United States Patent

[11] 3,615,817

[72] Inventors **William T. Jordan**
Pittsburgh, Pa.;
Cort A. Zimmerman, Idaho Falls, Idaho

[21] Appl. No. **796,579**
[22] Filed **Feb. 4, 1969**
[45] Patented **Oct. 26, 1971**
[73] Assignee **The United States of America as represented by the United States Atomic Energy Commission**

[54] **METHOD OF DECONTAMINATING RADIOACTIVE METAL SURFACES**
2 Claims, No Drawings

[52] **U.S. Cl.** **134/3,** 134/22, 134/41, 252/80, 252/142
[51] **Int. Cl.** **C23g 1/08**
[50] **Field of Search** 134/28, 41, 22, 3, 2; 252/142, 80, 146–151

[56] **References Cited**

UNITED STATES PATENTS

3,013,909	12/1961	Pancer et al.	134/3
3,033,794	5/1962	Morris	134/41 X
3,037,887	6/1962	Brenner et al.	134/22
3,436,262	4/1969	Crowe et al.	134/22 X
3,437,521	4/1969	Buist	134/22 X
3,496,017	2/1970	Weed	134/22 X
3,511,784	5/1970	Riggs	134/3 X

Primary Examiner—Joseph Scovronek
Assistant Examiner—D. G. Millman
Attorney—Roland A. Anderson

ABSTRACT: A method of decontaminating radioactive metal surfaces and particularly difficultly accessible radioactive surfaces such as the ceiling and walls of a reactor vessel. The decontamination is accomplished by carrying a decontaminating reagent to the surfaces in a foam. Consecutive applications of alkaline permanganate and oxalic acid in foam give particularly good results. A nonionic foaming agent should be employed when the foaming agent may come into contact with a solution containing aluminum ions.

METHOD OF DECONTAMINATING RADIOACTIVE METAL SURFACES

CONTRACTUAL ORIGIN OF THE INVENTION

The invention described herein was made in the course of, or under, a contract with the UNITED STATES ATOMIC ENERGY COMMISSION.

BACKGROUND OF THE INVENTION

This invention relates to a method of decontaminating radioactive metal surfaces. In more detail, the invention relates to a method of decontaminating difficulty accessible surfaces such as the walls and ceiling of a reactor vessel. In still more detail, the invention relates to a method of decontaminating radioactive surfaces wherein the decontaminating agent will be directed into a waste system containing aluminum ions.

During the operation of a nuclear reactor, radioactive contamination accumulates on the walls and contents of the main reactor vessel of the reactor above the reactor core. The consequent health hazard to maintenance men severely limits the length of time they may safely spend in this portion of the reactor during a shutdown. Similarly, other surfaces exposed to an atmosphere containing radioactive particles, such as those of a hot cell, may become contaminated and require decontaminating treatment.

Such surfaces could, of course, be decontaminated by scrubbing them with a solution containing a chemical reagent which will remove the radioactive contamination from the surfaces. Scrubbing the surfaces is, however, not possible due to the difficulty of access to the surfaces and the radioactivity of the surfaces. The surfaces could be sprayed with the solution without undue hazard to personnel, but experience has shown that adequate decontamination cannot be obtained in this manner.

Detergent foams have long been used in large industrial cleaning operations and their use for cleaning and removal of particulate radioactive contamination from surfaces has been reported in the literature. In some situations, however—as in the case of a reactor vessel—the radioactive contamination is bonded strongly to the surface and foams, as used heretofore, do not remove the radioactive material to an adequate extent.

SUMMARY OF THE INVENTION

According to the present invention, decontamination is attained by employing a foam containing a chemical reagent which will attack the radioactive contamination. The chemical reagent may be, for example, oxalic acid or alkaline permanganate or consecutive applications of oxalic acid and alkaline permanganate. The foam may be and preferably is produced by a nonionic foaming agent containing as active ingredient a condensation product of a hydrocarbon-substituted phenol with formaldehyde into which hydrophyllic groups have been introduced.

SPECIFIC EMBODIMENT OF THE INVENTION

As will become apparent hereinafter, the incorporation of decontaminating chemicals in foams for removal of radioactive contamination has several advantages.

