THE USE OF AMMONIA IN THE CHLORINATION OF WATER.

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IN the course of some experiments on the effect of color, turbidity, and temperature on the chlorination of water, the writer thought it would be interesting to determine the relative efficiencies of various hypochlorites. Nothing worthy of mention was observed until ammonium hypochlorite was used; this was prepared in solution by the double decomposition of calcium hypochlorite and ammonium oxalate, and great care was exercised to prevent the addition of an excess of oxalate, which, if present, would introduce a factor of unknown value. It was anticipated that the reaction would proceed somewhat along the lines represented by the following equation:

$$\underset{\text{Calcium Hypochlorite}}{Ca(OCl)_2} + \underset{\text{Ammonium Oxalate}}{(NH_4)_2C_2O_4} = \underset{\text{Calcium Oxalate}}{CaC_2O_4} + \underset{\text{Ammonium Hypochlorite}}{2NH_4OCl}$$

The calcium oxalate was deposited by centrifuging at a high speed and the supernatant liquid removed for experimental work.

In testing the effect of this solution on a culture of B. Coli Communi or seeded into raw Ottawa River water, the author was very surprised to find that the germicidal value was very much in excess of the hypochlorite of calcium, sodium and potassium. The velocity of the reaction as calculated by the formula

$$K = \frac{\log \frac{N_1}{N_2}}{t_2 - t_1}$$

in which N_1 represents the number of organisms at t_1 and N_2 at t_2, showed that with 0.3 parts per million of available chlorine in each instance, the value of K for ammonium hypochlorite was twenty to thirty times as great as that of calcium hypochlorite. This experiment was confirmed by others which gave similar results.

In searching for an explanation of this phenomenon it occurred to the writer that it was probable that ammonium hypochlorite was exceedingly unstable in dilute solution and spontaneously decomposed into chloramine and water as represented by the following equation:

$$\underset{\text{Ammonium Hypochlorite}}{NH_4OCl} = \underset{\text{Chloramine}}{NH_2Cl} + \underset{\text{Water}}{H_2O}$$

Chloramine has been shown by Rideal (Journal R.S.I., 1910, 31, 33-45) to have a much greater germicidal action than an equivalent of chlorine. Rideal deducted this fact from experiments on the chlorination of sewage in which he found that "the first rapid consumption of chlorine or hypochlorite was succeeded by a slow action which continued for some hours, even days, and was attended by a germicidal power after free chlorine or hypochlorite had disappeared." . . . "It became evident that chlorine, in supplement to its oxidizing action, which had been exhausted, was acting by substitution for hydrogen in ammonia and organic compounds, yielding products more or less germicidal." Rideal supported this by determining the carbolic coefficients of hypochlorite, and of hypochlorite with the addition of an equivalent of ammonia. These gave values of 2.18 and 6.36 respectively. Although Rideal seems to have made this experiment merely for the purpose of explaining an observed phenomenon, it is curious that the possibilities of its practical application to water and sewage disinfection seem to have either been entirely overlooked or discarded on account of economic considerations.

After noting the above-mentioned facts in connection with ammonium hypochlorite, the writer followed up Rideal's work and produced dilute solutions of chloramine by the addition of ammonia to calcium hypochlorite solutions. These had the same germicidal power as the chloramine produced by double decomposition and were approximately three times as efficient as an equal quantity of hypochlorite.

The next step was to determine the relative proportions of hypochlorite and ammonia that would yield the greatest efficiency. The results obtained, though not entirely conclusive as to the most efficient ratio, showed that an increase in the ammonia beyond an equivalent of the chlorine (available chlorine : ammonia as NH_3 = 2 : 1 by weight) did not produce results commensurate with the increase of ammonia. Half an equivalent of ammonia, or chlorine : ammonia = 4 : 1 gave inferior results but the reduction in efficiency was very much smaller than the reduction in the ammonia. The relative proportions of chlorine and ammonia must also be considered from the economic standpoint and when this process is carried out on a large scale, these various considerations will demand a rather fine adjustment.

A remarkable feature of the treatment of water with a mixture of hypochlorite and ammonia is the almost entire absence of absorption. On adding bleach to the Ottawa River water so as to produce a mixture containing 10 parts per million of available chlorine, about 35 per cent. is absorbed in 5 minutes at 60° F. and 60 per cent. within one hour. If an equivalent of ammonia is first added to the bleach, only 1.4 per cent. of the available chlorine is absorbed in one hour and 3.2 per cent. in 20 hours. As there is practically no absorption of the germicidal agent, the longer the contact period the better will be the results obtained. For instantaneous sterilization the relative efficiency ratio of 3 : 1 for the mixture of chlorine and ammonia as compared with chlorine cannot be obtained, but with the increase of contact period the efficiency ratio also increases and after about 40 minutes the ratio becomes greater than 3 : 1. The germicidal action of the mixture continues to persist on account of non-absorption and for a comparatively long time, and as a consequence of this no aftergrowths are produced.

Cost.—Basing the calculations on a ratio of one equivalent of ammonia to one equivalent of available chlorine (0.5 part per million NH_3 to 1.0 p.p.m. available chlorine) a very conservative estimate of the most efficient ratio, this process becomes economical when the price of hypochlorite exceeds $2.08 per 100 pounds. This statement is based on the mixture produced being three times as efficient as hypochlorite: that 33 per cent. of available chlorine can be obtained from bleach and that ammonia can be purchased for 25 cents per pound. The efficiency ratios of 3 : 1 can be obtained under the conditions of chlorination usually found and no alteration in the point of application will be required. Bleach containing more than 33 per cent. of available chlorine can be obtained but very few plants actually extract more than this amount as there are certain losses which are unavoidable. The present price of ammonia (aqua 16° B.) is quoted in the United States at 2¼ to 2½ cents per pound. This solution contains 10.3 per cent. of NH_3 and the anhydrous ammonia is therefore worth 22 to 25 cents per pound. In Ottawa bleach can be obtained for $3.70 per 100 pounds, and by the adoption of the ammonia process the heavy dosage of one part per million of available chlorine re-