CCCLVIII.—*The Composition of Bleaching Powder. Part I.*

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THE exact composition of the substances contained in bleaching powder has long been a subject for discussion (see Lunge, " Sulphuric Acid and Alkali," 3rd edn., III, pp. 577—587; Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," II, pp. 262—265), which has centred chiefly around the question of the existence of a definite compound of calcium hypochlorite and calcium chloride in equimolecular proportion, to which was usually assigned the constitution $CaCl\cdot OCl$. Basic compounds containing hypochlorite and chloride have also been postulated by several authors. Lunge (*op. cit.*, p. 585) expressed the following opinion : " It is certain that no calcium chloride is present as such in ordinary bleaching powder." Similar views were held by O'Shea (J., 1883, **43**, 410) and by Orton and Jones (J., 1909, **95**, 751).

A study of the literature led to the conclusion that there is no positive evidence for the existence of a compound of calcium hypochlorite and chloride. Such a compound has never been isolated, and the evaporation at low temperature of solutions obtained by extraction of bleaching powder with water led to a separation of crystals of hydrated calcium hypochlorite, reported as $Ca(ClO)_2,4H_2O$ (Kingzett, J., 1875, **28**, 404; Orton and Jones, *loc. cit.*). At the same time, Orton and Jones obtained three crystalline preparations, containing calcium hypochlorite and chloride together with calcium oxide and water, which on analysis yielded a molecular ratio of hypochlorite to chloride of 1 : 1. These substances, which could not be recrystallised from water, were only approximately analysed, owing to the small quantities available and to the difficulty of complete separation from mother-liquor. There is, therefore, no certainty that any of them was a single definite compound, although it appears likely that one or more basic double salts may exist.

The preparation of calcium hypochlorite comparatively free from calcium chloride, and in some cases free from calcium oxide, has been exploited in recent years by the Chemische Fabrik Griesheim-Elektron (B.PP. 17859, 182927, 188662; D.R.-PP. 188524, 195896, 282746). Calcium hypochlorite, prepared by chlorinating a paste of calcium hydroxide and water and removing as much as possible of the mother-liquor, is stated to be a very stable compound when thoroughly dry, and superior in this respect, as well as in available chlorine, to the best ordinary bleaching powder. Basic compounds containing 1—4 mols. of calcium hydroxide to one of hypochlorite, prepared by a similar process, are claimed to have the same advantages. Two of these compounds, $Ca(ClO)_2,2CaO,2H_2O$ and $Ca(ClO)_2,4CaO,4H_2O$, were isolated, but not in crystalline condition.

The problem of the exact nature and proportions of the substances composing any particular sample of bleaching powder cannot be expected to be capable of solution, for there is no certainty that equilibrium has been established. The equilibrium composition of a bleaching powder giving any particular ultimate analysis (neglecting formation of chlorate) could be determined if data for equilibria in the quaternary system $Ca(ClO)_2$–$CaCl_2$–CaO–H_2O at the same temperature were available. Consequently, it was decided to attempt at a suitable temperature a preliminary investigation of the three ternary systems in which water is a component.

Solutions of hypochlorites decompose rapidly at the ordinary temperature only in the presence of hypochlorous acid, and if this be removed by addition of a slight excess of alkali, the solutions are comparatively stable, forming chloride and chlorate and evolving oxygen very slowly (Foerster and Jorre, *J. pr. Chem.*, 1899, **59**, 53; Foerster, *ibid.*, 1901, **63**, 141). Solutions of calcium hypochlorite which can contain only small concentrations of free hydroxide rapidly increase in stability as the temperature falls, partly because of the usual diminution of reaction rate and partly because less hypochlorous acid is formed by hydrolysis. The whole of the experimental work was therefore carried out at 0°, and in the system $Ca(ClO)_2$–$CaCl_2$–H_2O a minute amount of calcium hydroxide was allowed to be present in the solutions.

EXPERIMENTAL.