1. The decontamination effectiveness of the foam is greatly improved.
2. Due to the nature of foam the chemicals it contains can be held in contact with vertical and overhead structures for extended periods of time when compared to liquid sprays or other aqueous decontamination systems. Once applied, a sufficiently dry foam will adhere to the metal surface and work without external aid. Fresh reagent is continually brought into contact with the contaminated area as the foam breaks out.
3. The volume of radioactive waste solution generated by chemical reagent-in-foam decontamination is significantly less than for any other aqueous decontamination system presently available.

4. Foam can be applied from a distance, thus minimizing the danger of exposure to radiation for personnel.

A number of tests were carried out to determine the most effective foaming agents and decontaminating reagents for incorporation into a foam. First tests were carried out with an ionic foaming agent, Fome-Add—a proprietary product of DuBois Chemicals—to determine whether a stable foam could be prepared incorporating various possible decontaminating reagents. It was found that by proper adjustment of foaming agent concentration stable foams can be prepared incorporating all of the proposed decontaminating reagents. In order to counter the foam inhibitory effect of a significant concentration of ammonium citrate or Turco 4521 —a proprietary product of Turco Products, Inc. containing a citrate-oxalate mixture, a foam suppressant and a corrosion inhibitor—it is necessary to add a relatively large amount of foaming agent. Oxalic acid, on the other hand, does not require an excessive amount of foaming agent even at fairly high concentration and alkaline permanganate requires even less. However, incorporation of the foaming agent in alkaline permanganate results in rapid reduction of the deep purple permanganate to the green manganate ion and then to a precipitate of brown manganese dioxide.

For the purpose of determining the decontaminating properties of these foams, 4-inch lengths of contaminated ¾-inch type 304 stainless steel tubing were supplied from the Engineering Test Reactor which is located at the National Reactor Testing Station, Arco, Idaho. The radioactivity of each tubing sample was measured with a survey meter prior to placement in a 400-ml. glass beaker. The beaker was then filled with foam. When the foam had condensed, the sample was dried and the radioactivity again measured. From the two readings a decontamination factor was calculated.

TABLE I.—RADIATION AND FOAM DECONTAMINATION DATA

Decontamination process [1]	Initial activity, mR./hr.	Final activity, mR./hr.	D.F.
Fome-Add plus Sprex AC-3	35	20	[2] 1.8
Fome-Add	40	25	[2] 1.6
Fome-Add plus Sprex AC-3	44	34	1.3
Fome-Add plus Sprex AC-3 plus EDTA	43	29	1.5
Oxalic Acid-1	40	8	[2] 5
Oxalic Acid-2	35	4	[2] 9
Do	85	24	3.5
Do	95	46	2.1
Oxalic Acid-3	30	4	7
Do	52	13	4
2 Oxalic Acid-2	43	3	14
Do	85	10	8
Do	95	25	4
3 Oxalic Acid-2	95	17	6
4 Oxalic Acid-2	95	9	11
5 Oxalic Acid-2	95	7	14
4502-Oxalic Acid-1	30	2	[2] 15
4502-Oxalic Acid-2	40	2	[2] 20
Do	96	15	6
Do	140	39	3.6
Do	203	74	2.7
Ammonium citrate-1	35	25	[2] 1.4
Ammonium citrate-2	37	30	1.2
Ammonium citrate-2	59	52	1.1
4502-Ammonium citrate-1	35	7	[2] 5
4521	35	11	[2] 3
4502-4521	40	8	[2] 5
Citrate-oxalate	43	13	3
Do	73	18	4

[1] The number prefixing a foam reagent, e.g. 2 oxalic acid-2, indicates the number of times the foam was applied to the sample. The suffix number is the key to the foam composition given in Table II. A hyphen separating two reagents in column 1 indicates that the two foams were applied separately.

[2] These decontamination factors were computed from measurements taken with a G.M. survey meter. All others were calculated from Juno meter readings.

