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NEW APPROACHES TO THE PRTR DECONTAMINATION PROBLEM

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HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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NEW APPROACHES TO THE PRTR DECONTAMINATION PROBLEM

INTRODUCTION

Reactors, such as the PRTR, operating with heavy water as the primary coolant offer powerful incentives for developing decontamination processes that do not require removal of the heavy water during the decontamination operation. Removal of heavy water, no matter how carefully done, is involved, expensive and time consuming. It is desirable that processes be devised that would permit the fuel elements to remain in place during the decontamination.

A literature search and chemical property study was begun to find an effective decontamination procedure that permits leaving the coolant in the primary system. For heavy water coolants a further restriction is necessary: no hydrogen contamination or compounds containing hydrogen.

This report covers the results of this literature search and study of properties. It is focused on the system cooled with heavy water but the ideas advanced, with slight modification, could be applied to other pressurized water reactor systems.

SUMMARY AND CONCLUSIONS

A literature search and study of chemical properties was made to determine methods for decontaminating PRTR-like systems with the fuel in place and with no drainage of the heavy water coolant. The results of this study suggest that heavy water systems might be decontaminated with substantial savings in time and money by using ozone and certain acid anhydrides. The proposed decontamination operation is as follows:

1. Introduce ozone for PuO_2 or UO_2 oxidation and oxide film conditioning.
2. Deoxygenate and remove activated materials with ion exchange techniques.
3. Introduce acid anhydrides and defilm system.
4. Remove chemicals and activated materials with ion exchange techniques.
5. Resume operation.

DISCUSSION

There are two basic parts to the nuclear reactor decontamination problem: (a) the removal of activated corrosion products and impurities from the reactor system; and (b) the removal of fuel element rupture products. Activated corrosion product and impurity decontamination generally involves a two-step procedure, consisting of a film-conditioning step followed by a film-removal step.(1,2,3) This technique has been found to be effective for activated materials are either incorporated into the piping metal oxide crystal lattice, strongly adsorbed or retained as loosely adherent particulate matter on these oxide films.(4)

Rupture product decontamination involves the use of an oxidizing medium to change the valence of the fissionable material from + four to + six and remove this oxidized material from the system.(1,2,3) If appreciable leaching or release of fission products from the fissionable material has occurred, frequently, film-conditioning and film-removal steps are required for effective decontamination.

It was assumed in this work that the same general reactions outlined earlier for systems cooled with light water would be necessary to decontaminate heavy water cooled reactors. The basic ground rules for limiting the scope of this study were:

(1) Heavy water to be left in the primary system during decontamination.

(2) No hydrogen or light water contamination.

(3) No heavy water losses.

(4) The procedure must be simple and straightforward.

Other important considerations in determining the feasibility of using certain chemicals were:

(1) Is or will the chemical be readily available?

(2) Can it be readily removed from the heavy water system?

(3) Is it prohibitively corrosive?

(4) Does it offer chemical decontamination possibilities?

With regard to the latter, the chemicals must be able to oxidize the piping film, dissolve or complex the film, or oxidize rupture debris to a water soluble valence state to be an effective decontamination chemical.

Film Conditioning and Oxidation

One of the first considerations in this study was to find a replacement for the alkaline permanganate solutions that are presently used to condition reactor coolant system films. Ozone seems to offer this possibility. Its oxidizing power is apparent from the following couples:

$$O_2 + H_2O \rightleftharpoons O_3 + 2H^+ + 2e^-, \quad E^\circ = -2.07 \text{ volts}$$

$$O_2 + OH^- \rightleftharpoons O_3 + H_2O + 2e^-, \quad E^\circ = -1.24 \text{ volts}$$

In acidic solutions, ozone is exceeded in oxidizing power only by fluorine and materials such as oxygen difluoride, atomic oxygen, and the hydroxyl radical, whereas in alkaline solutions it is exceeded only by the hydroxyl radical.(5)

Normal deoxygenation procedures could be used to remove the decontaminant from the primary system, for ozone decomposes as follows:

$$O_3 \rightleftharpoons 3/2O_2 + 34.2 \text{ K calories}$$

Deoxygenation can be accomplished without disturbing the deuterium purity by

1. Use of oxygen-scavenging ion exchange resins.
2. Liquid phase catalytic recombination of O_2 with D_2 to form D_2O.
3. Mechanical deaeration devices.