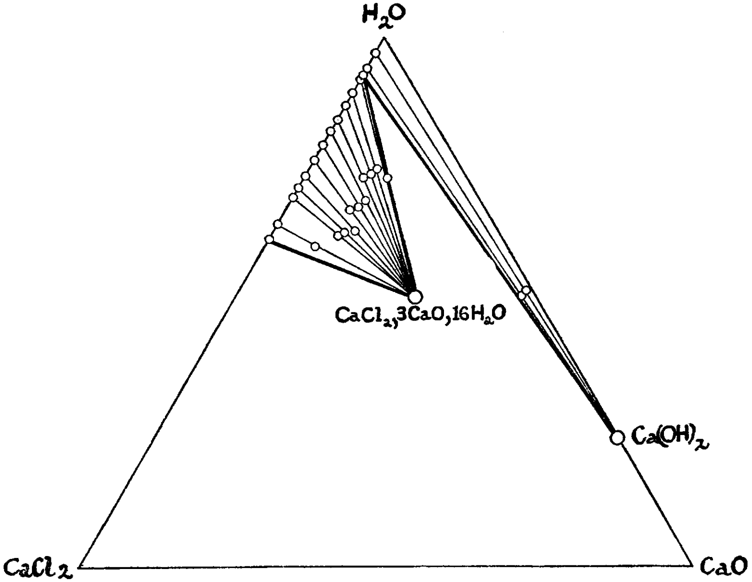
A. *Analytical Methods.*—Hypochlorite was estimated by the usual iodometric method, and chloride by the Volhard process if hypochlorite was absent. In the presence of hypochlorite, chloride was estimated by first determining the former, and then finding the total chloride present after the hypochlorite had been reduced by neutral hydrogen peroxide. The same method of reduction was employed when it was necessary to estimate hydroxide in the presence of hypochlorite. The accuracy of these methods was checked by a determination of total calcium by the oxalate–permanganate process in a few control experiments.

B. *The Preparation and Properties of Calcium Hypochlorite.*—The following procedure, based upon the process of the Chemische Fabrik Griesheim-Elektron (*loc. cit.*), was adopted. About 224 g. (4 g.-mols.) of calcium oxide, prepared by ignition of the pure precipitated carbonate, were treated with 650 c.c. of water, whereby a thin paste resulted, quite free from lumps. The cooled paste was introduced into a cylindrical gas-jar provided with a rubber stopper with holes for an inlet tube and a stirrer. The inlet tube reached well down into the jar, and the stirrer, which was of anchor-shape, was made long and wide enough to agitate the whole contents of the cylinder when rotated rapidly by a motor. Chlorine, washed with water, was supplied from a small battery of diaphragm cells, with hydrochloric acid as electrolyte, at an initial rate of about 105 g. per hour. The temperature was allowed to rise to about 40°, external cooling being used when necessary. Under these conditions, there was no visible indication of basic salts, the calcium hydroxide progressively disappearing. After about 70% of the theoretical quantity of chlorine had been admitted, a sudden separation of calcium hypochlorite occurred, and the contents of the flask became pasty once more. The temperature was then reduced to about 25°, and more chlorine was passed in at one-third of the above rate, until from 90% to 95% of the theoretical quantity had been supplied. (After the separation of calcium hypochlorite, chlorine is not absorbed so readily, and a more rapid stream of the gas is partly wasted.) It was not found practicable to chlorinate beyond the limit given, as any further quantity of chlorine caused the complete loss of the preparation by production of free hypochlorous acid.

The paste containing calcium hypochlorite was collected in a Buchner funnel on asbestos-paper, since ordinary filter-paper was rapidly destroyed. The filtration was somewhat slow, but when the characteristically soft mass was covered with asbestos-paper and well pressed, a fair separation from mother-liquor was effected. Comparatively little hypochlorite remained in solution. Further separation of mother-liquor was brought about by pressing the cake of hypochlorite between very thick plates of porous earthenware, specially made for the purpose. After a few hours, the apparently dry substance was desiccated in a vacuum over caustic soda. It formed pale greenish-yellow, almost odourless, apparently non-crystalline lumps, which developed a strong smell of hypochlorous acid on exposure to air.

Pure calcium hypochlorite was prepared by making a saturated solution of the crude product in water and filtering off the insoluble residue of calcium hydroxide or basic salt. The solution was evaporated under the diminished pressure afforded by a water-pump. Concentration progressed until the liquid was considerably supersaturated, and short, needle-shaped crystals finally appeared, at first slowly, then more rapidly. At this stage it was found best to stop the evaporation, and allow the crystals to be produced without agitation. A more granular product, easily filtered and dried as described above, then resulted. A repetition of the process yielded calcium hypochlorite free from chloride, and therefore free from chlorate. About ½% of calcium hydroxide (or an equivalent quantity of basic salt) was present, rendering unfiltered solutions slightly turbid. Analysis of the final product gave results for hypochlorite and total chlorine which agreed with one another within the limits of experimental error. When thoroughly desiccated, calcium hypochlorite shows no appreciable decomposition after several days, if kept out of contact with air. Concentrated aqueous solutions are greenish-yellow, and decompose at 25—35° at the rate of about 1% per day, evolving a very slow stream of oxygen in minute bubbles. At 0°, there is no decomposition or evolution of oxygen during the period of the experiments.

