the rate at which magnesium hydroxide loses water at various temperatures, this subject was investigated with the results indicated in the graphs, Fig. 1. The rate of loss was determined by heating 7- to 8-g. samples in platinum in an electrically heated muffle at the desired temperature for ten-minute (or longer) intervals. The crucible and contents were then cooled in a phosphorus pentoxide desiccator and weighed. The oxide produced by low temperature calcination was extremely hygroscopic and the greatest care was required to secure reproducible results. The oxide produced by calcination at 900 and 1000° was quite inert and could be exposed to the atmosphere of the balance case without detectable change over a period of an hour.

The technique adopted for the determination of the rate of solution of magnesium oxide in magnesium chloride solutions was as follows.

A weighed amount of magnesium oxide was triturated in a mortar with a 25-cc. portion of magnesium chloride solution. Mortar, pestle, magnesium oxide and magnesium chloride solution were previously brought to the working temperature selected. The solution was decanted into a test-tube of 125 cc. capacity. The heavy particles which remained, after decanting the liquid carrying considerable solid material in suspension, were ground with the liquid remaining until all the large particles were reduced to a uniform suspension. A second portion of magnesium chloride solution was then added and the same operations repeated. On decanting a third 25-cc. portion from the mortar, all solid particles appeared to have been removed. A fourth 25-cc. portion of magnesium chloride solution served to assure the complete removal of all solid particles and brought the volume of magnesium chloride solution to a total of 100 cc. The stoppered tube and contents were placed in a constant temperature bath and turned end over end at a velocity of fifteen turns per minute throughout the duration of the experiment. At intervals, 10-cc. portions of the contents of the tube were withdrawn and the amount of magnesium oxide in solution determined by filtering and titrating a 5-cc. portion of the filtrate with $N/5$ hydrochloric acid, using phenolphthalein as an indicator.

The above described procedure proved to yield reproducible results, whereas no success was attained in attempting to prepare samples of magnesium oxide of like particle size by screening.

The graphs in Fig. 2 represent results obtained by following the foregoing procedure at a temperature of 30° . The graphs for magnesium oxide prepared at 500 and 600° fall regularly between those for 400 and 700° and are therefore omitted. At higher temperatures, up to 40° , the curves fall in the same relation to one another with the time decreased; at lower temperatures, down to 10° , the time is increased with decrease in temperature. The figures in brackets represent the time and temperature of calcination of magnesium hydroxide.

From the graphs, it is apparent that there is a definite relationship between the thermal treatment of the magnesium oxide and the rate of solution as well as the amount of oxide dissolved. The rate of precipitation of the new compound, once saturation is attained, is substantially the same in all cases.

An increase in the ratio of the amount of oxide to the amount of magnesium chloride solution decreases the time required to attain saturation and the amount of oxide dissolved increases [Graph 2 g., twenty-one hours, 400°]. A decrease in the ratio of oxide to solution retards the rate of formation of the insoluble precipitate to a marked degree [Graph 0.5 g., twenty-one hours, 400°].

In all cases the concentration of magnesium oxide in the solutions decreased as more and more precipitate was formed, finally approaching the solubility of magnesium hydroxide in the solution under investigation.

The following procedure was developed for the preparation of the precipitate. A sample of oxide of known thermal history was triturated in a mortar with magnesium chloride solution, as previously described, and the suspension, contained in a stoppered tube, was then agitated in a constant temperature bath. After the lapse of sufficient time to effect saturation of the solution with oxide, as indicated by the graph correspond-

ing to that oxide, the concentration of the magnesium chloride solution used, and the temperature, the excess oxide was removed from the solution by filtration. The clear filtrate was placed in a clean flask and returned to the constant temperature bath. Here it was allowed to remain until sufficient precipitate collected to provide a sample for analysis. The precipitate was then removed by filtration, dried rapidly by suction, and washed with 75- to 100-cc. portions of absolute alcohol prepared as recommended by G. Frederick Smith.³ The washing with alcohol was conducted by removing the

