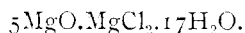


BASIC MAGNESIUM CHLORIDES¹

BY W. O. ROBINSON AND W. H. WAGGAMAN.

Sorel² describes a cement made by mixing calcined magnesia with a concentrated solution of magnesium chloride. This material much resembled marble and was used in mosaics with beautiful effect. When mixed with other material its "flocculating power" was so great that three or four times its weight of foreign material could be used. Sorel states that this cementing material was not affected by water, a statement which later workers have shown to be incorrect.

Bender³ prepared a basic magnesium chloride by a method similar to that of Sorel's. The magnesia usta of commerce was ignited and over this was poured a strong solution of magnesium chloride. This material was dried in air for six months, then analyzed. Different portions contained different amounts of magnesium carbonates, resulting from the absorption of carbon dioxide from the air. Bender assumed that all the carbon dioxide was combined with the magnesia to form normal, anhydrous, magnesium carbonate, and by deducting the requisite amount of magnesia corresponding to the carbon dioxide content, he found the substance to be represented by the formula



His analyses agreed poorly and the molecular ratio of the average was about $5\frac{1}{2} : 1$.

Davis⁴ found fine needle-like crystals which had deposited in mass on the bottom and sides of a reagent bottle containing magnesium ammonium chloride with an excess of ammonia. The material was divided into two parts, A and B. A was washed with a small amount of cold water until

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² Comptes rendus, **65**, 102 (1867).

³ Liebig's Ann., **159**, 341 (1871).

⁴ Chem. News, **25**, 258 (1872).

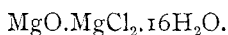
free from ammonium salts. The analyses showed the composition of this residue to be $5\text{MgO} \cdot \text{MgCl}_2 \cdot 13\text{H}_2\text{O}$. B was washed with a much larger quantity of water for several days. It contained no chlorine and the ratio of magnesia to water was between $\text{MgO} \cdot \text{H}_2\text{O}$ and $4\text{MgO} \cdot 5\text{H}_2\text{O}$.

Krause¹ claimed that Bender's² analyses were not accurate, for the basic residue was allowed to stand in air until carbon dioxide had been absorbed, and that the assumption that the carbon dioxide had combined to form a normal anhydrous carbonate was improbable, for with such an excess of base, a basic carbonate would have formed.

Krause prepared his oxychloride by shaking up magnesium oxide in a solution containing a large excess of magnesium chloride, and heating and cooling with intermittent shaking until nothing but acicular crystals could be observed with the aid of the microscope. The mother liquor was then decanted off and the residue washed with water until only an opalescence was observed by the silver nitrate test. An analysis of the material dried at 110° showed:



André³ formed a basic magnesium chloride by adding 20 grams of calcined magnesium oxide to a boiling mixture of 500 grams water and 400 grams crystallized magnesium chloride. The analysis of the solid residue gave the molecular ratios indicated by the following formula:



André states that the crystals immediately decomposed on washing with water or alcohol. It is probable that André analyzed a mixture of mother liquor and basic magnesium chloride.

Since basic magnesium chloride is decomposed by washing, it is evident that the previous analyses have been made

¹ Liebig's Ann., 165, 38 (1873).

² Loc. cit.

³ Comptes rendus, 94, 444 (1882).

on decomposed material, or as in André's case on a salt contaminated by mother liquor.

It has seemed that the composition of the basic magnesium chlorides and the ranges of concentration of solution over which they can exist could best be determined by a study of the solubility of magnesium hydroxide in solution of magnesium chloride of various concentrations. The 25° isotherm has been determined.

The magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) used in the research was found to contain no impurity other than a very slight trace of calcium. The magnesium oxide was prepared from this sample by precipitating with ammonia and washing. It was then strongly ignited, pulverized, and put in containers protected from the air.

Twenty bottles were made up in regular steps of concentration from pure water to a saturated solution of magnesium chloride. A small amount (1 gram to 200 cc solution) of magnesium oxide was then added and the bottles were placed in a thermostat where they were subjected to constant shaking. It was noticed that the residue tended to collect in lumps. These were broken down from time to time. At the end of six months the residues had become homogeneous, and analyses of the solutions from several bottles at intervals of two months, showed no change in concentration. By means of a microscopic examination it was found that the residue of the dilute solutions were kernel-like and amorphous, while the residues in the concentrated solution were composed of very fine, acicular crystals.

