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CORROSION INHIBITION BY HYDROGEN PEROXIDE IN DECONTAMINATION SOLUTIONS

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ABSTRACT

Under controlled conditions, hydrogen peroxide is an effective corrosion inhibitor for mildly acidic decontamination solutions used in contact with carbon steel. At Oak Ridge National Laboratory, solutions of 0.4 M ammonium oxalate with 0.3 M hydrogen peroxide at pH 4.0-4.5 have been developed for the low-corrosion decontamination of carbon steel. The solutions are used at 95°C and contain 0.2 M ammonium acetate, citrate, or glycolate as a pH buffer and peroxide stabilizer. Under these conditions of concentration, temperature, and pH, corrosion of carbon steel is 0.01 to 0.02 mil/hr. Without peroxide, corrosion is higher by a factor of 10 to 100, depending on the type of steel. Unlike most corrosion inhibitors, peroxide leaves no film on the steel to retard decontamination. Other advantages are that it oxidizes uranium dioxide to a soluble form and aids in the decontamination from ruthenium and cerium. Disadvantages are that it accelerates corrosion of some types of carbon steel at about 0.05 M H_2O_2 and has a useful life at 95°C of only a few hours. Hydrogen peroxide also inhibits the corrosion of stainless steel by strong acids such as oxalic, sulfuric, and hydrofluoric, normally considered too corrosive for extensive use in decontamination.

(An invited paper for oral presentation at the Decontamination Symposium in the national ACS meeting in Washington, D. C., March 27, 1962)

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The passivation of carbon steel by hydrogen peroxide in acidic solution under certain conditions has been known for several years. In 1952, Marshall (1) described a method of chemically polishing carbon steel by immersion in a mixture of 2.5% oxalic acid--1.3% hydrogen peroxide--0.01% sulfuric acid at room temperature. The steel removal rate was about 0.4 mil/hr. A protective layer of invisible oxide formed on the steel after withdrawal from the solution (2). Stainless steel was inert to the mixture. The electrode potential of iron in oxalic acid-peroxide mixtures was found by Hickling and Rostron in 1954 (3) to vary in a complex and interesting manner (Fig. 1). Although the authors were interested exclusively in the phenomenon of chemical polishing (region C in Fig. 1), they noted that at higher concentrations of peroxide (region D) the iron became passive to corrosion. At all concentrations below those producing passivity, peroxide accelerated the corrosion of steel.

Schumb, Satterfield, and Wentworth, in their monumental review of thousands of papers on hydrogen peroxide (4), warn that the inhibitive behavior of the substance on iron surfaces is capricious, and should not lead to consideration of its use in practice. It is explorations into the possibility of using hydrogen peroxide as a safe corrosion inhibitor in decontamination solutions, however, that we shall discuss today. A more detailed progress report on the decontamination research program at ORNL will be published shortly in the AEC literature.

At Oak Ridge National Laboratory, our interest in hydrogen peroxide as a component of decontamination solutions did not begin with Marshall and Hickling's work, of which we were unaware at the time, but began instead with the findings that a boiling mixture of 1 M hydrogen peroxide and 0.4 M oxalic acid was the

best decontaminant yet tried for niobium, and was also excellent for ruthenium on stainless steel. The addition of peroxide to 0.8 M oxalic acid lowered the corrosion rate from 0.011 ± 0.001 mil/hr, with a dull discolored finish, to 0.000 ± 0.001 mil/hr, with a bright luster (5). The boiling solution consumed carbon steel at a rate of about 12 mil/hr, leaving a very bright surface until the peroxide became depleted. Oxalic acid-peroxide mixtures were also rapid solvents for uranium dioxide, the proposed nuclear fuel of the Experimental Gas-Cooled Reactor (EGCR), which is now under construction in Oak Ridge. Thus hot oxalic acid-peroxide might be very useful for the decontamination of stainless steel, but it appeared to be much too corrosive for carbon steel.

Our second interest in hydrogen peroxide in the field of decontamination arose when we started developing methods and solutions for the decontamination of carbon steel EGCR components. It was necessary to have a noncorrosive solvent for both powdered and massive UO_2. The solvent which we found most effective was a mixture of ammonium oxalate and hydrogen peroxide, first proposed by Kraus of the Manhattan Project in 1944 (6). The hot solution, like oxalic acid-H_2O_2, was also an excellent decontaminant but, unlike oxalic acid-H_2O_2, caused no appreciable corrosion to mild carbon steel. The steel, after treatment with the hot solution, was, in fact, cleaner and brighter in appearance than before. The corrosion rate of carbon steel was less than 0.01 mil/hr.

