178. *The System Magnesium Chloride–Lime–Water.*

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THE work now recorded is a continuation of that previously published (J., 1932, 2008 *) on the physical chemistry of magnesium oxychloride cement. Lime is invariably present in commercial samples of magnesia and appears to exert a deleterious influence on the cement when present in amounts exceeding 2%. In order to study the effect of lime, the four-component (reciprocal salt pair) system $MgCl_2$–CaO–H_2O has been examined at 25°. Before describing this system it is desirable to discuss the four three-component systems MgO–$MgCl_2$–H_2O; CaO–$CaCl_2$–H_2O; MgO–CaO–H_2O; and $MgCl_2$–$CaCl_2$–H_2O at 25°: the first has been described in the previous paper (*loc. cit.*) and the second by Milikan (*Z. physikal. Chem.*, 1918, **92**, 60), the solid phases being $Mg(OH)_2$; $3MgO,MgCl_2,11H_2O$; $MgCl_2,6H_2O$ and $Ca(OH)_2$; $3CaO,CaCl_2,16H_2O$; $CaO,CaCl_2,2H_2O$; $CaCl_2,6H_2O$ respectively. The third and the fourth system are first described.

The System MgO–CaO–H_2O *at* 25°.—On account of the low solubilities of $Ca(OH)_2$ and $Mg(OH)_2$, the usual method of treating such 3-component systems is inapplicable. A method, analogous to a well-known method of studying salt hydrates, has therefore been used. Known weights of CaO, MgO, and H_2O were placed in a tube, shaken in a thermostat at 25° for 3 months, and the concn. of CaO in the filtered solution then determined by titration with acid. From the initial wts. taken and the measured solubility of CaO, the ratio *R*, undissolved CaO/undissolved CaO + MgO, was calculated. The results obtained are shown in Table I, in which the solubility of CaO is expressed in g. per 100 g. soln., and *R* in mols.

TABLE I.

Solubility of CaO	0·117	0·116	0·115	0·115	0·116	0·115
R	1·00	0·77	0·53	0·33	0·125	0·037

To illustrate the theory of the method, suppose a compound CaO,MgO,xH_2O to be formed. Solids for which *R* lay in the range 1·0—0·5 would be mixtures of $Ca(OH)_2$ and this compound, and the concentration of CaO in the soln. in contact with them would be the same as that in a sat. soln. of pure $Ca(OH)_2$. All solids for which *R* was in the range 0·5—0 would be mixtures of $Mg(OH)_2$ and the compound. The concn. of CaO in the soln. in contact with them would be constant, but would be lower than that of a sat. soln. of pure $Ca(OH)_2$. Thus if concns. of CaO be plotted as ordinates against *R* as abscissæ, the resulting graph should be a series of steps, each vertical portion indicating a compound. The relative amounts of CaO and of MgO in each compound will be given by the corresponding value of *R*, but the amount of water in the compounds cannot be determined by this method. The figures given in Table I indicate therefore that no compound is formed, and that the only solid phases present are $Ca(OH)_2$ and $Mg(OH)_2$.

The System $MgCl_2$–$CaCl_2$–H_2O *at* 25°.—This system has been described by Lee and Egerton (J., 1923, **123**, 706), the solid phases present being $MgCl_2,6H_2O$; $CaCl_2,2MgCl_2,12H_2O$ (tachydrite); and $CaCl_2,6H_2O$. During investigation of the 4-component system it was found that solutions saturated with $MgCl_2,6H_2O$ and $3MgO,MgCl_2,11H_2O$, or with $CaCl_2,2MgCl_2,12H_2O$ and $3MgO,MgCl_2,11H_2O$, were identical in composition with those saturated with $MgCl_2,6H_2O$ or $CaCl_2,2MgCl_2,12H_2O$ alone as determined by Lee and Egerton. There was, however, an appreciable difference between our data for the composition of solutions saturated with $CaCl_2,6H_2O$ and $3MgO,MgCl_2,11H_2O$ and those of Lee and Egerton for the composition of solutions saturated with $CaCl_2,6H_2O$ alone. The solubility of $CaCl_2,6H_2O$ in solutions containing $MgCl_2$ was therefore determined. One of Lee and Egerton's points was found to be in error, and the form of the curve for the solubility of $CaCl_2,6H_2O$ is rather different from that given by them.