The bottles were allowed to settle and the clear solution drawn off and analyzed for magnesium and chlorine. They were also titrated against standard hydrochloric acid $N/50$, using phenolphthalein as indicator. On account of the small amounts present the determinations are necessarily poor. They are given in Table I, and when plotted show two distinct curves.

TABLE I
Showing the solubility of MgO in solutions of MgCl₂ at 25°

Percent MgCl ₂	Percent MgO as Mg(OH) ₂
2.36	0.00008
4.47	0.00028
6.79	0.00048
9.02	0.00080
13.14	0.00115
15.15	0.00195
17.53	0.00240
18.52	0.00250
22.04	0.00245
23.78	0.00235
25.13	0.00230
26.88	0.00250
28.34	0.00230
29.80	0.00240
30.04	0.00250
34.22	0.0030

TABLE II

Serial No.	Solution			Residue		Solid phase
	Sp. gr.	Percent MgO	Percent HCl	Percent MgO	Percent HCl	
1	1.019	0.99	1.77	41.56	0.99	Indefinite solid solution
2	1.038	2.02	3.85	12.90	2.91	" " "
3	1.056	2.88	5.16	19.21	4.00	" " "
4	1.075	3.82	6.80	17.17	5.20	" " "
5	1.111	5.57	9.94	19.95	7.67	" " "
6	1.129	6.42	11.52	15.86	9.86	" " "
7	1.141	7.13	12.76	22.74	14.88	2MgO.HCl.5H ₂ O
8	1.162	7.85	14.17	23.71	15.70	"
9	1.192	9.34	16.51	22.01	16.98	"
10	1.209	10.08	17.83	22.59	17.63	"
11	1.226	10.65	19.16	24.40	18.24	"
12	1.245	11.39	20.68	24.91	18.93	"
13	1.256	12.01	21.53	23.80	19.69	"
14	1.274	12.63	22.73	25.64	19.95	"
15	1.282	13.24	23.92	26.38	20.18	"
16	1.302	13.86	24.58	—	—	"
17	1.321	14.49	26.05	25.50	21.80	"
18 ¹	1.345	15.19	27.38	—	—	MgCl ₂ .6H ₂ O

¹ Represents a saturated solution of MgCl₂.6H₂O. Concentration 55.76 grams anhydrous MgCl₂ to 100 grams H₂O.

The residues were sucked as completely as possible from the mother liquor, but not washed at all, and analyzed for magnesia and chlorine. The results are given in Table II. When plotted on the triangular diagram shown in Fig. 1 it is plain that an indefinite solid solution of magnesia-chlorine and water exists up to a concentration of about 10 grams MgCl_2 to 100 cc solution, and that beyond this concentration up to a saturated solution of magnesium chloride there exists a basic magnesium chloride of definite composition.

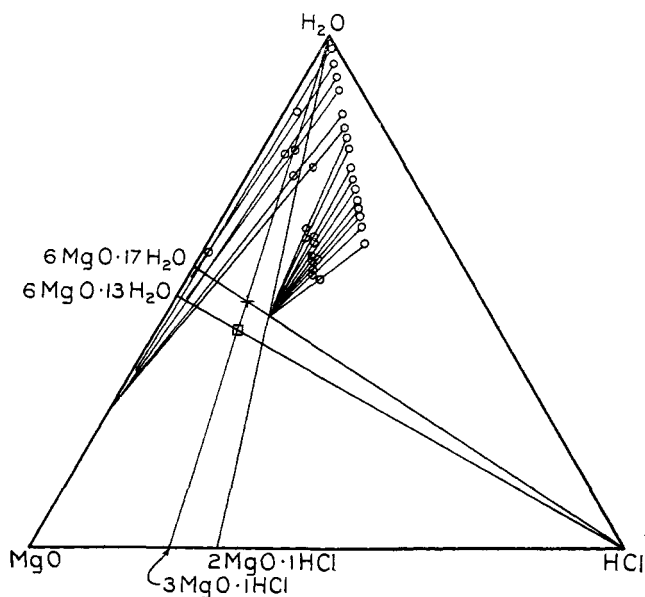
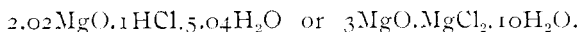


Fig. 1

This solid, by scaling off on the triangular diagram, was found to consist of



In this paper a study of the system magnesia (MgO), hydrochloric acid (HCl) and water (H_2O) at 25° with the

MgO in excess has been outlined. A hitherto undescribed basic magnesium chloride of definite composition has been identified and the limits of concentration of aqueous solution over which it is stable as solid phase have been determined.

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