OAK RIDGE NATIONAL LABORATORY
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ORNL-TM-301 Nc 9
COPY NO. - 17
DATE - July 31, 1962

DECONTAMINATION STUDIES FOR THE GAS-COOLED REACTOR PROGRAM: SUMMARY FOR PERIOD OF DECEMBER 1, 1961-JULY 31, 1962

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ABSTRACT

A periodic summary of ORNL gas-cooled reactor decontamination studies, with a guide to publications, is presented for discussion at the August 23-24 meeting of the Reactor Decontamination Information Exchange Group at Chalk River.

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The development and laboratory testing of oxalate-peroxide mixtures as low-corrosion metal decontaminants was continued (1-6). In the reports cited, there is discussion of the electrode potential method for the determination of metal corrosion passivity conditions at various formulations and temperatures, a "fail-safe" oxalate-peroxide-citrate solution of long life, acetate rusting of carbon steel, basic versene with triethanolamine as a decontaminant, the removal of blue oxide from carbon steel, the absence of crevice and stress corrosion cracking on carbon steel in oxalate-peroxide solutions, ammonia-oxygen combustion in the gas phase, and corrosion inhibition by H_2O_2 in phosphate-sulfate-peroxide-fluoride solutions. The ORNL work on the inhibition of corrosion by hydrogen peroxide in decontamination solutions was reviewed at the March ACS meeting in Washington (7). A detailed report on all of the decontamination development work on the GCR program is in preparation (8).

Recent developments in the formulation and use of oxalate-peroxide solutions, which have not yet been published, include the acetate effect in oxalate-citrate-peroxide, the inhibition of fluoride corrosion by hydrogen peroxide and aluminum ions, optimum formulations for 60°C decontamination, and the effect of 500°C baking on subsequent decontamination from fission products. Details are as follows:

Acetate Effect in Oxalate-Citrate-Peroxide. The life of 0.4 M oxalate-0.34 M H_2O_2-100 ppm Fe^{+++} at pH 4.0 and 95°C was not extended by 0.1 to 0.8 M acetate addition as much as had been experienced with 0.16 M citrate. With acetate concentrations of 0.1, 0.2, 0.4, and 0.8 M the peroxide was exhausted after about 8 hr at 95°C and two overnight periods at room temperature. The pH stability increased with increasing acetate, but low pH resulted in an earlier loss of corrosion

passivity on carbon steel. The corrosion rate at failure was also higher when the pH was lower. For example, with 0.8 M acetate after 6 hr the solution became corrosive at 0.1 M H_2O_2, pH 4.38, at a rate of 1.6 mils/hr during the peak rate, and 0.25 mils/hr after the peak rate. With 0.1 M acetate, however, after 7 3/4 hr the solution became corrosive at 0.003 M H_2O_2, pH 7.55, and the peak rate was only 0.13 mils/hr followed by a rate of 0.07 mil/hr. The addition of 0.2 M ammonium acetate to the previous optimum 0.4 M oxalate-0.16 M citrate-0.34 M peroxide formula at pH 4.0 and 95°C, containing 100 ppm Fe^{+++} as a peroxide destruction catalyst, lengthened the low-corrosion life almost 50% from 12 to 17.5 hr. The corrosion rate on carbon steel during this life was 0.002 mils/hr. When the H_2O_2 had decreased to about 0.03 M in 17.5 hr, corrosion occurred for about 45 min at about 0.14 mils/hr (pH 4.8), and then decreased to about 0.09 mils/hr. Several other formula combinations had shorter lives. Stress and crevice corrosion samples of the one type of steel tested did not show abnormal attack. Steel in acetate-containing solutions did not have as bright a surface as in non-acetate solutions.

Inhibition of Fluoride Corrosion by Hydrogen Peroxide and Aluminum Ions. Fluoride ion is an excellent decontaminant for several fission products and transuranics, but its corrosivity to metals has been a drawback to wide usage. The inhibition of fluoride corrosivity by H_2O_2 was studied by the electrode potential method. The first fluoride solution was 0.05 M NaF in 0.4 M ammonium oxalate-0.2 M ammonium acetate at pH 4.0, 95°C. The electrode potentials of carbon steel, types 304 and 347 stainless, and types 1100 and X8001 aluminum were observed vs an H_2O_2 concentration from 0 to 3 M. At zero H_2O_2, potentials (vs the calomel

electrode) were, in the above order, -705, -545, -535, -960, and -855 millivolts, all indicating corrosivity. At 0.11 M H_2O_2 the stainless steels became passive at about +180 mv. At 0.3 M H_2O_2 the carbon steel entered the oscillating phase at about +35 mv associated with brightening, and at 0.6 M H_2O_2 it became passive at about +245 mv. The aluminum potential was still -500 mv at 3 M H_2O_2. Fifteen minute corrosion rates taken at 3 M H_2O_2 were the following in mils/hr: carbon steel 0.012, stainless steels (very bright) 0.003 and 0.006, aluminums 1.8. In a similar run with 0.2 M NaF, the stainless steels went passive at 0.12 M H_2O_2 and the carbon steel at 1.1 M H_2O_2.