Such a powerful oxidizing agent might also serve as the medium for oxidizing uranium or plutonium in rupture debris to a higher valence. In addition, there is a possibility that two decontamination steps might be accomplished with one reagent, i.e. ozone might oxidize fissionable material and condition oxide films simultaneously. This would greatly simplify the whole rupture debris decontamination process.

Its oxidation potential in an acid medium is such that it might speed up the dissolution of such difficultly soluble materials as fired plutonium dioxide.

There is the possibility that ozone might make the desired valence changes but not be able to effect a totally efficient removal of the rupture debris because of adsorption or deposition reactions. Certain acid anhydrides could be added, in this case, for acidification and complexing action to avoid these troublesome reactions. Acidification could be readily accomplished by injecting an acid anhydride such as carbon dioxide, sulfur dioxide or mellitic anhydride into the heavy water. The reaction is as follows:

$$CO_2 + D_2O \longrightarrow D_2CO_3$$

where D is used for ${}_1H^2$ (deuterium).

The behavior of ozone in water is not well defined. It is known, however, that it is more soluble in water at room temperature than is oxygen.(5) It is also known that certain oxides can cause the decomposition of ozone.(6)

The alkaline permanganate solution that is presently used for reactor coolant system film conditioning requires high concentrations of caustic (~ 18% NaOH) and potassium permanganate (~ 3% $KMnO_4$). These high concentrations present serious waste disposal problems for spent solutions. A successful ozone process would give a substantial concentration savings and there would be no problem with large volumes of waste. In addition, alkaline permanganate solutions are effective only at temperatures in excess of 100 C. The potential of the ozone reaction suggests a possibility of using this reagent at a somewhat lower temperature.

Alkaline permanganate solutions are also known to cause dendritic corrosion on Stellite Alloys (1,2,3,6). The difficulty with which the alkaline permanganate is rinsed from systems often permits the alkaline permanganate to remain in the dendritic openings and proceed to attack the Stellite over prolonged periods of time. Although little is known about the corrosion expected by ozone in reactor decontamination, the use of ozone would eliminate long-term corrosion effects since ozone decomposes fairly rapidly, especially at elevated temperatures.

Ozone usage is not new at Hanford. At the present time it is employed in the Redox process. Ozone is produced by ozonators in the 202-S Building. This method could be used in experimental studies to determine its feasibility as a decontamination reagent or conceivably it could be used on reactor primary systems. If it were desirable to use ozone in larger quantities, it could be obtained commercially by the time it was required.(8)

Before ozone could be used in-reactor an extensive program would be required to determine its decomposition rate and its decontamination, handling, and corrosion characteristics. Its chemical possibilities are such, however, that such a program appears to have merit.

Film Removal

Film removal in stainless steel systems is best accomplished in acid media. As discussed above, in order to minimize contamination of D_2O by H_2O, it may be necessary to add acid anhydrides. Several acid anhydrides, especially those listed in Table I, offer good film stripping possibilities for PRTR-like systems.

TABLE I

Hydrogen-Free Acid Anhydrides

Substance	State at 25C	First hydrogen dissociation of acid	Heat of solution (gm cal/mole)	Acid
1. Mellitic anhydride $C(CO)_6$	solid	-	-	mellitic acid
2. Carbon suboxide C_3O_2	gas	1.8×10^{-3}	-	malonic acid
3. Sulfur dioxide SO_2	gas	1.5×10^{-2}	1,500	sulfurous acid
4. Sulfur trioxide SO_3	liquid	strong	39,170	sulfuric acid
5. Carbon dioxide CO_2	gas	4.3×10^{-7}	-	carbonic acid
6. Phosphorus pentoxide	solid	7.52×10^{-3}	53,600	phosphoric acid

Phosphoric acid has been used for reactor loop decontamination.(9) Some of the others such as mellitic acid and malonic acid have been selected because they have polybasic organic acid properties similar to organic acids that have been successfully used for decontamination work.