FIG. 1.



C. *The System* $CaCl_2$–CaO–H_2O.—This system has already been examined at 10°, 25°, 40°, 48°, and 50° (Milikan, *Z. physikal. Chem.*, 1917, **92**, 59), basic compounds $CaCl_2,3CaO,16H_2O$; $CaCl_2,CaO,2H_2O$; and $CaCl_2,CaO.5(?4)H_2O$ being reported. The third was obtained only at 48° and 50°, whilst the range of existence of the first increases and that of the second diminishes as the temperature falls. The results (Table I and Fig. 1) obtained at 0° show that $CaCl_2,3CaO,16H_2O$

is the only basic salt obtainable at that temperature It forms well-defined, transparent, needle-shaped crystals, which may attain a length of several mm. if the mother-liquor does not contain too much calcium chloride.

Suitable complexes were rotated in a thermostat for about 24 hours, which was found to be a sufficient time for establishment of equilibrium, and the composition of the solid phases was deduced by the residue method. The separation of residues from solutions was achieved in the following manner. The disc of a Gooch crucible was placed in the bottom of a small cylindrical funnel and covered with a pad of asbestos well pressed down, which was then thoroughly dried. The funnel was stoppered loosely, fitted to the neck of a filter-flask connected to the water pump, and immersed in the ice and water of the thermostat, only the top projecting. The filtration could then be carried out at 0°, no matter how slowly the solution drained through the asbestos pad. The same process was adopted in the examination of the two systems about to be described.

TABLE I.

	Composition, %.				
	Solution.		Residue.		
$d_4^{0°}$.	$CaCl_2$.	CaO.	$CaCl_2$.	CaO.	Solid phase.
1·025	2·7	0·214	1·0	46·5	$Ca(OH)_2$.
1·048	5·5	0·226	2·0	46·8	
1·056	6·8	0·216	—	—	$Ca(OH)_2 + CaCl_2,3CaO,16H_2O$.
1·067	7·6	0·212	12·7	13·7	$CaCl_2,3CaO,16H_2O$.
1·089	10·2	0·186	13·5	11·2	
1·111	12·5	0·172	15·0	10·7	
1·133	15·2	0·164	16·6	9·8	
1·155	17·4	0·152	18·4	12·4	
1·186	20·0	0·148	20·2	11·8	
1·213	22·8	0·145	21·8	10·7	
1·240	25·6	0·142	23·0	13·4	
1·265	28·0	0·138	24·9	11·9	
1·280	29·7	0·152	26·1	11·1	
1·338	34·9	0·190	31·0	8·3	
1·370	37·6	—	—	—	$CaCl_2,6H_2O$.

D. *The System* $Ca(ClO)_2$–$CaCl_2$–H_2O.—The investigation of this system presented no special difficulty. When calcium hypochlorite was intended to be present as solid phase, it was added in excess to suitable solutions of calcium chloride. It was necessary to have these solutions, particularly when concentrated, free from calcium hydroxide, otherwise the hydroxide, always present in small amount in solid calcium hypochlorite, was converted into basic chloride, and did not pass entirely into solution. A corresponding error in the composition of the residues, which became slightly too rich in calcium chloride, was then produced.

The experimental figures, reproduced in Table II and Fig. 2, show definitely that no compound of calcium hypochlorite and calcium chloride can be formed in aqueous solution at 0°, and that the composition of the hydrate of the former salt is $Ca(ClO)_2,3H_2O$, and not $Ca(ClO)_2,4H_2O$ as reported by Kingzett and by Orton and Jones (*loc. cit.*). The solubility of this hydrate in water at 0° is 21·8%.

FIG. 2.