Fome-Add is an ionic foaming agent produced by DuBois Chemicals, Sprex AC-3 is an alkaline metal cleaner produced by DuBois Chemicals, EDTA is the disodium salt of ethylenediaminetetraacetic acid, 4502is an alkaline permanganate produced by Turco Products and the composition of 4521 was given previously. The results for any particular foam should be compared to those obtained for the application of the foam generated from a solution of Fome-Add and Sprex AC-3. This is the foam currently being used in reactor decon-

tamination at the Engineering Test Reactor and was selected as a standard for these studies. The compositions of all the foams given in table I are described in table II. The concentrations given in the last column are the corresponding amounts to be added to a 55-gallon drum from which foam is generated on a large-scale basis.

TABLE II.—FOAM COMPOSITIONS

Foam	Composition	Comcentration	Amount per 55 gal.
Fome-Add plus Sprex	Sprex AC-3	10.9 g/l	5 lb.
	Fome-Add	4.5 ml./l	1 qt.
Fome-Add	Fome-Add	13 ml./l	2.86 qt.
Oxalic acid-1	Oxalic acid	20 ml./l	9.2 lb.
	Fome-Add	18 ml./l	3.96 qt.
Oxalic acid-2	Oxalic acid	40 g./l	18.4 lb.
	Fome-Add	14 ml./l	3.08 qt.
Oxalic acid-3	Oxalic acid	40 g./l	18.4 lb.
	Fome-Add	12.5 ml./l	2.75 qt.
Ammonium citrate-1	Ammonium citrate	15 g./l	6.9 lb.
	Fome-Add	19.5 ml./l	4.29 qt.
Ammonium citrate-2	Ammonium citrate	20 g./l	9.2 lb.
	Fome-Add	33.5 ml/l	7.37 qt.
4521	Turco 4521	15 g./l	6.9 lb.
	Fome-Add	21 ml./l	4.62 qt.
Citrate-oxalate	Oxalic acid	25 g./l	11.5 lb.
	Ammonium citrate	15 g./l	9.2 lb.
	Fome-Add	35 ml./l	7.7 qt.
Fome-Add plus Sprex plus EDTA	Sprex AC-3	10.9 g./l	5 lb.
	Disodium salt of EDTA	3 g./l	1.38 lb.
	Fome-Add	4.5 ml./l	1 qt.
4502	Turco 4502	14 g./l	6.44 lb.
	Fome-Add	4 ml./l	.88 qt.

It is evident from these results that the decontamination factor depends on the nature of the sample. Thus to obtain a meaningful comparison, the efficiencies of foams when applied to samples of about the same level of radioactivity should be compared. The decontamination factors for application of a number of foams to samples initially reading between 35 and 43 mr./hr. with a Juno meter from about three-fourth inch are presented in table III.

TABLE III.—RELATIVE EFFECTIVENESS OF REAGENTS IN FOAM

Process [1]	Initial activity, mR./hr.	Final activity, mR./hr.	D.F.
Fome-Add plus Sprex	35	20	[2] 1.8
Fome-Add	40	25	[2] 1.6
Oxalic Acid-1	40	8	[2] 5
Oxalic Acid-2	35	4	[2] 9
Ammonium citrate-1	35	25	[2] 1.4
Amonium citrate-2	37	30	1.2
4521	35	11	[2] 3
Citrate-oxalate	43	13	3
2 Oxalic Acid-2	43	3	14
4502-Oxalic Acid-2	40	2	[2] 20
4502-Ammonium citrate	35	7	[2] 5
4502-4521	40	8	[2] 5

[1] The terminology used in column one is explained in footnote, Table I.
[2] Explained in footnote, Table I.

On the basis of the tabulated results, reagents may be arranged in order of their effectiveness in foam decontamination of stainless steel. For a one-step process, reagents are effective in the order

oxalic > 4521 > ammonium citrate.

The same order applies for the two-step process in which one of the reagent-improved foams follows initial application of the alkaline permanganate foam.

The highest decontamination factor was obtained by the two-step alkaline permanganate—oxalic acid foam process. A double application of the oxalic acid foam was slightly less effective. Gamma scans of the test samples and the condensed decontaminating solutions indicate the reason for the increased efficiency of the two-step process. Gamma scan data on the condensed foaming solutions subsequent to decontamination show that alkaline permanganate is selective for Ru^{103}, Cr^{51}, I^{131} and Ce^{141} but does not remove Zr–Nb^{95}. These later isotopes are removed by oxalic acid.