The solubility of the metastable hydrate α-$CaCl_2,4H_2O$ in solutions containing $MgCl_2$ was also determined because it was thought that the discrepancy between our results and those of Lee and Egerton might be due to the fact that these authors had obtained this

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* In this paper, p. 2010, l. 7 from bottom, *for* " 1·27 " *read* " 2·7."

hydrate instead of the stable $CaCl_2,6H_2O$ as solid phase, but the results obtained do not support this surmise.

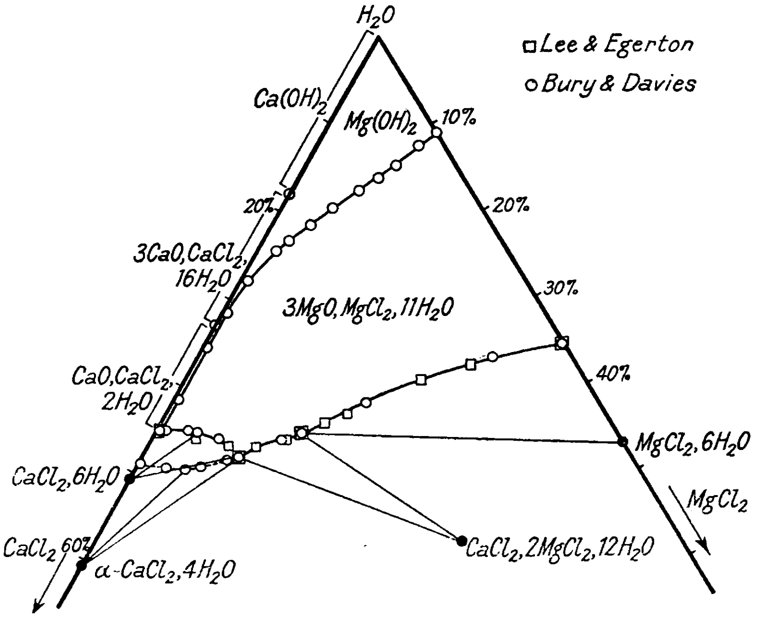
Exptl. and analytical methods were the same as those used in studying the 4-component system, except that equilibrium is established in a few days. The nature of the solid phases present was determined by inspection with a microscope; a few analyses of moist solids were also made, but are not quoted. The results are given in Table II, which includes some measurements with $Mg(OH)_2$ or $3MgO,MgCl_2,11H_2O$ as solid phases obtained during the study of the 4-component system; these contain a trace of free MgO. All analyses quoted are the mean of 2 concordant determinations and are expressed in g. per 100 g. soln. The results, together with other material, are shown in the fig., plotted on triangular co-ordinates. As can be seen, the two triple points $CaCl_2,6H_2O$–$CaCl_2,2MgCl_2,12H_2O$–Soln. and α-$CaCl_2,4H_2O$–$CaCl_2,2MgCl_2,12H_2O$–Soln. coincide within the limits of exptl. error at this temp.

TABLE II.

Analyses of saturated solutions for system $CaCl_2$–$MgCl_2$–H_2O.

$MgCl_2$, %.	$CaCl_2$, %.	MgO, %.	Solid phases.	$MgCl_2$, %.	$CaCl_2$, %.	MgO, %.	Solid phases.	$MgCl_2$, %.	$CaCl_2$, %.	MgO, %.	Solid phases.
—	45·00	0·002	C, H.	13·58	33·36	0·002	X, T.	5·97	43·42	—	A.
0·168	44·88	0·002	C, H, X.	14·60	31·32	0·002	X, T, M.	6·01	43·38	—	A.
0·612	44·55	0·002	C, X.	19·32	22·94	0·002	X, M.	6·24	43·19	—	A.
3·098	42·14	—	C.	29·25	7·87	0·002	X, M.	7·30	41·99	—	A.
4·115	41·48	—	C.	29·84	7·46	0·002	X, M.	8·52	40·03	—	A.
6·47	39·58	—	C.	—	48·80	—	A.	9·43	38·88	—	A, T.
8·14	38·82	0·002	C, X.	2·739	46·49	—	A.	9·38	38·94	—	A, T.
9·42	38·80	0·002	C, X, T.	4·742	44·71	—	A.				

Solid phases : C = $CaCl_2,6H_2O$; H = $Mg(OH)_2$; X = $3MgO,MgCl_2,11H_2O$;
T = $CaCl_2,2MgCl_2,12H_2O$; M = $MgCl_2,6H_2O$; A = α-$CaCl_2,4H_2O$.



