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INVENTION REPORT - DEVELOPMENT OF A SOLUTION TO
OXIDIZE AND DISSOLVE URANIUM METAL AND ITS OXIDES

R. D. Weed

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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INVENTION REPORT - DEVELOPMENT OF A SOLUTION TO
OXIDIZE AND DISSOLVE URANIUM METAL AND ITS OXIDES

INTRODUCTION

Following a fuel element cladding failure, large quantities of metallic uranium can be corroded and deposited throughout a high-temperature pressurized-water nuclear reactor core-coolant recirculation system. This contaminating material is in the form of uranium oxides (UO_2 , U_3O_8 , and UO_3) and may include particulate chunks of metallic uranium. A large percentage of the remaining fission products are associated with this particulate oxide material. Decontamination of such a system requires the dissolution of these oxides for removal from the system.

Laboratory^(1,2,3) evaluations have evolved three solutions which can effectively dissolve quantities of uranium oxides.

The peroxide-bicarbonate solution^(1,2) (0.25 M H_2O_2 , 0.25 M Na_2CO_3 , 0.25 M NaHCO_3 , 0.01 M EDTA, 1.0 g/l 8-quinolinol) was found to be effective in dissolving the finely divided uranium oxides but ineffective in dissolving large particles of metallic uranium. In laboratory tests, the permanganate-bicarbonate solution⁽²⁾ (40 g/l KMnO_4 , 27 g/l Na_2CO_3 , 21 g/l NaHCO_3) was superior to the peroxide-bicarbonate solution but subsequent tests in dynamic loops proved the reverse to be true. The formation and precipitation of MnO_2 was undesirable in the dynamic system.

The peroxide-oxalate solutions^(2,3) was originally composed of oxalic acid and hydrogen peroxide with the pH adjusted to approximately 4.5 with ammonium hydroxide. To eliminate the handling of the aqueous ammonia and its gas (NH_3) formation with elevated temperatures the solution was recomposed using 2.3 g/l of oxalic acid, 32 g/l of sodium oxalate, and 15 g/l of hydrogen peroxide, the pH remained at 4.5.

Although these peroxide-oxalate solutions provided good uranium oxide dissolution rates and would dissolve large chunks of metallic uranium and uranium oxides that the peroxide-bicarbonate solutions would not dissolve, it was found that the peroxide-oxalate solutions were very unstable. The pH would progressively increase with time (from 4.5) accompanied by rapid H_2O_2 losses. This stability problem was solved by the addition of 10 g/l of sodium acetate and 5 g/l of acetic acid. These ingredients adequately buffered the solution, preventing the peroxide losses, and did not affect the uranium oxide dissolution rates.

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During the laboratory testing, the acetic acid-sodium acetate buffered solution reacted rather violently giving a tremendous temperature rise and boiling over the solution in the flask. In a literature review, an article by Daniel Swern⁽⁴⁾ contained the following information:

Grundman and Trischmann employed 30 per cent hydrogen peroxide and emphasized that the reaction temperature should not be too low during the addition of the reactants; otherwise complete mixing may occur before any reaction has taken place, at which point the reaction may proceed with explosive violence. The reaction temperature employed was 40 C.

It was apparent that peracetic acid had been made during these reaction periods in the laboratory; therefore, the choice of peracetic acid was made. The new composition became known as the oxalic-peroxide-peracetic solution. It is composed of the following chemicals:

Oxalic acid	2.3 grams/liter
Sodium oxalate	32.0 grams/liter
Hydrogen peroxide	15.0 grams/liter
8-Quinolinol	1.0 gram/liter
Peracetic acid (40%)	12.5 grams/liter

DISCUSSION

The preliminary scanning tests were conducted without the addition of the 8-quinolinol. In the laboratory, glass equipment was used in testing, but the dynamic systems are of steel which catalyzes the decomposition of H_2O_2 requiring the addition of the 8-quinolinol as a stabilizer suppressant for H_2O_2 decomposition. Its addition to the solution did not affect the oxidation of uranium and its oxides.

