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**METHOD AND COMPOSITION FOR DECONTAMINATION OF STAINLESS STEEL SURFACES****Ronald D. Weed, Richland, Wash., assignor to the United States of America as represented by the United States Atomic Energy Commission****No Drawing. Filed Apr. 28, 1966, Ser. No. 546,489****Int. Cl. C23g 1/08, 1/20****U.S. Cl. 134-2****3 Claims****ABSTRACT OF THE DISCLOSURE**

The tenacious magnetite film containing included radioactive contaminants which forms on stainless steel heat exchange surfaces of nuclear reactors is removed by a two step treatment. The first step utilizes a hot, alkaline, aqueous solution of potassium permanganate. The second utilizes a hot aqueous solution of oxalic acid, dibasic ammonium citrate, ferric sulfate or nitrate and diethyl thiourea.

**CONTRACTUAL ORIGIN OF THE INVENTION**

This invention was made in the course of or under a contract with the United States Atomic Energy Commission.

**Introduction**

The invention relates to a method of and a composition for the removal of radioactive contamination from metal surfaces. It is effective for removing the extremely tenacious radioactive film which forms on stainless steel surfaces on long exposure to hot water containing radioisotopes. It is also effective for removing the less tenacious radioactive films formed on carbon steel, zircaloy, brass, bronze and other metals. At the same time there is no objectionable corrosion to any of these metals.

The principal object of the invention is the decontamination of nuclear reactor cooling systems composed primarily of stainless steel. The radioactive corrosion films characteristic of recirculating water-cooled nuclear reactors must be periodically removed to permit contact maintenance and continuity of operation. Before these systems can be cleaned, procedures and processes must be developed which are suitable for use in the system. These processes must meet certain criteria which are discussed in the following paragraphs.

A decontamination reagent must dissolve the radioactive corrosion film and remove it from the system. Large nuclear plants are no exception to other types of plants; they are built with inherent low velocity areas and other traps where particulate material will settle out. The particulates in these areas must be dissolved for successful removal. Therefore, a successful decontamination reagent must dissolve as well as remove the radioactive corrosion film because if it is only removed from the piping surfaces and not dissolved, it will settle out in the low velocity areas and traps.

A successful decontamination reagent must remove and dissolve radioactive films formed during extended periods of continuous operation (up to at least two or three years). From the limited data available in the AEC literature, it is probable that cleaning will not be required oftener unless under unusual circumstances or demands. It is desirable, in power reactor operation, to keep the down time at a minimum and possibly reach five years of continuous operation before cleaning. Therefore, the removal of these long term films is an essential requirement.

A successful decontamination reagent must not be excessively corrosive to the materials of construction in the

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primary system. The reactor system will be constructed of primarily one or two materials, but there will be small quantities of many other types of materials in the system. These lesser materials will be found in such places as valves and sampling devices. All of these materials must be compatible with the reagent if they are in either direct or indirect contact with the solution, this is particularly true if the components are in a critical location, e.g., a drain valve plug, seat or stem.

The film which forms on stainless steel surfaces in the cooling systems in water cooled nuclear reactors appears to be primarily magnetite mixed with oxides of nickel and chromium. Radioactive ions present in the water are included in or adsorbed on this film so that they cannot be removed without removing the film itself. It is known in the art to decontaminate stainless steel nuclear reactor cooling systems by treatment with alkaline potassium permanganate followed by oxalic acid. However, previously known oxalic acid containing solutions have tended to deposit a secondary film on the surfaces. Sometimes the secondary film takes the form of a precipitate settling out in the low velocity regions and dead legs of the cooling system. This secondary film contains a considerable amount of radioactivity and its formation partially nullifies the decontamination.

**General Description of Invention**

In my procedure I first treat the system with the conventional alkaline potassium permanganate. This serves primarily for the removal of chromium and conditions the film so that it is dissolved in the acid medium. In the subsequent treatment I utilize a novel oxalic acid-containing aqueous solution which prevents the formation of the secondary film referred to above. This solution has the following composition:

	G./l.
Oxalic acid -----	20-30
Dibasic ammonium citrate -----	40-60
Ferric sulfate or nitrate -----	1.7-2.4
Diethyl thiourea -----	0.8-1.2

The ratio of oxalic acid to dibasic ammonium citrate should not be greater than  $\frac{1}{2}$ , otherwise secondary film formation may occur.

The preferred composition at present is as follows:

	G./l.
Oxalic acid -----	25
Dibasic ammonium citrate -----	50
Ferric sulfate -----	2
Diethyl thiourea -----	1

This solution, which is designated "RDW-3," was used in the experimental tests and the reactor decontamination subsequently described. If significant surfaces of carbon steel or of stainless steel of the 400 series are present, it is preferable to use 1.2 g./l. of diethyl thiourea in the RDW-3 solution.