At the present time there is no known supplier of carbon suboxide. If it proved to have desirable properties, C_3O_2 can be produced by dehydrating malonic acid with phosphorus (V) oxide in a vacuum at 140-150 C.(5) The other items listed in Table I are available commercially.

In order to facilitate removal of these substances from the D_2O after decontamination is effected, it is desirable that they be effective in comparatively low concentrations. Under these conditions they could be removed by ion exchange or similar techniques. New liquid ion exchange techniques might well allow somewhat higher chemical concentrations than the presently available solid resins. A continuous feed and bleed of liquid resin to a shielded waste container would provide for greater flexibility in meeting moderately concentrated chemical solutions than do isolated solid resin beds.

In many cases, the effectiveness of these acid anhydrides might be enhanced by materials commonly known in the metal cleaning industry as "activators" or synergistic chemicals. It is quite possible that either mellitic acid or malonic acid would act in this manner with sulfuric acid. The polybasic acid, oxalic acid, a lower homolog of malonic acid, is known to provide effective decontamination with sulfuric acid.(2,10) The determination of these properties will require a considerable research and development effort. The same applies to minimum effective chemical concentration, kinetics, and corrosion determinations. The properties of any candidate must be determined before it is used in-reactor.

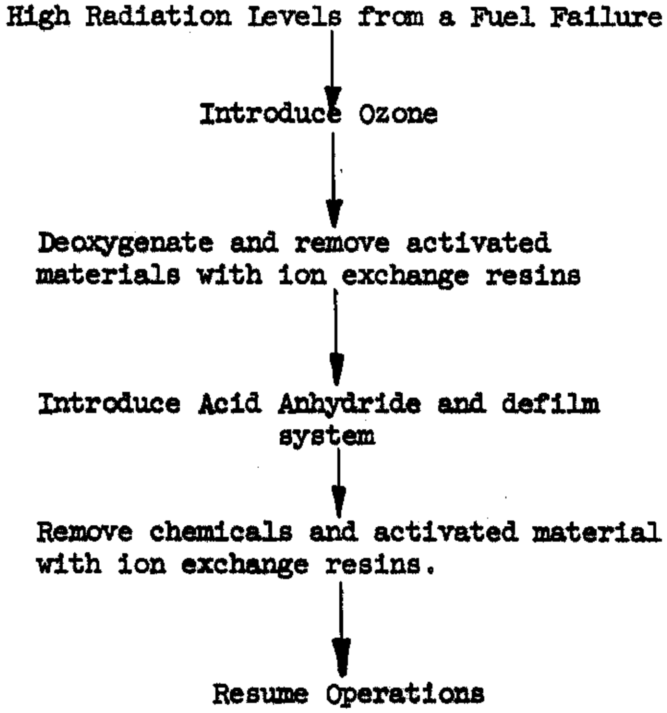
The possibilities offered by these chemicals in avoiding heavy water drainage and deterium purity degradation are such that serious consideration should be given to a study of their decontamination effectiveness.

Decontamination Sequence

A suggested operational sequence will indicate the ease, simplicity, and straightforwardness that could be obtained using the proposed procedure.

TABLE II

Suggested Operational Sequence



At no time during the proposed sequence is it necessary to drain and replace the heavy water. The procedure used for decontaminating PRTR following the rupture of August 21, 1962 required ~ 14 weeks(11) Optimistically, this time could be reduced by careful planning to 8 weeks if the same procedure were used. A substantial savings in time and personnel radiation exposure would be obtained by just avoiding the discharge and charging of heavy water and fuel elements. The procedure as now used under ideal conditions generates at least 12 system volumes of radioactive liquid waste that must be transported to disposed facilities. Radioactive waste from the proposed procedure would be concentrated on ion exchange resins. Here there is a waste handling incentive even though transportation of the high radiation level resins would require shielding.

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LDP:mf

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