The Four-component (*Reciprocal Salt Pair*) *System* CaO–$MgCl_2$–H_2O *at* 25°.—$Mg(OH)_2$ and $3MgO,MgCl_2,11H_2O$ are much less sol. than any other solid phases encountered in studying this system, and consequently one or the other of these is almost invariably present as solid phase. These two solids also play a prominent rôle in the 3-component system MgO–$MgCl_2$–H_2O and in its exptl. behaviour, and in the difficulties encountered in its study, the 4-component system is very similar to the 3-component system. Even in favourable circumstances, equilibrium is only established very slowly, metastable equilibria are readily established, and mixtures tend to set to cements or gels. It was found that continuous shaking for 2 months at 25° was necessary, and metastable equilibria could be avoided by inoculation with a trace of powdered magnesium oxychloride cement. As the amount of $CaCl_2$ in the system increases, the tendency to form cement decreases, while the tendency to form gels increases; 0·2 g. MgO swells in contact with 100 c.c of a $CaCl_2$-rich soln. containing a little $MgCl_2$ and the whole of the soln. sets to a gel. Gel formation prevents stirring, and equilibrium can only be attained in reasonable time by using such small amounts of MgO that no firm gel is formed. This in turn makes it difficult to fix the concns. of solns. in equilibrium with $Mg(OH)_2$ and $3MgO,MgCl_2,11H_2O$ simultaneously, for small amounts of MgO are converted completely into one or the other of these unless the concn. of the initial soln. used is almost coincident with the concn. of the equilibrium soln.

To overcome this difficulty, and to cover the field systematically, a system of " traverses " was used. Two solns., of accurately known but very different composition, were mixed in various proportions: 0·2 g. of MgO, or sometimes of CaO, was then added to each mixture. After equilibrium had been established, the solns. were analysed, and the nature of the solid phase determined. As a rule, the solid phase was $3MgO,MgCl_2,11H_2O$ in the solns. containing most $MgCl_2$, and $Mg(OH)_2$ in solns. containing least $MgCl_2$. Once the triple point $Mg(OH)_2$–$3MgO,MgCl_2,11H_2O$–Soln. had been bracketed, the interval was systematically investigated in a second series of expts.

Solns. and moist solids were analysed for Cl by Volhard's method, and for Ca and Mg. The moist solid was dissolved in dil. HNO_3 and aliquot portions taken. Blasdale's procedure (*J. Amer. Chem. Soc.*, **1909**, **31**, **917**) for the estimation of Ca in the presence of Mg was followed, the Ca being then weighed as $CaCO_3$ after ignition in an electric furnace at 500—520° (Willard and Boldyreff, *ibid.*, **1930**, **52**, **1888**). Mg was estimated as $Mg_2P_2O_7$ with the precautions recommended by Epperson (*ibid.*, **1928**, **50**, **321**). Solns. were always slightly alk., although if they contained much $CaCl_2$ or $MgCl_2$ this could not be detected from analyses of Ca, Mg, and Cl, which were present in equiv. proportions within the limits of exptl. error. The free base in soln. was therefore determined by titration with HCl.

Analyses of sat. solns. are given in Tables III and IV, all results being the mean of 2 concordant determinations. In Table III are also given analyses of moist solids in contact with these solns. Analyses are expressed as g. of the various components per 100 g. soln. or moist solid. The results fall naturally into 2 sections: Table III includes all analyses in which $MgCl_2$ was found present in solution. For this part of the system $MgCl_2$, $CaCl_2$, and MgO can most conveniently be regarded as the components of the system. In this section solns. invariably contain about 0·002% MgO in addition to the other components listed. Table IV includes all analyses in which no Mg can be detected in soln.: for this part of the system CaO, $CaCl_2$,

TABLE III.

Analyses of saturated solutions and moist solids for system $CaO–MgCl_2–H_2O$.