Unfortunately, the oxalate-peroxide solution, which was so effective a solvent for uranium dioxide and such a good noncorrosive fission product decontaminant for carbon steel, was also unstable in the presence of iron, its dissolved salts, or suspended

iron oxides. For example, although 0.1 M ammonium oxalate with 0.3 M hydrogen peroxide was little changed by being heated and stirred in glass at 95°C for several hours, the addition of 100 ppm Fe^{+++} caused the hydrogen peroxide to decompose in 20 min. Stabilizers such as 8-hydroxy-quinoline, pyrophosphate, and Versene either had little effect or, as in the case of Versene, actually accelerated the decomposition. Physical signs of the decomposition were the evolution of oxygen and an increasing rise in pH. Although the hydrogen peroxide was decomposed, the oxalate ion was scarcely affected. The solution simply became a basic solution of the oxalate salt, without further capability of either dissolving UO_2 or decontaminating metal surfaces from the more stubborn fission products.

The two routes by which oxalate-peroxide mixtures decompose may be represented in a simplified way:

$$H_2O_2 + C_2O_4^{=} + 2H^+ = 2H_2O + 2CO_2 \qquad (1)$$

$$2H_2O_2 = 2H_2O + O_2 \qquad (2)$$

Reaction 1 takes place in the presence of acid, as shown, consumes hydrogen ion, and hence raises the pH. The reaction is driven to the right by excess acid, and to a lesser extent by excess peroxide or oxalate. As the reaction proceeds and the pH rises, or one of the other components is used up, the reaction slows down or stops. For example, a 5% solution of oxalic acid with excess peroxide may be boiled to dryness in the course of about 2 hr without leaving any organic residue. If the oxalic acid is first partly neutralized with ammonia to a pH of 4, oxidation of the oxalate to CO_2 will be only partial in several hours, the pH will rise, and reaction 2 will supervene. Reaction 2 takes place at an increasing rate from about pH 4.5

to 6.0, as the acid reserve diminishes, and becomes complete in a few minutes in a heated solution between pH 6.0 and about 6.5. Both reactions 1 and 2 are catalyzed by dissolved iron. The second reaction is more affected by iron as the pH rises and the solution approaches neutrality.

It was in the course of providing increased stability by lowering the pH and adding buffering agents that we rediscovered the fact, already published by Marshall and Hickling, that hydrogen peroxide can act both as a corrosion accelerator and inhibitor on carbon steel in acidic oxalate solutions. In Fig. 2, the corrosion rate of a carbon steel in an oxalate solution was increased from about 0.07 mil/hr to 1.2 mil/hr by 0.05 M H_2O_2, and then decreased to 0.02 mil/hr by 0.2 M H_2O_2. Weighed coupons of the steel were suspended in 0.3 M ammonium oxalate solutions at 95°C and pH 4.0, containing different concentrations of H_2O_2. The coupons were weighed again after 1 hr and the corrosion calculated by weight loss. The corrosion maxima at 0.05 to 0.10 M H_2O_2 correspond to region B of Fig. 1. We found these maxima to occur only with mild steels, and not with stainless steel, aluminum, titanium, Zircaloy-2, Croloy, or high carbon 440-C, which is used in ball bearings. The maxima disappear when the pH is raised to 4.5 or 5.0, except when citrate is present. Acetate, which is a good buffer and helps prolong the life of these solutions, was first tried at Hanford (7), and is also under study at Argonne National Laboratory. Unfortunately, acetic acid vapors, corrosive to carbon steel, are liberated from acetate-buffered solutions at elevated temperatures. Glycolate and citrate do not seem to share this property. Note that citrate accelerated corrosion at the lower peroxide concentrations, but helped to inhibit corrosion at 0.2 M