Other tests have shown that corrosion of the metal surface to which the foam is applied by the foam is not a problem. However, it is also necessary to consider the effect of the foam on the waste system into which it may pass and also on the reactor water chemistry when a reactor vessel is being decontaminated. While slightly better decontamination is obtained with consecution applications of foams containing permanganate and oxalic acid than with foams containing oxalic acid alone, the improvement is not sufficient to outweigh the disadvantage of having to prepare and use two different foams. In particular oxalic acid foams alone are preferred for reactor use since it is not desirable to permit manganese ions to enter the reactor coolant system since an additional radioactive species would be added to the coolant. Since the foam condenses to the surface of the coolant water above the reactor core in reactor vessel decontamination, at least some of the foam components will diffuse into the body of the coolant system. Thus oxalic acid alone is preferred for reactor use.

Another problem that creates concern, however, whether the two-step or one-step process is employed, arises from the fact that all radioactive wastes at the site ultimately are directed into the radioactive waste system. This is primarily waste from the chemical processing plant which contains aluminum nitrate.

It was discovered that the ionic foaming agent used in the initial experiments precipitated a particularly undesirable waxy solid upon contact with an aluminum nitrate solution. Since waste from the chemical processing plant contains aluminum nitrate, this ionic foaming agent cannot be permitted to enter the waste system. Thus the only alternatives are to prevent the foam condensate from entering the waste system or to find a foaming agent which would not react with aluminum ions. Fortunately, the search for an alternative foaming agent was successful and its use forms an important part of the present invention.

It was found that a nonionic foaming agent could be used with good results so far as decontamination is concerned and also that it would not create any problems in the waste system. A specific product found acceptable contains as the active ingredient a condensation product of a hydrocarbon-substituted phenol with formaldehyde into which a hydrophyllic group is introduced. Such products form the subject matter of U.S. Pat. No. 2,454,541. The product is a proprietary product of Turco Products, identified as Turco 4527. It was first determined that Turco 4527 has suitable foaming characteristics. From the standpoint of decontamination, the stability factors of greatest interest are the rate of drainage of liquid from the foam and the expansion (volume of foam/volume of liquid in the foam). A low drainage rate and a low-expansion favor decontamination. Experiments have shown that, as the concentration of foaming agent is increased, the rate of drainage decreases and, as the concentration of foaming agent is increased, the expansion increases. These two foaming properties thus tend to compensate for each other so that the con-

centration of foaming agent should have little effect on the decontaminating ability of the decontaminating foam. Experimental proof of this will be given hereinafter.

It was also determined that Turco 4527 is compatible with the decontaminating reagents to be used. Both oxalic acid and Turco 4521 had practically no effect on the foaming properties of Turco 4527. On the other hand, oxalic acid has a moderate inhibitory effect and Turco 4521 has a very pronounced inhibitory effect on Fome-Add.

In order to evaluate the decontaminating efficiencies of the solutions containing Turco 4527, a number of contaminated 4-inch lengths of 1-inch OD stainless steel lead tubing were obtained from the Engineering Test Reactor. This tubing had been exposed to reactor cooling water above the reactor core at a temperature of 44° C. The contamination resulting from this type of exposure consists primarily of fission products from fuel element leakage absorbed in the film of hydrated metal oxides which forms on stainless steel in water. The film has a dull yellow cast and it is possible to estimate the rough effectiveness of a decontamination step by visual inspection.

The extent of contamination removal was estimated by taking radiation readings before and after each treatment. From the two measurements a decontamination factor (D.F.) was calculated. The readings were taken with a Juno survey meter placed three-fourth inch from the surface of the specimen which was enclosed in one layer of polyethylene. The tubing was not uniformly contaminated and initial radiation readings varied by as much as 30 percent per sample as it was rotated under the metering device. Therefore, high and low readings were taken each time and, correspondingly, two decontamination factors calculated. The samples were placed in 400 ml. glass beakers so that they leaned at approximately a 60° angle. The beaker was then filled with foam. When the foam had completely broken out, the samples were rinsed with water and acetone and dried prior to taking a final reading.

