

The Hypochlorite Issue

Oxidation of polymers, and in particular polyolefins, has always been a concern, especially for applications at elevated temperatures. The oxidation reaction is temperature-sensitive --- which means that the reaction proceeds much faster at elevated temperature. The typical rule-of-thumb is that the reaction doubles its rate for every 10°C rise in temperature, i.e., the reaction proceeds on the order of 32 times faster at 60°C (140°F) than at 10°C (50°F). To protect polyolefins in these situations, antioxidants are added to the formulations --- some are there to protect the polymer during exposure to high processing temperatures, while an additional amount or a different antioxidant is added to protect the polymer during service.

Recently, polyolefin piping in hot water applications has come under fire for premature failure due to oxidation. The hypothesis is that small amounts (1-3 ppm) of “chlorine” in the water may have caused the unsuspected increase in the rate of oxidation. Experiments have shown that exposure to high concentrations of hypochlorite at high temperatures can indeed result in the oxidation of the polymer, possibly at somewhat higher rates than originally anticipated, therefore, it has been concluded that there is a need to measure the “chlorine resistance” of materials destined to be used as materials in these applications.

An ASTM test method has been developed to measure this so-called “chlorine resistance”, referred to now as “oxidative resistance” --- but clearly Note 1 of the proposed method points out that only chlorine solutions have been considered. The premise of the method is based on the Arrhenius Rate Process which is used to measure the rate of change (in this case, time-to-failure) at several elevated temperatures, and project the data to lower temperatures and longer times in order to establish a lifetime prediction at reasonable use conditions. The method is well thought out and well presented --- the problem, however, is the “presumed” interpretation that a material that gives a better performance in this test is more resistant to chlorine, and, therefore, will perform better in a hot water plumbing system.

A little-known fact runs clearly in the face of this premise --- **there is essentially no free chlorine present in the hot water system.** The hypochlorite ion (OCl^-) and hypochlorous acid (HOCl) are particularly unstable at elevated temperature and oxidize rapidly to form chlorates, a chlorine compound which has virtually no disinfecting power --- basically a salt.

In an experiment using a 40-gallon water heater with a cold water feed having a 1.1 ppm chlorine residual, samples of hot water flowing at a precalibrated rate of 1.5 gallons per minute indicated no presence of free chlorine for twenty minutes. At the 20-minute mark, the first sign of chlorine was measured to be 0.1 ppm. Keep in mind that by this point 75% of the volume of water in the water heater had been replaced, which lowered the water temperature to 130°F from its original temperature of 138°F due to the continual addition of

fresh water. After that, the chlorine residual slowly rose as the temperature of the water declined. After 36 minutes into the experiment the chlorine residual essentially leveled out at 1.0 ppm with a water temperature of 104°F and was stable for the next 2 hours. The residual chlorine was also monitored while the water heater was allowed to restabilize. The chlorine residual had dropped to 0.5 ppm after 1-1/2 hours and was no longer detectable after 4 to 5 hours.

Understanding the ramifications of this experiment, one cannot hold the concentration of a free chlorine solution constant at elevated temperature. Even in a once-through test procedure it would take hours for the tank of solution to reach temperature which would mean that the concentration of free chlorine would be significantly reduced or nil. In order to maintain the concentration, additional hypochlorite has to be continually added to the solution to compensate for the chlorine lost due to chlorate formation. At the same time pH has to be monitored and adjusted to compensate for the hydrochloric acid (HCl) which is generated as a reaction by-product of the chlorate formation. The solution is basically unstable under these conditions, and does not, in any way, represent actual conditions of a hot water system.

The use of the Arrhenius principal to project the reaction rate at other conditions is based on the simple premise that only temperature is driving the rate of the reaction, within the limits of the experiment. If anything else is occurring, the Arrhenius model may not be valid.

Oxidation of polyolefin materials in hot water plumbing systems is a fact that cannot be ignored --- but must be understood. While it is clear that free chlorine can react with polyolefins, it is also evident that free chlorine does not exist in the hot water system to any appreciable amount. One has to recognize that the reaction of small amounts of free chlorine may not be responsible for the oxidation which is occurring in the field. Any test method which presumes to be capable of predicting the oxidative performance of polyolefins must be capable of realistic predictions. Clearly, a method which is based on exposure to an unstable solution of hypochlorite at elevated temperature which is maintained by forcing the solution to be in that “controlled” state, must be considered suspect.

It is essential that we understand the process which is occurring in order to find the solution. To accomplish that end we must first understand the chemistry and then develop an appropriate procedure for estimating service life. Until this is accomplished appropriately, the method we are developing may yield totally inappropriate conclusions.

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