Corrosivity of Peroxyacetic Acid Solution to Copper Refrigeration Tubing

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Background

Antimicrobial ice (Patent Pending, Enviro Tech Chemical Services, Inc), prepared by flash-freezing an aqueous solution of peroxyacetic acid (PAA), is applied to seafood during its storage and transportation to mitigate against spoilage and pathogenic microorganisms. Typically, the ice is prepared to contain between 50 and 100 ppm PAA. Because of its outstanding thermal conductivity properties (390 W/ m K @ 273 K), copper tubing and coil is commonly used with refrigeration equipment. It was therefore considered necessary to determine the corrosion rate of PAA solutions to copper. An experiment was designed to simulate worst-case scenario conditions whereby a chilled solution of 100 ppm PAA was contacted with a section of copper tubing for a 30-day period. Corrosion of copper causes copper ions to be released into the contacting solution. Copper ions catalyze the degradation of PAA by reducing its concentration. Therefore, the 100 ppm solution of PAA was replaced at least once, and sometimes twice a day for 5 days out of the week. The copper tubing was weighed before and after a 30-day contact period, and the weight loss was used to calculate the corrosion rate. The two days of the week that the 100 ppm PAA solution was not replenished were <u>not</u> factored into the calculation.

Method

A small section of a ½" copper pipe, similar in dimensions and size to the copper refrigeration piping used in the field, was used in the experiment. Oil and grease that may have created a barrier to attack by the PAA solution was removed by cleaning with isopropyl alcohol (IPA). The initial weight of the copper pipe was measured with an analytical balance, and a micrometer was used to measure its initial dimensions.

Perasan MP-2 was diluted with chilled city water to a nominal 100ppm PAA solution. A clean glass bottle, containing the copper pipe, was filled with PAA solution to a specified level (marked on the bottle). The glass bottle, containing the copper pipe and the PAA solution was stored in the refrigerator at 38 ^{o}C throughout the test period.

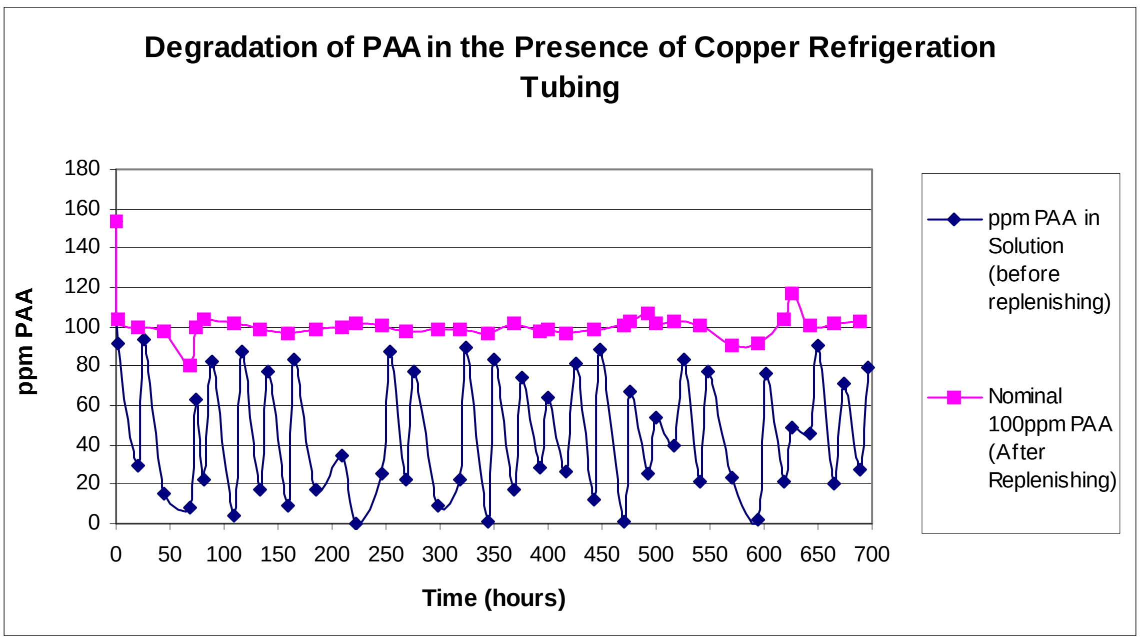
The PAA solution was analyzed for PAA using a HACH DR/700 Colorimeter and 10mL Total Chlorine Pillow Packs, based on a method developed by Enviro Tech. The solution was tested after four hours to determine the levels of PAA and copper. An Analyst 200 Atomic Absorption Spectrometer with a copper lamp was used to analyze the level of copper in solution after four hours. The PAA solution was tested once in the morning and once in the afternoon. If the PAA level dropped below 70ppm PAA, the solution was disposed of, and a fresh nominal 100ppm PAA solution was added in place of the older solution. A record was kept of each time the solution had to be replenished.

The experiment was conducted over a six-week period, but because the extended period of time included weekends, the solution was only tested during the five-day workweek (a total of 30 days were taken into account in this experiment). The pipe was stored in the same test solution, from Friday's test, over the weekend.

After the six weeks, the pipe was removed from the solution, dried and weighed. Visual observations were recorded and corrosion rate was calculated.

Results

PAA is unstable in the presence of metals ions. There was an average of 40% decline in PAA four hours into the experiment. The copper ions present in the PAA solution indicate that corrosion of the copper pipe was occurring. The copper ions present in solution accelerated the degradation of PAA causing the decline in activity. The amount of copper was analyzed in the PAA solution after four hours using the Analyst 200 Atomic Absorption Spectrometer. The copper level tested at 10.6ppm. Due to the rapid initial degradation of PAA, the activity of the solution was tested up to twice a day for 30 days. If the PAA dropped below an acceptable level (70 ppm), a fresh nominal 100ppm solution replaced the old solution. The graph below illustrates the degradation of PAA over the 30-day experimental period and each time the PAA solution was replenished.



The surface area of copper pipe exposed to the PAA solution was calculated using a geometric formula along with micrometer measurements of its inner diameter (I.D) and outer diameter (O.D). The corrosion rate was calculated using the formula:

Corrosion Rate (mpy) = (534)(W) / (D)(A)(T)

Where:

W = 735.0 mg (represents the weight of the pipe lost over the 30 day period)
D = 8.02 g/mL (density of the copper pipe)
A = 14.8996 in^2 (area of exposed surface represented by square inches)
T = 720 hr (represents the time in hours that the pipe was exposed to the PAA solution, not including 2 days of the week that the PAA solution was not replenished)

The corrosion rate was calculated to be 4.56 mils per year (mpy)

Microscopic examination of the exposed copper pipe revealed that the type of corrosion was general in nature, taking place evenly over the exposed surface. There was no microscopic evidence of a pitting corrosion mechanism that would cause the pipe to develop pinhole leaks.

Conclusion:
The general industry standards have ranges in place for metal corrosion levels, and are:

- Very Good levels are less than 5 mpy
- Acceptable/marginal range from 5-10 mpy
- Corrosive is any level about 10 mpy

The corrosion rate calculated from this experiment, 4.56 mpy falls in the Very Good range bordering the Acceptable. This experiment indicates that use solutions containing up to 100 ppm PAA will not adversely impact copper refrigeration piping over the lifetime of the equipment. Lower levels of Perasan MP-2 would proportionately reduce the corrosion rate of the PAA solution on copper.