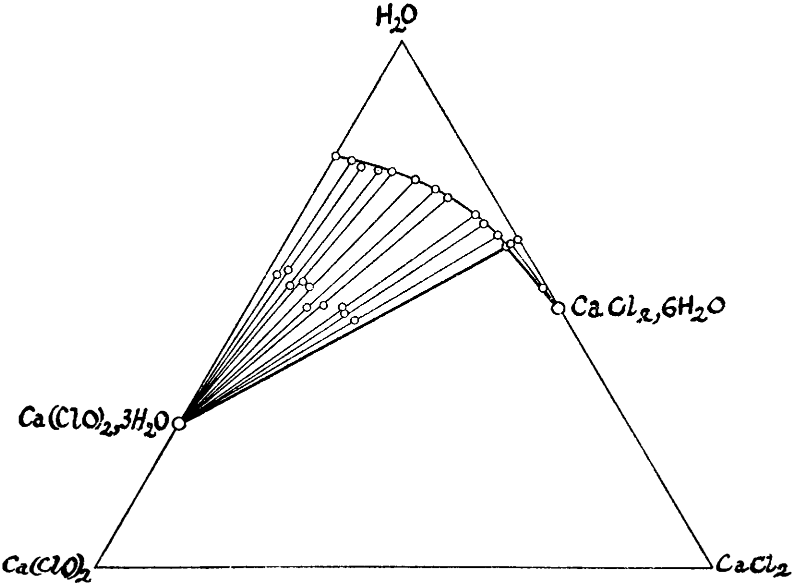
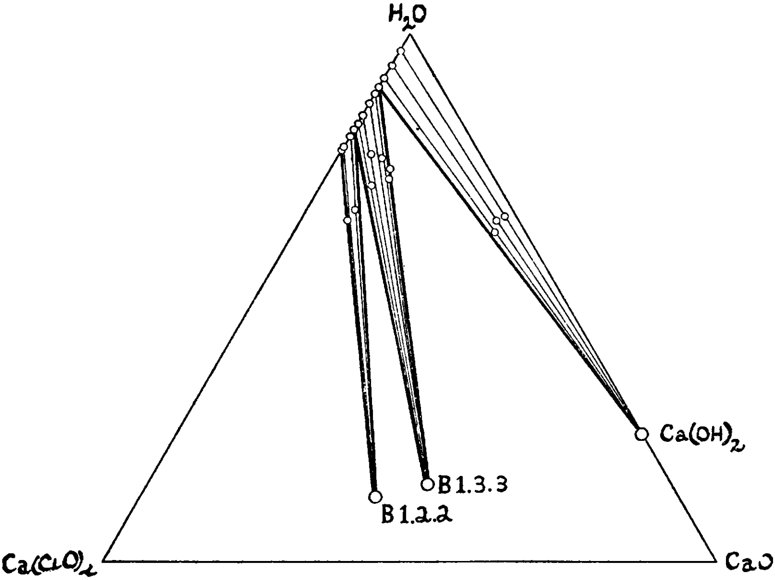


TABLE II.

	Composition, %.				
	Solution.		Residue.		
$d_{4^\circ}^{0^\circ}$.	$Ca(ClO)_2$.	$CaCl_2$.	$Ca(ClO)_2$.	$CaCl_2$.	Solid phase.
1·213	21·8	—	—	—	$Ca(ClO)_2,3H_2O$.
1·220	19·6	3·1	42·5	1·8	
1·228	18·6	5·3	40·2	3·1	
1·234	16·1	8·4	41·5	5·0	
1·238	14·0	10·8	38·9	6·7	
1·255	11·0	15·4	38·5	8·1	
1·270	8·8	19·4	40·8	9·7	
1·285	7·4	22·2	37·8	12·1	
1·322	4·5	28·5	35·0	15·5	
1·333	4·2	30·7	35·2	16·4	
1·366	2·9	34·0	34·1	18·9	
1·388	2·6	36·4	—	—	$Ca(ClO)_2,3H_2O + CaCl_2,6H_2O$.
1·382	1·6	36·9	0·7	46·3	$CaCl_2,6H_2O$.
1·370	—	37·6	—	—	

E. *The System* $Ca(ClO)_2$–CaO–H_2O.—An extended series of measurements was undertaken, the procedure being in all cases to add solid calcium hypochlorite to milk of lime, and to agitate the resulting complexes for periods varying from 1 to 5 days before analysis. In order to avoid the presence of lumps, freshly burned calcium oxide was slaked in boiling water. Since accurate adjustment of the inital compositions of the complexes was sometimes necessary, the percentage of anhydrous substance in the calcium hypochlorite was determined immediately before use. Two basic salts were found (see Table III and Fig. 3) of formulæ $Ca(ClO)_2,2CaO,2H_2O$ and $Ca(ClO)_2,3CaO,3H_2O$. These are referred to as B 1.2.2 and B 1.3.3, respectively.