The characteristics of the solution initially tested are as follows: Original pH - 4.30; pH after one hour of refluxing at 80 C - 4.68; grams of total uranium dissolved per liter - 18.7.

The data presented in Tables I and II were obtained for the solution whose composition is given above. The results in Table I indicate that the solution is near saturation with the dissolved uranium. The solution is still able to

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TABLE I

Data For Dissolution Of Uranium Oxides With
The Oxalic-Peroxide-Peracetic Solution

Amount of Oxides Added to Solution									Temperature
25 g/l			50 g/l			75 g/l			
Initial pH	Final pH	gms U/Liter in Solution	Initial pH	Final pH	gms U/Liter in Solution	Initial pH	Final pH	gms U/Liter in Solution	
4.12	4.32	16.9	4.30	4.50	19.8	*	*	*	80
4.30	4.53	16.6	*	*	*	*	*	*	60
4.30	4.51	15.1	4.30	4.52	23.9	4.38	4.57	24.2	40

* Tests not conducted.

TABLE II

Corrosion (mils/hour) of Materials In
The Oxalic-Peroxide-Peracetic Solution

Materials							Temperature
CS	304 SS	302 SS	Inconel-X	Zircaloy	Brass	Admiralty Brass	
0.01	0.001	0.001	0.001	N.D.*	5.34	3.96	80
0.002	N.D.	0.001	N.D.	N.D.	2.27	1.91	60
0.001	N.D.	N.D.	N.D.	N.D.	-	0.74	40

* N.D. = None detected.

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oxidize uranium and has oxidized up to the 75 grams of mixed oxides per liter. However, a considerable portion of the oxidized uranium is precipitated as the uranyl oxalate ($\text{UO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$) which is soluble in alkaline solutions.

The corrosion data in Table II indicate that the brass and brass alloys are the primary materials corroded in this solution. Corrosion of the major materials of construction, carbon steel, stainless steel, Inconel-X, and Zircaloy by the solution was insignificant.

In comparing this solution with other chemical solutions used for the purpose of oxidizing and dissolving uranium oxides, it is noted that this solution is either less corrosive to the materials of construction, more effective in oxidizing the uranium oxides, or chemically stable when being heated and cooled. Nitric acid is a good oxidizing media for uranium oxides but is too corrosive for use in carbon steel systems. Some mixtures of phosphoric acid and hydrogen peroxide are good oxidants but are severe corrodants. The peroxide-bicarbonate solution was suitable from the corrosion point of view and does oxidize and dissolve the uranium oxides. However, the solution described in this paper oxidizes and dissolves greater quantities of the uranium oxides than the peroxide-bicarbonate solution. The permanganate-bicarbonate solution is not suitable for use because of the precipitation of manganese dioxide and besides it is less effective than the oxalic-peroxide-peracetic solution for oxidizing and dissolving uranium oxides. The initial solution of hydrogen peroxide, oxalic acid, and sodium oxalate was chemically unstable under heated conditions in the presence of a catalyst such as iron and steel. Other additions such as 8-quinolinol increased the stability but the acetic acid-sodium acetate addition gave the pH stability. Complete chemical stability was still lacking because of the existing reaction between hydrogen peroxide, acetic acid, and sodium acetate. The addition of peracetic acid to replace the acetic-acetate addition gave the desired stability.

Also, the oxalic-peroxide-peracetic solution surpasses the comparative solutions in that it is nearly as effective at 40 C as at 80 C. These other solutions must be used at 60 C or above for effective oxidation and dissolution.

Claims:

The oxalic-peroxide-peracetic solution is a superior oxidizing and dissolving solution for the uranium oxides present in a nuclear reactor primary system. This solution has been used to decontaminate an ex-reactor system from 17 r/hr to 0.9 r/hr. This solution also has been used to dissolve plutonium oxides during the Plutonium Recycle Test Reactor decontamination.

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