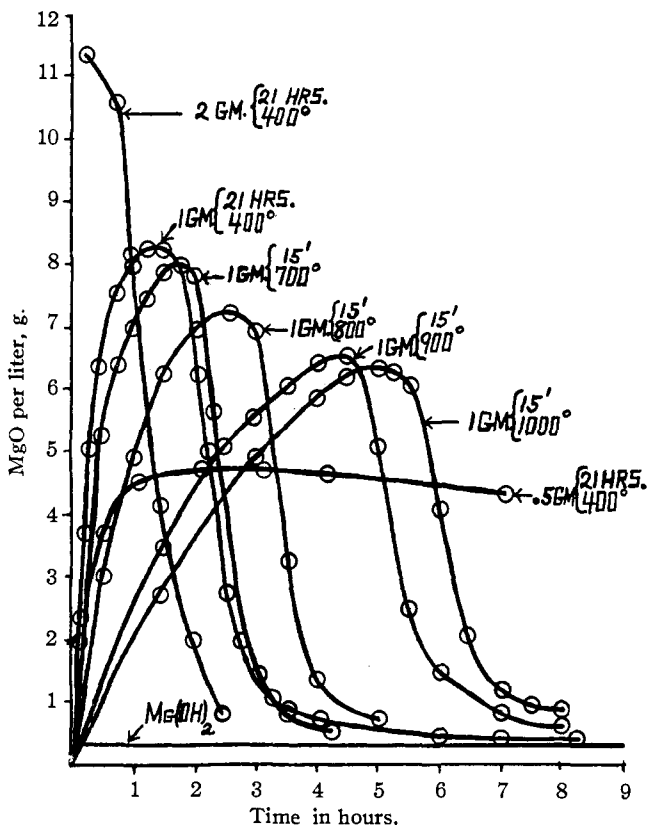


Fig. 2.—Solubility of magnesium oxide in magnesium chloride solution of sp. gr. 1.179; temperature 30°.

gelatinous precipitate to a flask and stirring with a rod while covered with a small portion of alcohol. More alcohol was then added and the mixture shaken violently until a uniform suspension of precipitate in alcohol was attained. The alcohol was then removed by filtration, with suction, and the operation repeated with additional portions of alcohol until successive portions of filtrate, when tested, indicated a low constant chlorine content. This was found to correspond to 0.213 g. of soluble material per liter. From six to eight portions of alcohol were required to complete the washing. The material was then heated at a temperature of 100° to constant weight. As the material was hygroscopic, it was introduced into weighing bottles while warm and samples for

³ Smith, *Ind. Eng. Chem., Anal. Ed.*, 1, 2, 72 (1929).

analysis were measured by determining the weight of bottle and contents before and after pouring out samples.

The precipitates, while forming, appeared to consist of minute crystals. On removal from the solutions they were observed to have all of the characteristics of a gel. On washing with alcohol the precipitates lost their gel-like properties and became decidedly crystalline. This change was accompanied by a marked decrease in volume. It was observed, however, that if a washed and dried precipitate were again treated with magnesium chloride solution, it again attained the gel-like character and regained its former volume.

Many efforts to obtain reproducible results on analysis of samples prepared in this way were unsuccessful, until it was realized that there was a relationship between the time the precipitate remained in the chloride solution and the composition of the precipitate. A few results are tabulated to illustrate the effect of time of contact of the precipitates with the magnesium chloride solutions from which they were precipitated. The chlorine content is assumed to be present in the form of magnesium chloride.

