Sterilization of water by chloric peroxide and by ozone.

OFFICE OF CONSUL-GENERAL OF THE UNITED STATES,
Paris, France, October 6, 1900.

SIR: I have the honor to submit the following report upon the sterilization of potable water in large and small quantities by two processes, both depending on the action upon albuminous matter and other organic material of unstable oxygen compounds, in one case chloric peroxide, in the other ozone.

The first method was reported upon by M. Bergé, of Brussels, at the fourth international congress of applied chemistry, at which I had the honor to represent the Service; and the latter, perfected by Messrs. Marmier and Abraham, was mentioned in the discussion of this paper, and again at the tenth international congress of hygiene and demography.

I have obtained such data as are available on both methods, and would present the following brief account of each:

The first process depends upon the solubility in water of the unstable chloric peroxide gas, which by its strong oxidizing power is strongly bactericidal and at the same time acts upon much of the organic matter found in ordinary water, especially compounds of nitrogen and sulphur. The chloric peroxide is generated by means of sulphuric acid and potassic chlorate according to the following equation:

$$3\,K\,cl\,O_3 + 2\,H_2SO_4 = K\,cl\,O_4 + 2\,KHSO_4 + H_2O + 2\,cl\,O_2$$

It is then dissolved in water to form a sterilizing solution of standard strength and this solution is mixed with the water to be sterilized regularly and in a proportion depending upon the original purity of the water. The details are thus described by M. Bergé:

Sulphuric acid at 58° B. decomposes slowly the chlorate of potassium. A current of air draws out the gas in proportion to its production. This air charged with peroxide of chlorine can be led directly into the water to be purified. It is more practicable, however, to prepare by aid of this latter a concentrated solution of peroxide which poured regularly into the water sterilizes it in a continuous fashion.

Diagram 1 is the scheme of the apparatus used for the preparation of solutions of peroxide of chlorine. A pump forces air into a reservoir. This air is dried more or less by passing first into a lead chamber containing sulphuric acid. From there it enters at the bottom of a second lead chamber, also containing sulphuric acid, but connected with a second chamber above containing the chlorate and having an annealed shaft passing through its center, which by a to-and fro movement assures the regular and continuous arrival of the chlorate. The air charged with peroxide arrives at the base of a tower filled with porous stones, and is dissolved there to form the sterilizing liquid which is collected in a reservoir.

It only remains to have an apparatus to add this liquid regularly to the water to be sterilized and to mix the same. After this it is let stand in a reservoir fifteen minutes, and then is poured in a cascade over coke. After ten minutes contact with the coke it is delivered for consumption.

"The expense of the production of the peroxide is very slight, in fact the dose of potassic chlorate varies according to the waters from one-half to 3 grams per meter cube. Valuing the chlorate at $20 per 100 kilograms and the 300 kilograms of H_2SO_4 necessary for its decomposition at $6, we arrive at the expense of thirteen five hundredths of a cent per meter, cube, gramme of water to be sterilized."

At Ostend, Belgium, where a station has been equipped to sterilize by this process 5,000 cubic meters daily of water after it has passed through sand filters, the expense is twenty-six five-hundredths of a cent per cubic meter, as this water requires 2 grams of potassic chlorate per cubic meter.

Many tests made by competent bacteriologists have demonstrated that at the end of fifteen minutes the sterilization of the water is assured. After that by passing the water over a cascade or ærator made of coke it is possible to deliver it directly for consumption, as this process destroys all the reagent in the water. According to M. Bergé this last procedure is not necessary in practice except as an additional precaution in case the water should be immediately drunk. Beside such excess is destroyed in a very few minutes in the water simply standing in the tanks, and even if remaining, it is claimed, has no injurious effects.

Dr. Desguin, former president of the Royal Academy of Medicine of Belgium, in his experiments on the persistence of this reagent dissolved in water, employed a solution three or more times the normal strength. He wrote:

"In this case the odor persists a little longer, the color, when the proportion was exaggerated, changed and became a yellowish green, but the odor and the color became normal in less than two hours; as to the taste it always remained the same as in other tests."

A priori we can conclude from what precedes that water sterilized by chloric peroxide should unite all the requirements of potable water; first, because the chloric peroxide, being gaseous and unstable, disappears rapidly; secondly, because it is destroyed immediately in contact with organic matters, and so can not enter the stomach; thirdly, because the composition of water is improved in regard to the sulphur, nitrogen, and organic matter it contains; and fourthly, because a certain quantity of oxygen in solution renders it more limpid, lighter, and consequently more digestive.

To arrive at the above conclusions many tests are reported showing that using water strongly treated with chloric peroxide for artificial digestion, fermentation, and for aquariums containing fish and plants all the processes of nature proceed as well or better with this solution as with ordinary water.

Before this process was adopted for the city of Ostende, Brussels, a series of tests were made with favorable results. The following is from the report made on these experiments:

"The action of chloric peroxide is remarkably energetic. In spite of the brevity of its action (about fifteen seconds) the proportion of organic matter is reduced almost by half; and this mineralization of the organic material is most striking in the proportional diminution of nitrogen and of sulphur—in organic combination—with augmentation of the amounts of nitric and sulphuric acid. Besides all microscopic germs are killed."