FIG. 3.



The salt B 1.2.2 was formed in a few hours from complexes containing from 21·8% to about 16% of calcium hypochlorite, but subsequent investigation showed that its range of stable existence at 0° extends only from 21·8% to 18·0%. Prepared as described above, it was rather voluminous and not visibly crystalline. In consequence, residues containing B 1.2.2 consisted chiefly of solution, although an apparently good filtration had been achieved. Nevertheless, the residue method was quite capable of giving the composition of the solid phase with certainty. The range of stable existence of B 1.2.2 is probably greater above 0°, as it was observed that preparations of B 1.3.3 decomposed on being allowed to warm to room temperature, producing minute crystals. When the rise

TABLE III.

	Composition, %.				
	Solution.		Residue.		
$d_4^{0^\circ}$.	$Ca(ClO)_2$.	CaO.	$Ca(ClO)_2$.	CaO.	Solid phase.
1·030	3·0	0·106	1·85	32·6	$Ca(OH)_2$.
1·053	5·7	0·105	3·5	31·9	
1·077	8·2	0·110	4·8	32·6	
* 1·103	11·0	0·114	12·7	31·2	Variable.
* 1·122	12·7	—	10·6	19·5	
* 1·133	14·0	0·111	13·4	35·0	
1·093	9·9	0·091	15·9	9·8	B 1.3.3.
1·104	11·1	0·093	16·9	10·5	
1·123	13·0	0·093	16·3	7·35	
1·142	15·1	0·077	17·6	5·2	
1·161	16·9	—	20·3	8·3	
1·168	17·8	—	19·2	3·7	
1·171	18·0	—	22·4	6·7	B 1.3.3 + B 1.2.2.
* 1·154	16·1	—	16·3	7·4	B 1.2.2.
* 1·172	17·7	0·105	21·4	6·8	
1·173	18·2	—	24·0	8·1	
1·189	19·2	0·113	25·3	7·9	
1·188	19·8	0·106	25·0	7·2	
1·203	21·2	0·106	27·3	7·7	
1·213	21·8	—	—	—	$Ca(ClO)_2,3H_2O$.

* Metastable equilibria.

of temperature was slow, these were larger, taking the form of thin plates, 1—2 mm. in diameter, of great transparency and high lustre, entirely free from the greenish-yellow tint of the normal hypochlorite. They were transformed once more into B 1.3.3 on cooling to 0°. An excellent separation of residue from solution was possible, and the subsequent analyses proved conclusively that the crystalline substance was B 1.2.2.

The compound B 1.3.3 was formed after a few hours when calcium hydroxide was agitated at 0° with a solution containing not less than 15% of hypochlorite. It is definitely different in appearance from B 1.2.2, excessively voluminous, and not visibly crystalline. In consequence, the compositions of solutions and corresponding residues were quite close together. A complex consisting of 50 c.c. of the above solution with about 1 g. of calcium hydroxide became of the consistency of cream, and larger amounts of calcium hydroxide produced a semi-solid mass—a fact which suggests that the basic salt may be highly hydrated; but all the evidence (see Fig. 3) is against this supposition. Over a range of solutions containing from 18·0% to 9·9% of calcium hypochlorite, the tie-lines converge fairly well upon the point representing B 1.3.3. They converge better on a point slightly to the right of this along a line joining the points representing B 1.3.3 and calcium hydroxide. This would indicate a basic salt of approximate composition B 2.7.7, but the discrepancy may be due to experimental error or to the peculiarities of the system itself.

Introduction of a suspension of B 1.3.3. into preparations in which B 1.2.2 had been formed as solid phase revealed the metastable existence of the latter in contact with solutions containing from 18·0% to about 16% of hypochlorite, the change of solid phase occurring after a few hours' rotation. Owing to the relatively small quantities of calcium hydroxide which could be used, and the correspondingly small amounts of hypochlorite taken up in forming B 1.2.2 or B 1.3.3, it was not easy to obtain a residue containing both basic salts. This was finally produced by inoculating with B 1.3.3 a series of preparations which differed only very slightly from one another in initial composition, and in which B 1.2.2 had already been formed. The difference in appearance of the two basic salts confirmed the analytical results.