The extent of corrosion reduction of fluoride by Al^{+++} was also measured. In 0.4 M oxalate-0.2 M acetate-0.2 M fluoride without H_2O_2, at 95°C and pH 4.0, types 304 and 347 stainless steels were active at -300 mv, but when 0.2 M Al^{+++} was added as the nitrate the steels became passive at about +200 mv. Carbon steel became passive at 0.38 M H_2O_2 in the mixture, instead of the 1.1 M H_2O_2 required when no Al^{+++} was added. When 1 M H_2O_2 was used in the oxalate-acetate-fluoride solution, without Al^{+++} the corrosion rate on aluminum was 6 to 9 mils/hr, with 0.067 M Al^{+++} it was 2.1 mils/hr, and with 0.2 M Al^{+++} it was 0.27 mils/hr.

The tendency toward corrosion was greater when 0.16 M citrate was added to the oxalate-acetate-fluoride-aluminum formula. When peroxide was added the stainless steels became passive at 0.1 M H_2O_2 and the carbon steel at 0.4 M H_2O_2. The aluminums remained active even at 1 M H_2O_2. Corrosion rates at 1 M H_2O_2 in mils/hr were 0.012 for carbon steel, 0.003 for type 304, 0.000 for type 347, and 0.66 and 0.63 for 1100 and X8001 aluminums, respectively. The stainless steels

acquired a very bright finish during the tests.

Aluminum ion was so effective a corrosion inhibitor for fluoride on steel surfaces that 0.05 M F^- and Al^{+++} could be added to the optimum oxalate-peroxide formula without the need for increasing the peroxide, although the useful life of the solution was somewhat shortened. When 0.05 M F^- and 0.05 M Al^{+++} were added to 0.4 M oxalate-0.16 M citrate-0.34 M H_2O_2-100 ppm Fe^{+++} at pH 4.0 and 95°C, the noncorrosive life to carbon steel was 6.5 hr. Addition of 0.1 M acetate lengthened the life to 11 hr, and 0.2 M acetate to 11.5 hr. In the 0.2 M acetate solution, corrosion to carbon steel during the first 11.5 hr was less than 0.001 mils/hr. During a short corrosion peak thereafter it was 0.15 mils/hr, and after the peak, when the H_2O_2 was all decomposed, at pH 5.4, the corrosion was 0.09 mils/hr.

Optimum Formulas for 60°C Decontamination. The development of long lived "fail-safe" oxalate-peroxide formulas for use at 60°C was successful. The fundamental mixture, to which additions were made, was 0.4 M ammonium oxalate-1.0 M H_2O_2-100 ppm Fe^{+++} at pH 2.50 and 60°C. A preferred citrate concentration was found to be 0.1 M. With no citrate, in 79 hr the H_2O_2 had fallen to 0.005 M and the pH had risen to 7.95, but with 0.1 M citrate the H_2O_2 was still 0.7 M and the pH 4.19. With 0.47 M citrate, carbon steel was rapidly corroded. In the 0.1 M citrate solution, initial corrosion to carbon steel was about 0.001 mils/hr, and this rate decreased with time. There was no stress corrosion cracking or crevice corrosion. The initial corrosion rate on types 1100 and X8001 Al in the 0.1 M citrate formula was about 0.02 mils/hr, and the final rate was about 0.01 mils/hr.

A very stable and low-corrosive oxalate-peroxide formula containing fluoride

was found. In 144 hr at 60°C, a mixture consisting of 0.4 M oxalate-0.1 M citrate-0.2 M acetate-0.05 M F^--0.05 M Al^{+++}, initially at pH 2.5, with 100 ppm Fe^{+++} added to decrease life, still contained 0.7 M H_2O_2 at pH 4.24. Corrosion on carbon steel and aluminum during the first hour were 0.006 and 0.44 mils, and during the 127th hour were <0.001 and 0.1 mils, respectively. After 144 hr in a similar mixture without acetate, the H_2O_2 was 0.05 M and the pH 7.5. Without citrate, the H_2O_2 was again 0.05 M, and the pH 6.4. Without citrate, fluoride, and aluminum, the life ended also at about 144 hr, but with the aluminum corrosion lower by a factor of about 20 than when F^- was present.

Effect of 500°C Baking on Subsequent Decontamination from Fission Products. When stainless steels were contaminated with $ZrNb^{95}$, Ce^{144}, or $BaLa^{140}$ in non-acidic solutions, dried, baked at 500°C in O_2-free helium, rinsed in hot water, and then treated with decontaminating reagents, results were poor. Type 347 SS had decontamination factors from $ZrNb^{95}$ of only 1.5 to 5 in 20 min at 95°C, and scarcely higher in 3 1/2 hr, with oxalate-peroxide reagents. The same low results were obtained with type 302 SS, showing that they were not caused by isotopic exchange with the columbium stabilizer. Boiling Turco 4501, normally quite effective on $ZrNb^{95}$, produced additional decontamination factors of only 1.1 to 1.2. Equally poor results on stainless steels were obtained with cerium and barium-lanthanum when treated with oxalate-peroxide. Carbon steel decontamination factors were somewhat better, being 20-40 in 20 min and 250-320 in 3 1/2 hr with $ZrNb^{95}$, 17 in 20 min for Ce^{144}, and about 3 for $BaLa^{140}$ in 20 min. Baked aluminum had decontamination factors of 3×10^3 in 20 min for $ZrNb^{95}$, 700 to 1×10^4 for

$BaLa^{140}$, and 60 to 100 for Ce^{144}. The higher decontamination factors for aluminum were partly due to the higher corrosion rate of fluoride on aluminum than on steels. In general, baking at lower temperatures did not fix the fission products as firmly to the metals as at 500°C.

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