TABLE I
EFFECT OF TIME OF CONTACT WITH MAGNESIUM CHLORIDE SOLUTIONS ON COMPOSITION OF PRECIPITATE

Time precipitate remained in solution	MgO, 1 g., 30 hours, 400°. MgCl ₂ , 100 cc. Sp. gr., 1.179. Temp., 25°		
	MgO, %	Composition of precipitate MgCl ₂ , %	H ₂ O, %
1 hour	44.61	20.34	35.05
10 hours	44.34	21.38	34.28
24 hours	38.84	25.08	36.08
10 days	35.96	26.84	37.20
9 months	36.51	27.07	36.42

With such evidence, strongly indicative that the ratio of MgCl₂ to MgO increased with time of exposure of the precipitate to the solution in which it formed, an effort was made to determine whether the precipitate, as formed, was homogeneous. Two portions of a precipitate were collected. One portion represented that which formed at first and which was removed from solution within one hour after precipitation started. The second portion was the precipitate which formed between one hour after and four hours after precipitation started. After removal of the second portion, a further small amount of precipitate formed but this was discarded. On analysis of the two portions of precipitate, the following results were obtained.

TABLE II
COMPOSITION OF INITIAL AND FINAL PORTIONS OF PRECIPITATE

Period of time after precipitation started during which sample was formed	MgO, 1 g., 30 hours, 400°. MgCl ₂ , 100 cc. Sp. gr., 1.179. Temp., 25°			
	MgO, %	MgCl ₂ , %	H ₂ O, %	Ratio MgO : MgCl ₂
0 → 1 hour	42.42	20.09	37.49	4.97 : 1
1 hour → 4 hours	42.51	20.07	37.42	5.00 : 1

From the above and similar data it was concluded that the precipitate, as formed, was uniform in composition.

To determine definitely whether a precipitate changed in composition on further contact with the solution in which precipitation took place, the following experiment was conducted. Five grams of magnesium oxide (30 hours, 400°) was treated with 250 cc. of magnesium chloride solution of sp. gr. 1.179 at a temperature of 25°. The precipitate formed after filtering remained in contact with the solution at constant temperature for a period of ten days. On analysis the precipitate was found to have the following composition: MgO, 42.35%; MgCl₂, 20.85%; H₂O, 36.80%; ratio of MgO:MgCl₂, 4.79:1. Further data relating to such changes are presented later.

To determine whether the precipitates differed in composition when prepared from samples of magnesium oxide of different thermal history, experiments were conducted from which the following results were obtained.

TABLE III
COMPOSITION OF INITIAL PRECIPITATES OBTAINED FROM MAGNESIUM OXIDE SAMPLES OF DIFFERENT THERMAL HISTORY

Type of MgO	MgO, %	MgCl ₂ , %	H ₂ O, %	Composition of precipitates	
				MgO, 1 g.	MgCl ₂ , 100 cc. Sp. gr., 1.179. Temp., 25°
				Ratio	
				MgO : MgCl ₂	
21 hours, 400°	44.62	20.39	34.99	5.12 : 1.00	
36 hours, 500°	42.56	20.08	37.36	5.01 : 1.00	
30 min., 800°	42.72	19.93	37.35	5.06 : 1.00	
10 min., 1000°	44.68	20.28	35.04	5.20 : 1.00	

It is evident that within the range covered, the mole ratio of magnesium oxide to magnesium chloride approaches 5:1, irrespective of the thermal treatment of the oxide from which the precipitates are prepared.

Temperature was found to have a marked effect on the velocity of the reaction. At 20° only a slight precipitate formed within twenty-four hours; in forty-eight hours precipitation was complete. Raising the temperature from 25 to 30° increased the rate of solution of oxide approximately 50%. Change in temperature was found to have no detectable effect on the ratio of magnesium oxide to magnesium chloride in the precipitates as is illustrated in Table IV.

TABLE IV
EFFECT OF TEMPERATURE ON COMPOSITION OF INITIAL PRECIPITATES

Temperature during formation, °C.	MgO, 1 g., 30 hours, 400°. MgCl ₂ , 100 cc. Sp. gr., 1.179			
	Composition of precipitates			
	MgO, %	MgCl ₂ , %	H ₂ O, %	Ratio MgO:MgCl ₂
20	44.35	21.38	34.27	4.89 : 1.00
25	42.41	20.11	37.48	4.98 : 1.00
30	42.72	20.05	37.23	5.03 : 1.00

To determine whether the composition of the precipitate was influenced by the specific gravity of the magnesium chloride solutions employed, precipitates were made at 25° using magnesium oxide prepared at 400°, and magnesium chloride solutions of sp. gr. 1.124, 1.142, 1.148, 1.151, 1.160, 1.179 and 1.265. The results of the analysis of these precipitates are shown in the graphs, Fig. 3.