The equilibrium of B 1.3.3 and calcium hydroxide with solution could not be determined satisfactorily in spite of many attempts. The separation of B 1.3.3 did not always occur spontaneously when calcium hydroxide was agitated with solutions containing less than about 14% of calcium hypochlorite. Inoculation from another preparation caused it to separate, less and less readily, however, as the concentration of the solution fell. Below a concentration of 10% the appearance of the suspended solid and of the residues was entirely that of calcium hydroxide, even after inoculation and subsequent rotation for several days, but analysis revealed a small proportion of hypochlorite in the solid phase. The best available approximation to the conditions of the equilibrium in question was obtained as follows. About 40 c.c. of a solution containing some 13% of calcium hypochlorite in contact with 2·5 g. of calcium hydroxide were seeded with B 1.3.3 and rotated for several days. A large quantity of B 1.3.3 separated, but, owing probably to its slow formation, did not make the preparation unmanageable. The solution contained 9·9% hypochlorite, and the residue was practically free from hydroxide. Similar treatment of preparations in which the initial concentrations of the solutions varied from 12% to 10% yielded final solutions more concentrated than the above and residues of B 1.3.3 and calcium hydroxide. Reproducible results could not be obtained, and after a number of experiments the figure 9·9% was taken as a provisional lower limit to the range of stable existence of B 1.3.3 in contact with solution.

The concentration of calcium hydroxide in the solutions was small and its variation smaller, furnishing no guide to the establishment of equilibrium. In some cases, it was not determined.

When agitated with solutions containing from 14% to 10% of calcium hypochlorite, calcium hydroxide took up varying small quantities of hypochlorite, which increased with both the concentration of the solution and the time of agitation. Below 10%, the quantity was negligible. The appearance of the solid phase and residues was that of calcium hydroxide. This effect points to adsorption, mixed crystal formation, or production of some basic salt in variable amounts; but no decision between these possibilities could be made. Some of the analytical results are included in Table III, marked with an asterisk to indicate that they represent metastable conditions. Only equilibria believed to be stable are shown in Fig. 3.

Of the basic salts reported by the Chemische Fabrik Griesheim-Elektron (*loc. cit.*), only two (B 1.2.2 and B 1.3.3) have been found to exist at 0° in contact with solutions containing hypochlorite and hydroxide. There is no definite evidence at this temperature of any other basic salt.

Conclusions.

Although equilibria in the appropriate quaternary system have not been investigated, it is possible to discuss at the present stage the probable composition of bleaching powder. A fresh sample, prepared by chlorinating nearly dry calcium hydroxide and containing about 35% of available chlorine, is roughly of the composition $2Ca(ClO)_2 + 2CaCl_2 + 3Ca(OH)_2 + 4H_2O$. No compound of calcium hypochlorite and chloride exists at 0°, and the same is probably true at higher temperatures, as indicated by the method given for the preparation of the former salt. If present separately, the hypochlorite and chloride cannot be wholly in the form of trihydrate and hexahydrate, respectively, because the amount of water present is too small. Lower degrees of hydration, at least of the calcium chloride, are possible. Further, in ordinary good bleaching powder, the proportion of calcium hydroxide is too small to convert completely either the hypochlorite or the chloride present into any of the known basic salts, except $CaCl_2,CaO,2H_2O$. The extent to which these substances are present in dry bleaching powder prepared in the usual way is necessarily problematical, and is further limited in the case of $CaCl_2,3CaO,16H_2O$ by the amount of water available. The equilibrium distribution of the water and calcium hydroxide present, and the possibility of formation of a basic double salt cannot be discussed on the basis of the data at present available, but it appears likely that, in a solid preparation, basic salt formation, if it occurs at all, would be slow, and that fresh bleaching powder is therefore simply a mixture of calcium hydroxide with more or less hydrated hypochlorite and chloride.

Summary.

1. A method was developed for the isolation of relatively pure calcium hypochlorite.

2. The ternary systems $CaCl_2$–CaO–H_2O, $Ca(ClO)_2$–$CaCl_2$–H_2O, and $Ca(ClO)_2$–CaO–H_2O have been investigated at 0°.

3. Basic salts $CaCl_2,3CaO,16H_2O$; $Ca(ClO)_2,CaO,2H_2O$; and $Ca(ClO)_2,3CaO,3H_2O$ were identified.

4. No double salt was formed by calcium hypochlorite and calcium chloride.

5. The probable composition of bleaching powder has been discussed in the light of these results.

It is proposed to extend this investigation, and to attempt the isolation of the hypochlorites of metals other than calcium.

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[*Received, June 22nd,* 1927.]