It would thus seem from these data that the sterilization of water for alimentation by chloric peroxide is efficacious, is cheap for large or small quantities of water, and that by means of a comparatively simple apparatus the required chemical reactions are induced regularly, and without the danger of explosion feared by some. It also appears that water sterilized in this way and left several hours in open vessels, or cascaded a few minutes over a porous substance, such as coke, is sterile, but contains no sterilizing or poisonous substance, but that concentrated solutions of this peroxide can be made and preserved in closed vessels a considerable time, to be used later in treating water found far from the sterilizing plant.

It would appear that the above method, together with that of the small portable apparatus, might be a valuable adjunct to army-camp equipment, replacing the expensive and cumbersome water boilers.

The second method of utilizing ozone as a sterilizing agent has had to contend with the following difficulties:

First. The necessity of obtaining a strong solution of ozone in air which alone is sterilizing. This has been done by a specially constructed ozonator employing currents of very high voltage.

Second. The slight solubility of ozone in water, making it necessary to submit the water in finely divided particles to the immediate contact with the gas to insure the sterilization. This has been done by means of a sterilizing column, loosely filled with porous stone, in which the water falls in a very fine rain, while the strongly ozonated air is aspirated upward from the bottom to the top.

The patented apparatus is thus described:

"The liquid at *a* (diagram 2) is forced by a centrifugal pump *b* to the summit *c* of the column *d*, whose interior arrangement has for ulterior object to divide the water into small particles upon which the ozone acts. A tank *g* receives the water, which taken up by an elevating pump *t* is discharged into the distributing reservoir.

"The ozonated air is drawn into the lower part of the sterilizing chamber (column) which it transverses from below upward.

"The circulation of the ozone is assured by a ventilator *m*, aspirating the atmospheric air to make it pass first into a desiccation *l*, into the ozonator *k* and finally into the column *d*."

The ventilator *m* has in the later models been replaced by an exhaust or pump placed at the top of the column, thus avoiding any condensation of the ozonated air.

"The desiccator is simply a cylinder containing concentrated sulphuric acid which absorbs the vapor contained in the air.

"The electric current necessary for the production of the effluvia is furnished by a transformer *t*, whose primary circuit (1) receives the current of a motor *n*, operated by the engine *v*, with its boiler.

"The secondary circuit (2) furnishes to the ozonator currents of a tension of about 40,000 volts.

"At *n* is placed upon the circuit of high tension, a deflagrator formed of two spheres between which plays an electric spark that is blown continually by means of a jet of compressed air or of steam."

An experimental plant was erected in 1898 at the waterworks at Emmerin (Lille), capable of sterilizing 5,000 cubic meters per twenty-four hours, and the municipality appointed later a commission consisting of Drs. Staes-Brame, Roux, and Calmette, and chemists Buisine and Bouriez to report upon the water of Emmerin both chemically and bacteriologically before and after treatment by this process. Their labors were continued during the months of December, 1898, and January, 1899, and in February a report was rendered giving the details of many experiments and observations which are detailed in another place:

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Now as to cost of construction and operating.

For small plants, that is, under a daily output of 5,000 cubic meters, this process is expensive both for construction and supervision, as a small plant requires an experienced electrician as much as a large one. For a plant of 5,000 cubic meters per twenty-four hours the cost of sterilizing the water is from $0.006 to $0.008 per meter, which includes interest on cost of plant (about $40,000), as well as running expenses. For a large plant of 100,000 cubic meters per twenty-four hours the original cost of installation (all parts in duplicate), would amount to about $160,000, but after this outlay the expense of operating would only amount to about $0.0008 to $0.0012 per cubic meter where coal is used to generate power, and where water power could be utilized the expense would be less than half the above. We add to this the interest on the original outlay for the plant and the cost per meter amounts to $0.002 to $0.004.

We thus see that the apparatus requires a considerable outlay of capital at the beginning and must be under the constant control of an electrician, but that in spite of this the proportionate expense is not high for large quantities of water, although always above that of the chloric peroxide process. It is not recommended commercially for small quantities of water, and the apparatus can not conveniently be made portable, as can the first process. However, it presents a means of sterilizing potable water in large quantities that is according to the best authority practically absolute, without the danger, real or imaginary, of adding chemically noxious substances to the water, as is urged by some against the method by chloric peroxide. And the two methods enable us to economically sterilize potable water in those cases where the sources can not be absolutely protected from pollution, and in hospitals, institutions and army camps where special precautions are necessary.

Respectfully,

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The SURGEON GENERAL,
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[Translation.]

By P. A. Surg. H. D. Geddings, U. S. M. H. S.

THE INDUSTRIAL STERILIZATION OF POTABLE WATERS BY OZONE, BY MEANS OF THE APPARATUS AND PROCESSES OF MESSRS. MARMIER AND ABRAHAM.

LILLE, *February 12, 1900.*

A Report

presented to the Municipality of Lille, by the Scientific Commission appointed by the Municipal Administration, and composed of

Dr. Staes-Braeme, Adjunct to the Mayor, President.

Dr. Roux, Member of the Institute of France, Member of the Academy of Medicine, sub-Director of the Pasteur Institute.

Dr. Buisine, Professor of Industrial Chemistry of the Faculty of Sciences of Lille.

Dr. Calmette, director of the Pasteur Institute of Lille.

Professor of the Faculty of Medicine of Lille.

Dr. Bouriez, Chemical Expert.

(Dr. Calmette, Secretary of the Commission.)

February, 1899.