Sat. solution.		Moist solid.			
$MgCl_2$, %.	$CaCl_2$, %.	$MgCl_2$, %.	$CaCl_2$, %.	MgO, %.	Solid phases.
8·46	1·864	4·87	1·38	31·44	H.
5·02	12·99	2·12	7·62	32·07	H.
2·562	15·91	1·24	8·96	33·13	H.
4·313	10·96	1·25	7·19	31·53	H.
3·186	20·02	1·77	11·63	24·84	H.
7·29	7·95	3·204	6·82	22·34	H.
0·532	22·87	0·317	14·55	26·53	H.
1·481	22·88	1·130	16·38	21·77	H.
0·546	26·21	0·550	16·48	24·42	H.
10·36	2·483	9·96	1·55	16·36	H, X.
9·89	2·537	11·09	2·33	7·41	H, X.
9·33	6·105	9·56	5·53	8·32	H, X.
8·11	8·59	7·30	6·48	17·24	H, X.
7·99	8·60	7·18	6·79	18·45	H, X.
6·40	11·10	8·21	9·88	3·81	H, X.
4·62	14·64	5·98	12·93	6·82	H, X.
3·82	18·17	6·68	16·32	8·01	H, X.
2·415	20·78	6·92	16·02	7·91	H, X.
1·680	22·89	5·91	18·40	6·71	H, X.
0·754	26·20	1·73	21·84	4·32	H, X.
0·498	27·30	0·732	20·43	22·76	H, X.
0·366	31·58	2·16	28·75	3·38	H, X.
0·330	36·09	1·25	33·87	2·44	H, X.
0·230	41·68	—	—	—	H, X.
14·69	4·160	16·73	3·120	7·69	X.
21·84	5·981	21·91	4·45	6·83	X.
12·07	3·353	14·05	2·621	7·37	X.
18·00	5·753	19·11	4·58	6·19	X.
6·96	22·43	10·20	18·65	5·36	X.
5·144	15·62	7·45	13·73	3·92	X.
2·850	25·51	5·92	21·91	5·02	X.
19·44	21·41	19·83	16·68	7·66	X.
11·63	12·30	14·03	9·78	7·80	X.
9·38	9·44	11·61	7·86	6·76	X.
1·808	23·27	6·58	17·92	5·75	X.
0·741	27·41	4·013	23·15	6·12	X.
0·597	34·97	3·75	28·71	7·71	X.
0·368	40·52	—	—	—	X.
0·477	32·08	4·11	27·10	5·48	X.

Solid phases: H = $Mg(OH)_2$; X = $3MgO,MgCl_2,11H_2O$.

TABLE IV.

Analyses of saturated solutions for system $CaO–MgCl_2–H_2O$ (*Section* 2).

Sat. solution.		Solid	Sat. solutions.		Solid	Sat. solutions.		Solid
CaO, %.	$CaCl_2$, %.	phases.	CaO, %.	$CaCl_2$, %.	phases.	CaO, %.	$CaCl_2$, %.	phases.
0·141	14·85	H, L.	0·168	29·05	H, O.	0·083	36·82	H, P.
0·150	18·06	H, L, O.	0·170	29·22	H, O.	0·091	37·10	H, P.
0·145	20·08	H, O.	0·235	32·98	H, O, P.	0·051	40·85	H, P.
0·145	23·56	H, O.	0·098	36·44	H, P.	0·034	44·92	H, P, C.

Solid phases : H = $Mg(OH)_2$; L = $Ca(OH)_2$; O = $3CaO,CaCl_2,16H_2O$;
P = $CaO,CaCl_2,2H_2O$; C = $CaCl_2,6H_2O$.

and MgO can most conveniently be taken as the components. In this section several analyses of moist solids were made, but these were not quoted, since, as will be shown later, the results are valueless.

The nature of the solid phases was determined by an extension of the method of graphical extrapolation used in 3-component systems. Any reciprocal salt pair $AX–BY–H_2O$ can be regarded as a system composed of the 3 components (AX + BX), (AY + BY), H_2O. (Since the system is a 4-component system, concns. may be so expressed that the concn. of any one of the 4 salts is zero.) Any of the usual methods of determining the compositions of solid phases in 3-component systems, by plotting compositions of sat. solns. and moist solids and extrapolating, gives the composition of the solid phase in terms of the components chosen; *i.e.*, the relative amounts of (A + B), X, Y, and H_2O in the solid phase can be determined. Similarly, the system can be regarded as composed of the 3 components (AX + AY), (BX + BY), H_2O and the composition of the solid phase in terms of these components determined. Combination gives the complete formula. The method is perfectly general and can be applied in conjunction with any of the well-known methods of graphical extrapolation, provided concns. of the salts are expressed in g.-mols., and not in g. Jānecke's method (*Z. anorg. Chem.*, **1906**, **51**, 132) was found most convenient for this system. For the $CaCl_2$-rich portion of the system, the composition of the sat. soln. and of the various solid phases that might be present all lay so near to a straight line that graphical methods were of little value.

The nature of the solid phases was also determined by inspection with a microscope. $Ca(OH)_2$ cannot be distinguished from $Mg(OH)_2$, nor $CaCl_2,6H_2O$ from $MgCl_2,6H_2O$; with this exception all the solid phases can readily be distinguished.