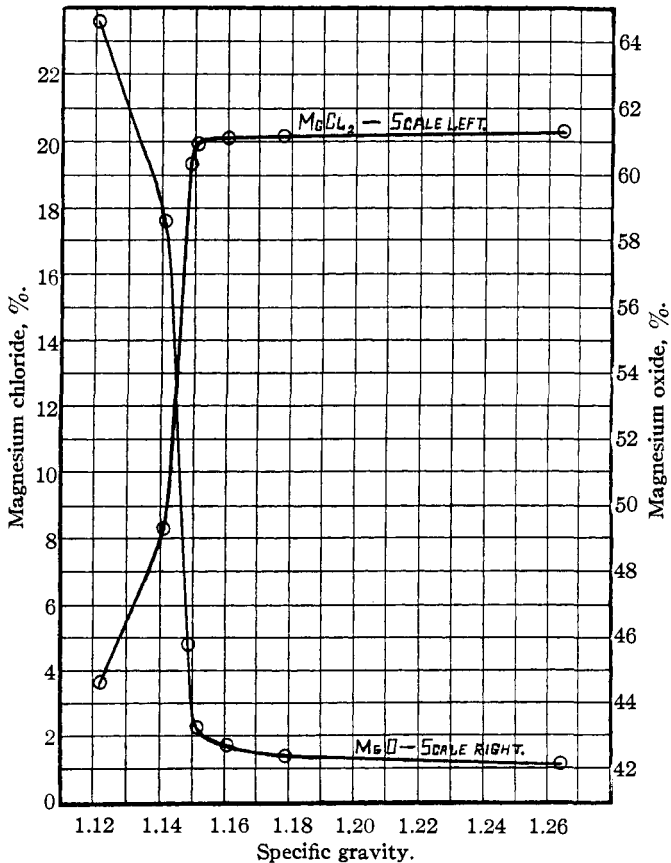


Fig. 3.—Composition of initial precipitates with change in specific gravity of magnesium chloride solutions.

The precipitates were removed from solution within five to six hours after the first contact of the oxide with the solutions. The precipitate produced in solution of sp. gr. 1.151 appeared to be more crystalline than those produced at higher concentrations. The precipitate formed in solution of sp. gr. 1.124 was decidedly flocculent.

It is obvious from the graphs that in solutions of sp. gr. below 1.16 the magnesium oxide content of the precipitates increases while the magnesium

chloride content decreases correspondingly. Such findings may be explained on the assumption that in solutions of low specific gravity, magnesium oxide combines with water to form magnesium hydroxide rather than a compound with magnesium chloride. From solutions of sp. gr. 1.16 up to sp. gr. 1.265 the initial precipitates consist of a combination of magnesium oxide, magnesium chloride and water in which the ratio of magnesium oxide to magnesium chloride is 5 to 1.

Robinson and Waggaman⁴ describe a compound formulated $3\text{MgO} \cdot \text{MgCl}_2 \cdot 10\text{H}_2\text{O}$. As this compound was formed after equilibrium was attained between the interacting constituents, it seemed of interest to investigate further the action of magnesium chloride solutions on the compounds just described. A precipitate corresponding to the 5 to 1 ratio was prepared. One-half was used for analysis, the other portion was covered with 50 cc. of magnesium chloride solution, sp. gr. 1.265, and agitated in a stoppered tube at 25° for ninety hours. The results of the analysis of the precipitates before and after treatment are given in Table V.