**Detailed Description**

The following examples are based on decontamination of the primary cooling system of the Plutonium Recycle Test Reactor located near Richland, Wash. It is a heavy water moderated and cooled reactor of the pressure tube, pressurized water type. A complete description of the PRTR is given in U.S. Atomic Energy Commission Report HW-61236, "Plutonium Recycle Test Reactor—Final Safeguards Analysis."

Except for the zircaloy-2 pressure tubes, in which the fuel elements are mounted, the primary cooling system is composed principally of type 304 stainless steel.

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## EXAMPLE I

## Experimental tests

Samples were cut from various "jumpers" in the primary cooling system of the PRTR. These jumpers had been subjected to filming by the circulating coolant for various periods ranging from 6 to 32 months.

The samples were treated at 100°–105° C. with 3% KMnO<sub>4</sub> solution containing varying concentrations of NaOH and then at 80° C. with the RDW-3 solution. Results are shown in Table I.

TABLE I.—DECONTAMINATION RESULTS FOR THE RDW-3 SOLUTION

	Jumper Number											
	1455	1546	1847-2	1847-1	1356	1249	1253	2049-T	2049-B	1154-B	1746-T	1746-B
Months of Filming.....	6	6	12	16	20	22	22	27	27	29	32	32
3% KMnO <sub>4</sub> -1% NaOH:												
IA <sup>a</sup> .....	5	4	31	12	24	28	25	55	48	120	38	180
FA <sup>b</sup> .....	1	1	8	2	5	7	4	6	2	<1	12	1
DF <sup>c</sup> .....	5	4	4	6	4.8	4	6.3	9.2	24	>120	3	180
3% KMnO <sub>4</sub> -5% NaOH:												
IA.....	6	4	32	12	33	28	29	50	70	120	40	190
FA.....	1	1	7	2	6	7	7	5	<1	<1	6	<1
DF.....	6	4	4.5	6	5.5	4	4	10	>70	>120	6.7	>190
3% KMnO <sub>4</sub> -10% NaOH:												
IA.....	5	4	26	10	38	35	27	45	80	130	35	180
FA.....	1	1	4	2	7	8	3	4	<1	<1	2	<1
DF.....	5	4	6.5	5	5.5	4.5	9	11.2	>80	>130	17.5	>180
3% KMnO <sub>4</sub> -18% NaOH:												
IA.....	5	4	29	13	24	27	24	50	45	120	39	160
FA.....	1	1	1	2	3	4	4	5	<1	<1	1	<1
DF.....	5	4	29	6.5	8	6.75	6	10	>45	>120	39	>160

<sup>a</sup> IA=Initial activity mrad/hr. <sup>b</sup> FA=Final activity mrad/hr.

<sup>c</sup> DF=Decontamination Factor=IA/FA.

No secondary films or precipitates were formed. It will be noted that the treatment was particularly effective on those samples exhibiting high initial activities.

Corrosion tests were then conducted on samples of various metals. One corrosion test was conducted with the RDW-3 solution at 80° C. for 120 hours; the total corrosion incurred by the carbon steel samples exposed was 0.22 mil and by the stainless steel samples was 0.01 mil. A pale yellow film was deposited on the carbon steel samples when the test was terminated; the solution was a clear yellow color with no precipitates present.

Another corrosion test was conducted for a 24-hour period at 82° C.; numerous other types of materials were charged during this test. The corrosion data obtained are presented in Table II. The corrosion attack on the carbon steels and the 440-A and 440-C stainless steels increased with increased exposure while the attack on the remaining alloys did not increase after the initial attack. The attack to all alloys was very low; the most attack (0.2 mil) was on Stellite A212 carbon steel. Pitting did not occur on any of the carbon steel alloys, but slight pitting up to 6 mils diameter occurred on the 400 series stainless steels.

There was no deposition with the RDW-3 solution in contrast with other oxalic acid containing solutions. The solution was a clear yellow, with no precipitates.

Dull grey passive oxides formed on the carbon steel and 400 series stainless steels; these oxides proved to be resistant to subsequent rusting when the samples were rinsed in warm tap water.

Tests were also conducted on zircaloy-2. No corrosion was apparent on the samples of this alloy.

