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Decontamination of EGCR and PBR, Revised Procedures.

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ABSTRACT

Revisions have been made in the tentative proposals first suggested in October 1960 for solutions and methods for the decontamination of the EGCR and PBR. Significant improvements in the oxalate-peroxide solution include greater stability, effectiveness, and economy, with considerable simplification of the waste disposal problem. Corrosion results are summarized.

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Tentative procedures for the decontamination of the EGCR charge and service machines and the Pebble Bed Reactor, based on low-corrosion solutions, were proposed in October 1960 (1-5). These procedures featured an initial detergent wash to remove dust and water-soluble contaminants, followed if necessary by a mixture of sodium oxalate and hydrogen peroxide at pH 5, to dissolve residual UO_2 and to further decontaminate the carbon steel surfaces. The oxalate-peroxide solution required pH adjustment approximately every half hour, in order to prevent a spontaneous pH rise followed by rapid decomposition. Development work has been continued on the oxalate-peroxide type of solution, resulting to date in the following changes:

(a) Ammonium oxalate used instead of sodium oxalate increased decontamination efficiency, prolonged solution life by its buffering action, increased the speed of dissolution of UO_2, lowered the cost, and facilitated waste disposal.

(b) Addition of citrate, glycolate or acetate further stabilized the solution by buffering action, and possibly helped to complex iron and increase decontamination.

(c) Lowering the peroxide concentration increased stability.

(d) Lowering the pH increased the effectiveness of the solution and further prolonged its life.

Extensive corrosion studies have greatly aided in the formulation of a solution which is approaching the optimum in safety and efficiency, as a one-solution decontaminant and UO_2 solvent for use on mild steel. Future work includes determining the effectiveness of this solution and other solutions on uranium mono- and di-carbide and graphite, as well as more extensive testing of various solutions as decontaminants for fission products and protactinium volatilized at high temperatures in helium.

Details of the formulation and usage of the oxalate-peroxide solution now recommended are as follows:

1. Solution composition

	For 100 gal	Molarity
ammonium oxalate	35.5 lb	0.40
acetic acid glacial	1.06 gal	0.~~10~~ 0.18
hydrogen peroxide 30%	5.2 gal	0.50
water	To 100 gal	

2. Mixing the solution

For each 100 gal of solution, run about 90 gal of cold water into the tank, then add, with stirring, first the oxalate, then the acid, and finally the peroxide. Make up to final volume with water. The pH will be about 4.2. Do not heat the solution in mild steel before adding the peroxide, as its corrosion rate on mild steel at 95°C without the peroxide is as high as 0.35 mil/hr. (Corrosion is more fully discussed in Sect. 6.) At room temperature, a little of the oxalate will remain undissolved, but all dissolves on warming.

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3. Purpose of solution ingredients

The oxalate ion, slightly acidified, is a very effective general purpose fission product complexer and decontaminant. Hydrogen peroxide serves the triple purpose of corrosion inhibitor, aid in the decontamination of ruthenium and cerium, and uranium oxidant so that the UO_2 will dissolve in the oxalate. The acetic acid lowers the pH to a level at which the solution is an efficient decontamination agent, without being so acidic as to be unduly corrosive. Acetate also has the important function of buffering the solution against the rise in pH which would otherwise occur, and which would result in rapid decomposition of the H_2O_2 with evolution of O_2. All ingredients are volatile, which will greatly simplify the waste disposal problem.

4. Effective life of the solution

The decontamination solution slowly decomposes with time, and this must be allowed for in its usage. At room temperature, the solution will remain effective for several days. At 95°C in a mild steel tank, in 17 hr the H_2O_2 level will have dropped to about 0.12 M, and the pH will have risen to about 5.1, which will make the solution less effective. The life of the solution is shortened by building up dissolved iron (causing a yellow color), by contacting with large surface areas such as in a spraying operation, and by prolonged heating. All contact with copper and its alloys must be prevented, since corrosion is high, and the dissolved copper rapidly decomposes the peroxide. Aged solutions can probably be reconstituted at least once, by re-addition of acetic acid and H_2O_2 after analysis (see below). Reconstitution has not yet been evaluated in the laboratory.