TABLE V
CHANGE IN COMPOSITION OF INITIAL PRECIPITATE WHEN AGITATED WITH MAGNESIUM CHLORIDE SOLUTION

Precipitate	Composition of precipitates				Ratio MgO : MgCl ₂ : H ₂ O
	MgO, %	MgCl ₂ , %	H ₂ O, %	MgO, %	
Initial precipitate	42.56	20.08	37.36	5.01	1.00 : 9.84
Precipitate after treatment with magnesium chloride for 90 hours	34.86	26.38	38.76	3.48	1.00 : 7.76

A precipitate was prepared and allowed to remain in contact with the solution for a period of ten days at 25°. Four samples of 2 g. each were placed in flasks, covered with 100 cc. of magnesium chloride solution, sp. gr. 1.325, the flasks stoppered and allowed to remain undisturbed in a constant temperature bath at 25° until removed for analysis. Analyses were made at intervals over two years with results indicated in Table VI.

TABLE VI
CHANGE IN COMPOSITION OF INITIAL PRECIPITATE ON UNDISTURBED CONTACT WITH MAGNESIUM CHLORIDE SOLUTION

Treatment of precipitate	Composition of precipitates				Ratio MgO : MgCl ₂ : H ₂ O
	MgO, %	MgCl ₂ , %	H ₂ O, %	MgO, %	
Original precipitate	42.35	20.86	36.79	4.79	1.00 : 9.32
After 5 months	38.30	24.99	36.71	3.62	1.00 : 7.76
After 11 months	36.55	27.25	36.20	3.16	1.00 : 7.02
After 18 months	36.45	27.39	36.16	3.14	1.00 : 6.98
After 24 months	36.49	27.11	36.40	3.17	1.00 : 7.09

The ratio of magnesium oxide to magnesium chloride described by Robinson and Waggaman is confirmed. The water content differs,

⁴ Robinson and Waggaman, *J. Phys. Chem.*, 13, 673 (1909).

probably due to the difference in the methods used in the preparation of samples for analysis.

Up to the present it has not been possible to devise any method for determining the water content of the precipitates. The gel-like appearance indicates that the amount of water is greater than indicated by the analyses. The water is obviously loosely held, for even protracted washing with absolute alcohol tends to reduce the water content as is evident from the data in Table VII.

TABLE VII

LOSS OF WATER BY $5\text{MgO}\cdot\text{MgCl}_2\cdot x\text{H}_2\text{O}$ ON WASHING WITH ALCOHOL	Composition of precipitate				Ratio MgO : MgCl ₂ : H ₂ O
	Number of times washed with anhydrous alcohol	MgO, %	MgCl ₂ , %	H ₂ O, %	
7 completed within an hour	42.56	20.08	37.36	5.01 : 1.00 : 9.84	
10 over a period of 4 days	51.27	24.14	24.59	5.06 : 1.00 : 5.43	

When exposed to the atmosphere of a phosphorus pentoxide desiccator, both compounds lose water steadily. The compounds were not in equilibrium with the desiccator atmosphere even after 111 hours at a pressure of 5 mm. On heating, both compounds will, in time, come to constant weight at any given temperature up to 200°. After heating for thirty-five hours at 200°, the 5 to 1 compound lost 17.16% of its weight after drying over phosphorus pentoxide at 5 mm. for 111 hours; the 3 to 1 compound lost 24.67%.

Summary

Magnesium oxide is shown to dissolve in magnesium chloride solutions with the subsequent precipitation of a compound in which the ratio of magnesium oxide to magnesium chloride is 5 to 1, loosely combined with an unknown amount of water.

The velocity of the reaction is determined principally by the thermal treatment of the magnesium oxide and by the temperature at which the reaction takes place.

The compound initially precipitated in solutions of magnesium chloride of concentrations above sp. gr. 1.16 may be formulated $5\text{MgO}\cdot\text{MgCl}_2\cdot x\text{H}_2\text{O}$.

The compound $5\text{MgO}\cdot\text{MgCl}_2\cdot x\text{H}_2\text{O}$ on continued treatment with magnesium chloride solution of sp. gr. above 1.16 is transposed to a new compound which may be formulated $3\text{MgO}\cdot\text{MgCl}_2\cdot y\text{H}_2\text{O}$.

No satisfactory method has been devised for determining the water content of the compounds as formed in solution.

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