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## A Method of Maintaining the Proper Copper Concentration in the Treatment of Water

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## A METHOD OF MAINTAINING THE PROPER COPPER CONCENTRATION IN THE TREATMENT OF WATER

O. R. SWEENEY AND O. G. FIFE

When water is impounded in a reservoir it usually becomes infested with algae. While not poisonous many of these algae impart disagreeable odors or tastes to the water, making it undesirable for drinking purposes. When the Croton dam was built as a part of the New York City water supply system, the water in the reservoir behind it became contaminated with algae. Upon the recommendation of Karl F. Kellerman, whose father, Professor Kellerman of Ohio State University, first noted the toxic effect of copper on algae, the water was treated with copper sulfate. This was effective and is being used quite generally in water reservoirs. The usual procedure is to place crystalline copper sulfate in a burlap bag attached by a rope to a boat and draw it back and forth slowly through the water. It must be done at the proper speed to produce the correct concentration necessary to kill the algae without killing the fish or making the water impotable.

Obviously there would be a great advantage in a material which, when added to water, would supply a concentration of copper ions just sufficient to prevent algae growth. If the material were to be placed in a reservoir of water where there would be ample time to come to equilibrium, the solubility of the material would be the only factor to take into consideration. Where there is an appreciable movement of the water the rate of solution may be of very great importance. Most of the algae do not grow readily in running water, hence in running water there is not the need for as high a concentration to prevent growth as in still water. If, however, the conditions are such that the water is flowing rapidly part of the time and not flowing for considerable periods a material with a relatively slow rate of solution may be desirable. During the rapid flow period when only a low concentration is needed, only small amounts of the compound will be dissolved, whereas, during periods of no movement the concentration of ions will become high approaching the total solubility figure.

Studies were therefore made to determine the amount of copper in water in which metallic copper and two copper compounds were placed. The concentration of copper was determined by comparison with standard solutions of copper sulfate varying in strength

from 1 part copper in 50,000 parts of water to 1 in 4,000,000. Two indicators were used: potassium-ferro-cyanide and logwood extract. The addition of 0.1 gram each of nitric acid and ammonium hydroxide to 25 cc. of 0.1N potassium-ferro-cyanide solution made it possible to detect as low as 1 part copper in 3,000,000 parts water. With logwood extract 1 part in 4,000,000 could be detected. In testing below this concentration the solution was concentrated by evaporation until the copper could be detected by one of the above methods.

The first material tried was made by fusing an intimate mixture of white sea sand and copper oxide. Samples of this material were placed in both distilled water and tap water for as long as 3 months without producing a concentration of copper ions which could be detected.

A piece of metallic copper 1 centimeter square was then placed in 500 cc. distilled water, producing copper concentrations shown in Table 1. The addition of carbon dioxide increased the rate of solution but resulted in a lower total solubility while sodium chloride increased both the rate of solution and total solubility. The effect of different amounts of sodium chloride upon the solubility in 24 hours is shown in Table 2.

An excess of a saturated solution of copper sulfate was next added, with stirring, to sodium silicate. A light blue precipitate which readily settled out was formed. This compound proved to be much less soluble than metallic copper as shown in Table 3.

The copper silicate compound and metallic copper offer interesting possibilities in algae control. Metallic copper when in water for 72 hours or longer will produce a copper concentration in the water sufficient to kill practically any algae. Where a lower concentration under similar conditions is desired the copper silicate compound may be used. In many cases the water will not remain in contact with the copper material long enough to build up maximum concentration of copper ions. Neither will this in all cases be necessary. Many algae, for example, are killed by a concentration of 0.25 parts per million produced by a one hour contact by the copper silicate material. Such a concentration is not toxic to some fish such as perch, sunfish, and black bass, although toxic to trout, carp, and catfish. Even lower concentrations should prevent growth though not sufficient to actually kill algae already growing vigorously. Since, as has been pointed out, not as much copper should be necessary in running water as in still water it may be possible to automatically regulate the amount

of copper necessary to prevent algae growth by allowing the water to flow over the copper or the copper silicate material as it passes into the storage reservoir. The material could, for example, be suspended from floats anchored in the water. The concentration of copper in the water would vary with the rate of flow, thus more or less adjusting it to the need. Metallic copper has been successfully used for several years to prevent algae growth in zeolitic water softeners.<sup>1</sup> Since concentrations less than 20 parts per million of copper in water are considered harmless if not beneficial to human beings, water treated in this way is potable.

<sup>1</sup>Sweeney, O. R. Method of Preventing the Growth of Algae. U. S. Pat. 1,915,874. June 27, 1933.

*Table 1. Solubility of Metallic Copper  
Copper Ions Parts Per Million*

No. of hours	Distilled water	Distilled water with CO <sub>2</sub>	Distilled water with 2 gr. per liter NaCl	Tap water (spongy copper)
1	0.33	0.33	0.50	0.50
2	—	0.50	—	
3	—	0.67	—	
4	—	1.00	—	
6	—	1.43	2.50	1.00
24	0.50	1.66	—	1.25
48	1.00	2.00	10.00	2.00
72	2.50	3.33	20.00	2.00
150	5.00	3.33	20.00	
300	5.00			

*Table 2. Effect of Sodium Chloride Concentration  
Upon the Solubility of Copper\**

Concentration of sodium chloride Parts per million	Concentration of copper Parts per million
0.2	0.33
2.0	0.33
20.0	0.33
100.0	0.67
1000.0	6.7
Sat. sol.	20.0

\* In 24 hours.

Table 3. Solubility of Copper Silicate Compound\*

Time in hours	Parts per million copper	
	Distilled water	Tap water
1	0.20	0.25
6	0.33	0.50
24	0.50	0.67
48		0.67
72	0.50	0.80
96		0.80
120		0.80

\* Compound produced by reaction of copper sulfate and sodium silicate. Composition not determined.

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