5. Analysis of the solution

(a) Peroxide by iodide method. In a 125-ml Erlenmeyer flask place 50 ml of 1 N H_2SO_4. Add 1.0 ml of saturated KI solution by pipet, and 2 drops of saturated ammonium molybdate solution from a medicine dropper. Add by pipet 1.000 ml of the decontamination solution to be tested, mix, and set aside for 5 to 10 min. Titrate to the disappearance of the iodine color with 0.1000 N thiosulfate solution. The buret reading in ml, divided by 20, gives the molarity of the peroxide.

(b) pH. Zero the pH meter on pH 4.00 buffer solution at least once a day. The pH reading of the decontamination solution is more reliable at room temperature than in a hot solution, because the electrodes are more likely to give trouble at elevated temperature.

(c) Oxalate and acetate. Analysis is not necessary. The oxalate is gradually consumed by the peroxide over a period of many hours in a hot solution, but a sufficient excess is present for decontamination purposes.

6. Corrosion by the solution at 95°C

Table 1, taken from an extensive series of corrosion vs H_2O_2 curves, lists the average

Table 1. Corrosion of Metals (mils/hr) in 0.3 M Oxalate-0.1 M Acetate-Peroxide Solutions at 95°C

pH	H_2O_2, M	Mild Steel A-109	Mild Steel 1020	Annealed 440 C	Aluminum	Titanium	Croloy 2-1/4*
4.0	0.00	0.08	0.008	0.6	0.013	0.00001	0.010
	0.05	1.8	1.8	0.075	0.075	0.0008	0.00008
	0.50	0.010	0.020	0.004	0.048	0.007	0.00002
4.5	0.00	0.35	0.072	0.35	0.020	0.00001	-
	0.05	0.005	0.011	0.002	0.044	0.0005	-
	0.50	0.004	0.008	0.004	0.042	0.004	-
5.0	0.00	0.23	0.09	0.14	0.020	0.00001	0.032
	0.05	0.005	0.007	0.003	0.048	0.0008	0.002
	0.50	0.004	0.006	0.006	0.042	0.012	0.0005

*Croloy at pH 4.0 was in glycolate instead of acetate, and at pH 5.0 was in oxalate-peroxide without additives.

corrosion figures in mils/hr for several metal types, calculated by the weight loss method. These data were all taken in solutions of 0.3 M instead of 0.4 M oxalate, but should apply also to 0.4 M oxalate. Although mild steel in pH 4 solution shows a corrosion peak at 0.05 M H_2O_2, strongly corrosive conditions will not be met in practice because the pH normally rises as the peroxide decreases. A misoperation such as failing to add hydrogen peroxide when the solution is prepared, or continued use of solution which has become depleted to 0.1 M H_2O_2 or below, could, however, cause relatively high corrosion of carbon steel, as shown in the table. The corrosion rates of 304 SS, 347 SS, and Zircaloy-2 were below 0.001 mils/hr in all cases.

7. Decontamination procedures

Decontamination of EGCR and PBR components should follow the outline in CF 60-10-63 (Rev.), p. 17.1-17.4, with a few changes. After the detergent wash, the new decontamination solution should be used. The contact should be for several hours for best results, or until the peroxide concentration falls to about 0.15 M. It is likely that lower temperatures, perhaps of the order of 60°C, can be used instead of the specified 95°C, if longer contact times are provided. This assumption is to be checked in the laboratory. If the

spray method is used, the longer contact times would make a recirculating system necessary for purposes of economy of solution and waste storage. It now appears that alkaline $KMnO_4$ treatments will probably not be necessary if the oxalate-peroxide reagent is contacted with the metal surfaces for the equivalent of 2 hr or more at 95°C. Repeated analyses and additions of oxalic acid will not be required, since the life of the new solution should usually be adequate for decontamination purposes.

ACKNOWLEDGEMENT

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