The system is represented graphically in the fig., in which percentages of $CaCl_2$ and $MgCl_2$ in the most significant sat. solns. are plotted on a triangular diagram. The fig. can be regarded as a projection of the usual pyramidal figure on the $CaCl_2–MgCl_2–H_2O$ side of the pyramid. In the pyramidal diagram the series of surfaces, which represent the concns. of the solns. sat. with the various solid phases, are practically coincident with this face, since $Ca(OH)_2$ and $Mg(OH)_2$ are so slightly sol.; consequently this projection is preferable to the usual projection on the base of the pyramid. Areas representing the composition of solns. sat. with $Mg(OH)_2$ and $3MgO,MgCl_2,11H_2O$ predominate in the figure, while areas representing the concns. of solns. sat. with the other solid phases are too small to appear. Thus the area representing the solubility of $CaCl_2,6H_2O$ in the 4-component system is a long six-sided figure, but this is indistinguishable on the small-scale diagram from the line representing its solubility in the 3-component system $CaCl_2–MgCl_2–H_2O$.

Application to Magnesium Oxychloride Cements.—A representative " unfilled " cement can be obtained by mixing 100 g. of magnesium oxide with 131 g. of a 20% magnesium chloride solution; as was shown in the previous paper, such a cement consists of three phases, $Mg(OH)_2$, $3MgO,MgCl_2,11H_2O$, and solution. The results recorded in this paper show that lime, if present in not too great amounts, reacts with an equivalent amount of magnesium chloride and goes into solution as calcium chloride, magnesium hydroxide being precipitated: no fresh solid phase appears until lime in excess of the quantity required to react with all the magnesium chloride has been added, whereupon basic calcium chlorides are formed. The small amounts of lime that may be present in commercial magnesia merely alter the relative amounts of the phases normally present and the concentration of the solution phase. By using graphical methods in conjunction with the figure, the results given in Table V have been obtained; in col. 1 are the amounts of lime

TABLE V.

Influence of lime on the constitution of magnesium oxychloride cement.

	Relative amounts of phases.			Concn. of soln. (g.-mols./1000 g. H_2O).	
CaO, %.	$Mg(OH)_2$, %.	X, %.	Soln., %.	$MgCl_2$.	$CaCl_2$.
0	42	47	11	1·28	—
1	43	44	13	1·06	0·66
2	44	41	15	0·79	1·30
3	44	40	16	0·59	1·79
4	46	36	18	0·41	2·25
5	47	34	19	0·28	2·61
10	53	18	29	0·06	3·81
15·2	60	0	40	0·06	4·37

present as impurity in the magnesia, the cement being otherwise the same as the representative cement described above. The concentrations of calcium and magnesium chlorides in the solution are given in g.-mols. per 1000 g. of water. The table shows that addition of lime causes progressive decrease in the amount of $3MgO,MgCl_2,11H_2O$ (denoted by X), which appears to act as binding material to the cement; it also causes a steady increase in amount of the solution phase, *i.e.*, the cement becomes more porous, and an increase in the total concentration of salt in the solution phase, which will make the cement more hygroscopic.

Two points must be emphasised. First, equilibrium conditions in a porous substance, like the cement, may be somewhat different from those in the experiments described above, since surface forces may not be negligible. Secondly, a study of equilibrium conditions alone cannot give a complete explanation of the influence of lime on magnesium oxychloride cements. A cement made from magnesia containing 10% of lime sets in 24 hours to an apparently excellent cement, but on " ageing," instead of becoming stronger like a pure cement, it contracts, becomes weaker and moist, and may finally turn to a moist paste. In our opinion, the most probable explanation of the change is that it is a kind of syneresis or recrystallisation of the $3MgO,MgCl_2,11H_2O$ gel that binds the cement together. Calcium chloride exerts a very marked influence on the gels described in the previous paper; the needle-like crystals which are the essential constituent of the gel are very much smaller, and the volume of gel containing a specified weight of oxychloride may be 10 times larger in the presence of calcium chloride. This suggests that in the presence of lime an unstable microcrystalline form of $3MgO,MgCl_2,11H_2O$ is formed when the cement sets; the slow recrystallisation of this causes the volume changes and the squeezing out of the solution phase, while the large crystals have poor binding properties, like the large crystals formed by the slow action of magnesium chloride solutions on magnesium hydroxide. Syneresis may be accompanied by chemical change due either to the slow establishment of equilibrium during the ageing period, or to the action of the atmosphere.

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