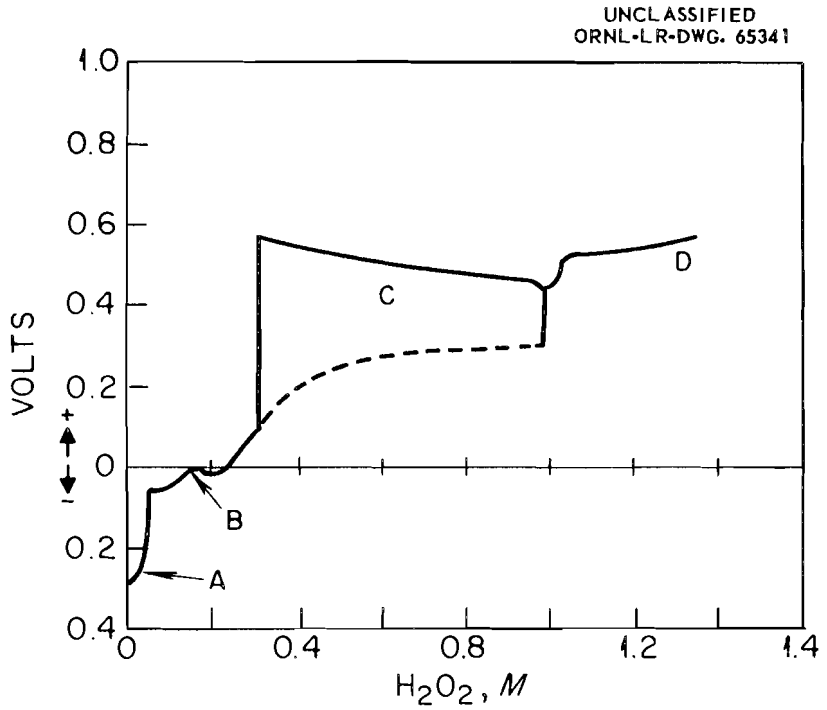

Fig. 1. Electrode potential vs hydrogen peroxide concentration, mild steel in 0.3 M $H_2C_2O_4$. (a) metal filmed, slight attack; (b) metal clean, rapid attack, O_2 evolution; (c) polishing region, oscillations; (d) passivity. (Hickling and Rostron, Trans. Inst. Met. Fin. 1955, 32, 229).

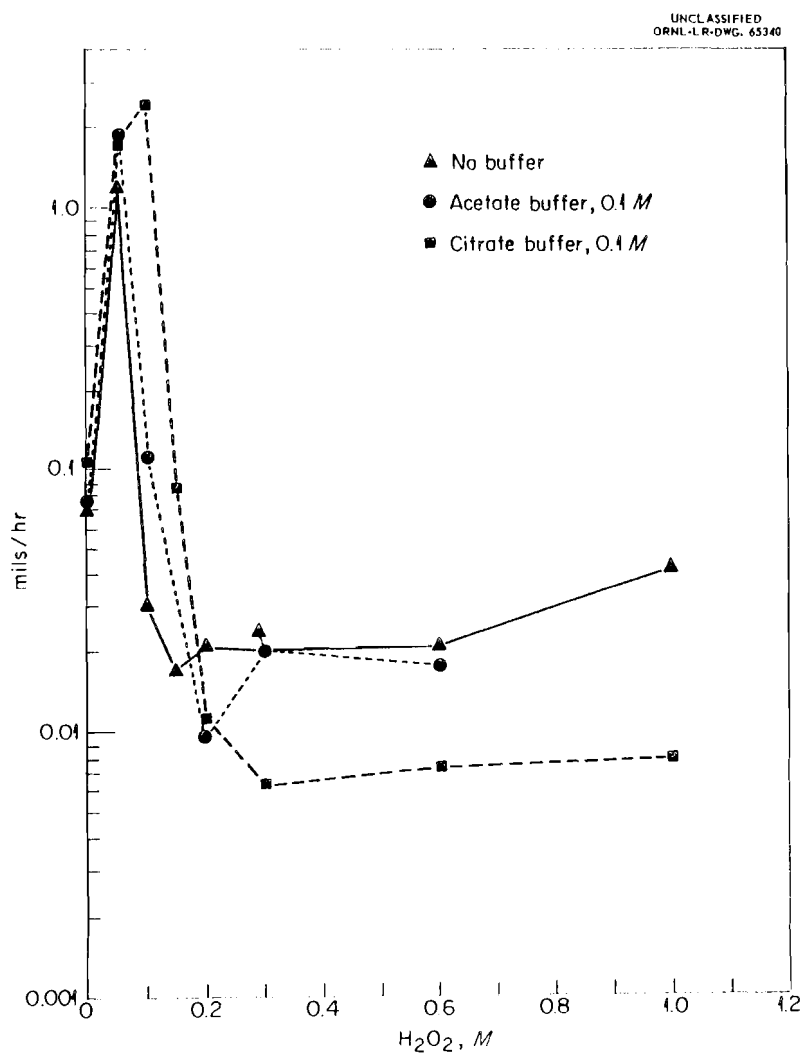

Fig. 2. Effect of H_2O_2 concentration and buffers on corrosion of type 1020 carbon

H_2O_2 and above.