Because of the angle at which the samples were placed and because of the difficulty of applying foam uniformly in such a small vessel, decontamination was not always uniform as indicated by residual areas of yellow film. Therefore, the decontamination factors reported here are considered to be the minimum which can be expected when the foam is properly applied.

The results of a number of decontamination experiments are presented in table IV. In all cases, multiplicate experiments were run; only one typical result for each case is given in table IV. It has been previously pointed out that caution must be exercised in comparing decontamination factors due to their dependence upon the nature and level of contamination. In this type of experiment, decontamination factors should be compared only for samples of approximately equal initial activities. The data in table IV are seen to satisfy this condition where all samples originally read approximately 100 mr./hr.

TABLE IV.—DECONTAMINATION DATA FOR REAGENT-IN-FOAM

Foam composition	Initial reading, mR./hr.	Final reading, mR./hr.	D.F.
1. 40 g./l. oxalic acid; 60 ml./l. Turco 4527	112	5	22
2. 40 g./l. Turco 4521; 64 ml./l. Turco 4527	100	45	2.2
3. 2M nitric acid; 50 ml./l. Turco 4527	98	52	1.9
4. 60 ml./l. Turco 4527	100	98	1.0
5. 40 g./l. oxalic acid; 16 ml./l. Fome-Add	95	6	16

The first significant conclusion to be drawn is that foam generated from Turco 4527 is effective in carrying reagents to the substrate. It should be noted that contamination removal is due to the reagents alone since test 4 of table IV shows Turco 4527 foam by itself does not decontaminate. Second, it is clear that oxalic acid-in-foam is far superior to Turco 4521-in-foam and nitric acid-in-foam as a stainless steel decontaminant. It is also worth noting that oxalic acid is at least as effective, and perhaps more effective, in Turco 4527 than in Fome-Add.

It was stated above that foam drainage and expansion are highly dependent upon foaming agent concentration. In order to determine how these properties affect decontamination, foams from solutions containing various proportions of Turco 4527 were applied to contaminated tubing specimens. The data, which appear in table V, demonstrate that there is very little, if any, effect. This seems to confirm the hypothesis made earlier that (for the concentration range tested) the effects of expansion and drainage on decontamination tend to compensate one another. Therefore, foam consistency can be varied over a certain range as desired without adversely affecting potency.

TABLE V.—EFFECT OF FOAMING AGENT CONCENTRATION ON DECONTAMINATION

Foam composition	Initial reading, mR./hr.	Final reading, mR./hr.	D.F.
40 g./l. oxalic acid; 40 ml./l. Turco 4527	92	4	23
40 g./l. oxalic acid; 60 ml./l. Turco 4527	112	5	22
40 g./l. oxalic acid; 80 ml./l. Turco 4527	100	5	20

It remains to be demonstrated that decontamination by foam is any better than spraying an equivalent volume of the same solution on a contaminated surface. If foam were not any more effective than this process, then it would be hard to justify in view of the somewhat greater simplicity of the second method. In order to settle the question, 50 ml. (more than twice the liquid volume in a foam application) of a solution, 40 g./l. in oxalic acid and 60 g./l. in Turco 4527, was sprayed from a squeeze bottle directly onto a section of tubing initially reading 88 mr./hr. The sample was rotated during the application to insure even contact and was left standing for 8 minutes following application before rinsing. The final reading was 63 mr./hr., giving a decontamination factor of only 1.4 compared to 22 for the same solution foamed. It should be noted that solution containing the foaming agent would be expected to be more effective than oxalic acid alone in aqueous solution due to the higher viscosity and the presence of a surface active agent.

It will be understood that the invention is not to be limited by the details given herein but that it may be modified within 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 decontaminating the radioactive surfaces of the reactor vessel of a nuclear reactor consisting of the steps of producing an aqueous foam from a solution of oxalic acid containing a nonionic foaming agent, carrying the oxalic acid to the surfaces to be decontaminated in the form of said aqueous foam, and contacting said surfaces with said foam whereby the oxalic acid attacks the radioactive contamination.

2. A method according to claim 1 wherein the surfaces are contacted with more than one application of a foam produced from a solution of oxalic acid and wherein the foaming agent contains as active ingredient a condensation product of a hydrocarbon-substituted phenol with formaldehyde into which hydrophyllic groups have been introduced.