TABLE II.—RESULTS OF RDW-3 CORROSION EVALUATION

Alloy	Penetration, mils <sup>1</sup>			Sample Appearance		
	8 hours	16 hours	24 hours	8 hours	16 hours	24 hours
Haynes 25.....	0.015	0.016	0.017	Shiny	Shiny	Shiny
304 SS, <sup>2</sup> stressed.....	0.0061	0.006	0.0067	do	do	Do.
304 SS, sensitized.....	0.0051	0.0065	0.0069	do	do	Do.
316 SS.....	0.0060	0.0042	0.0058	do	do	Do.
17-4 PH SS.....	0.024	0.015	0.021	do	do	Do.
416 SS.....	0.074	0.086	0.085	Dull grey	Dull grey	Dull grey—5 pits to 6 mils diameter.
440-A SS.....	0.063	0.069	0.11	Dull grey, slight attack at crevice area.	Dull grey, slight attack at crevice area.	Dull grey, surface roughening.
440-C SS.....	0.094	0.13	0.198	A few scattered 2-3 mil diameter pits.	Dull grey, no pits.	Surface very rough, a few 3 mil diameter pits.
Stellite A212 CS <sup>3</sup> .....	0.046	0.10	0.208	Dull grey	Dull grey	Dull grey.
A212 CS Welded to 304 SS.....	0.024	0.029	0.045	do	do	Do.
A245 CS.....	0.046	0.054	0.032	do	do	Do.
A108 CS.....	0.044	0.078	0.103	do	do	Do.

<sup>1</sup> Total mils penetration in time period given. <sup>2</sup> SS=stainless steel. <sup>3</sup> CS=carbon steel.

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## EXAMPLE II

## Reactor decontamination

The primary cooling system of the Plutonium Recycle Test Reactor was drained. It was then flushed by pumping water through it and draining. This was repeated several times. Next, an aqueous solution of 3% KMnO<sub>4</sub> and 10% NaOH was introduced into the system and circulated for six hours. It was maintained at 100°–105° C. by a heat exchanger for two of those hours. The heating and cooling each took two hours. It was then repeatedly

flushed with water until the latter had attained a pH between 10 and 11.

The RDW-3 solution was then circulated through the system for three hours. It was maintained at 80° C. for one hour. The system was then flushed with deionized water until the latter attained a resistivity of 10,000 ohm centimeters. The results are given in Table III.

TABLE III.—DECONTAMINATION FACTORS OBTAINED ON PRTR PRIMARY SYSTEM

System Location	Activity Levels (mR/hr.)		Decontamination Factor
	Before	After	
Inlet header, injection pumps.	60	5	12
Outlet header, injection pumps.....	100	5	20
Outlet line, DT-2 Tank.....	90	5	18
Inlet line, DT-2 Tank.....	100	5	20
Pressurizer, outlet piping.....	190	5	38
Inlet, primary pump, 2.....	220	5	44
Inlet, primary pump, 1.....	210	5	42
Inlet, lower ring header.....	300	10	30
Bypass, HX-1 and pressurizer.....	100	5	20
Piping, HX-1 to pressurizer.....	110	5	22
Volute, primary pump, 2.....	150	5	30
Volute, primary pump, 3.....	120	5	24
Inlet to Degasser.....	100	5	20
Bottom of HX-5 header.....	190	5	38
HX-1 general background on enclosure grating.....	25	6	4
HX-1 Secondary side:			
6" inside manhole.....	1,200	5	240
1' from the tubes.....	1,800	5	360
Maximum reading on tubes.....	4,500	25	180

In the above table the abbreviations used have the following meanings: DT-2=storage tank; HX-1=primary heat exchanger; HX-5=auxiliary heat exchanger. There are three primary pumps, numbered 1, 2 and 3.

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The zircaloy-2 pressure tubes were coated with an iron film containing contaminants. This film was completely removed, leaving a bright surface. To the best of my knowledge this represents the most successful nuclear reactor decontamination ever recorded.

While I have described specific embodiments of my process, it will be understood that various changes are possible. I, therefore, wish my invention to be limited only by the scope of the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of removing a tenacious magnetite film containing included radioactive contaminants from a nuclear reactor cooling system composed primarily of stainless steel, which system has been subject to extended circulation of hot water during recator operation, which method comprises:

- (a) circulating through said system of hot alkaline, aqueous, potassium permanganate solution and thereafter
- (b) circulating through said system a hot aqueous solution of the following composition:

	G./l.
Oxalic acid	20-30
Dibasic ammonium citrate	40-60
Feric sulfate or nitrate	1.7-2.4
Diethyl thiourea	0.8-1.2

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the ratio of oxalic acid to dibasic ammonium citrate being not greater than 1/2.

2. A method as defined in claim 1 wherein the solution employed in Step a. contains 3% potassium permanganate and 10% sodium hydroxide.

3. A method as defined in claim 2 wherein the solution employed in Step b. has the following composition:

	G./l.
Oxalic acid	25
Dibasic ammonium citrate	50
Ferric sulfate	2
Diethyl thiourea	1

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U.S. Cl. X.R.

134-3, 22, 27, 28, 29, 41; 252-82, 146, 301.1