The corrosion rates of several other metals in 0.3 M oxalate--0.1 M acetate solutions containing 0 to 0.5 M peroxide, at pH 4.0 and 95°C, were also measured (Table 1). The aluminum corrosion rate of about 0.05 mil/hr would not be prohibitive for many decontamination applications. Titanium showed an increasing corrosion rate with increasing peroxide, but remained relatively inert. Croloy 2 1/4, which is an alloy sometimes used in heat exchangers, showed the inhibition phenomenon. Rates were less than 0.001 mil/hr for 304 and 347 stainless steels, Inconel, and Zircaloy-2. Ball bearings of high carbon steel were corroded at 1.6 mil/hr at pH 5.1 in oxalate-citrate without peroxide, but at only 0.01 mil/hr when 0.33 M H_2O_2 was present at pH 4.0. We are currently studying corrosion rates and corrosion inhibition at still lower pH ranges, where, in general, higher peroxide concentrations and lower temperatures are used to guard against corrosive failure. One of our techniques is electrode potentials, as with Marshall and Hickling. Results will be reported in forthcoming ORNL publications.

Some typical decontamination results on laboratory coupons, with decontamination factors of 10^2-10^5, are shown in Table 2. For this test, duplicate metal coupons of carbon steel, 347 stainless, and aluminum were contaminated by a dry-on and mild heating technique with each of several pure fission products. The coupons were rinsed twice in hot water to remove soluble contaminants, dried, γ counted, washed 90 min in a modified household dishwasher (1 hr 75-95°C, then 0.5 hr at 95°C), rinsed, dried, and again γ counted. The formula used was 0.3 M $(NH_4)_2C_2O_4$--0.36 to 0.28 M H_2O_2, pH 4.1-4.4. The initial β -γ activity of each

Table 1. Corrosion in 0.3 M Oxalate--0.1 M Acetate-Peroxide Solutions at pH 4.0, 95°C

H_2O_2, M	Corrosion Rate, mils/hr			
	Al	440 C Steel	Ti	Croloy 2 1/4
0.00	0.013	0.60	0.00001	0.010
0.05	0.075	0.075	0.0008	0.00008
0.50	0.048	0.004	0.007	0.00002

Table 2. Decontamination by Oxalate-Peroxide

Isotope	Initial/Final γ Counts		
	Carbon Steel	347 Stainless	Aluminum
Ru-106	1.7×10^4	420	1.1×10^4
Zr-Nb-95	2.3×10^5	3.3×10^3	130
Sr-90	9.0×10^4	1.1×10^5	1.9×10^5
Cs-137	4.9×10^3	120	6.5×10^3
Y-91	2.0×10^4	7.5×10^3	3.2×10^4
Ce-144	2.5×10^5	9.6×10^4	1.8×10^5
I-131	980	5.1×10^3	1.6×10^4
Ba-La-140	2.1×10^4	1.5×10^4	2.1×10^5

coupon ranged from 30 to 1600 mr/hr. When one considers that these high decontamination factors are produced by one solution, which has a very low corrosion rate, it is evident that this type of solution deserves further investigation.

We have made preliminary explorations into the merits of hydrogen peroxide as a corrosion inhibitor with other acids. Results have been very gratifying with dilute sulfuric and hydrofluoric acids, but the study is still far from complete. As an example, the corrosion rate of type 347 stainless steel in 1 M HNO_3--1 M H_2O_2--0.1 M NaF at 70°C is only 0.0042 mil/hr, yet the solution is a highly effective decontaminant for plutonium. In 30 min at 70°C the decontamination was by a factor of 1000 on plutonium which had resisted other noncorrosive methods.

ACKNOWLEDGMENT

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