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YANKEE ATOMIC ELECTRIC COMPANY
RESEARCH AND DEVELOPMENT PROGRAM

A STUDY OF DECONTAMINATION AGENTS FOR USE IN THE YANKEE REACTOR

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WESTINGHOUSE ELECTRIC CORPORATION
ATOMIC POWER DEPARTMENT
PITTSBURGH, 30 P. O. BOX 355 PENNSYLVANIA

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Yankee Atomic Electric Company
Research And Development Program

A STUDY OF DECONTAMINATION AGENTS FOR USE IN
THE YANKEE REACTOR

by

R. M. Watkins
Nuclear Core Engineering

For The Yankee Atomic Electric Company
Under Research and Development Subcontract
No. 1 of USAEC-YAEC Contract AT(30-3)-222

November, 1958

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I. ABSTRACT

This report covers a study of chemical decontamination agents for possible use in the Yankee reactor. The necessity for chemical decontamination is discussed along with the properties sought in an ideal cleaning solution. A survey of available decontamination information is presented together with a description of the experimental test program carried out at the Westinghouse Atomic Power Department in an effort to develop new and improved chemical methods for the removal of oxide scale and radioactive contamination from Yankee reactor primary coolant system components. On the basis of bench scale testing of various cleanup procedures, a method employing basic permanganate and citrate solutions has been selected as offering the most promise for successful solution of Yankee primary loop contamination problems. Data are presented concerning the attack rates produced by these reagents on various reactor materials of construction, as is an evaluation of the possibility of caustic embrittlement of stainless steel resulting from the use of the basic permanganate solution. A discussion of future larger scale testing of the proposed decontaminants is also included.

II. INTRODUCTION AND STATEMENT OF THE PROBLEM

Radioactive contamination of the primary coolant system of the Yankee reactor will result from fission products (if released from defective fuel elements) and from corrosion products of fuel elements, control rods, and irradiated structural materials. There will be an unavoidable deposition of such materials on interior surfaces of the primary loop system and these may require removal in order to permit access for repair and replacement of components. The object of this investigation has been the development of an effective chemical cleanup agent so that this task may be accomplished.

The ideal decontaminating agent should have the ability to remove all of the occluded radioactivity from the deposited oxide layer or crud film. In order to do this it would be most advantageous if the crud film itself could be dissolved, thus bringing all the contaminants into solution or suspension. The activity could then be flushed from the system. It is of course important that the base metal suffer a minimum amount of attack during the decontamination process.

Unfortunately most of the known chemical decontaminating solutions which are strong enough to dissolve the oxide layer are also so powerful that they may seriously damage the system components, whereas those decontaminants which are safe to use in contact with the materials of construction of the system are usually not strong enough to dissolve the crud film. Thus, the problem resolves itself into the development of a chemical cleanup method which is at the same time both safe to employ and effective in achieving the desired decontamination results.

III. CONCLUSION

On the basis of bench tests of available cleanup procedures a method employing basic permanganate and citrate solutions has been selected for use in larger scale studies, as it apparently offers the most promise for successful Yankee reactor application. When properly applied, this procedure could provide a safe and efficient method of descaling the stainless steel primary coolant piping without causing serious damage to other materials in the system. The deposited crud film is dissolved by the treatment, thus bringing the activity within it into solution or suspension. The results of the bench scale tests have indicated that an overall decontamination factor of at least 10 (i.e., 90% activity removal) can be achieved through the use of this procedure.

It was concluded on the basis of results from fatigue tests, cold bend tests, and metallographic examinations, that no embrittlement problem exists as a result of the use of the basic permanganate reagent and that it may be safely employed in cleaning austenitic stainless steel without significant danger of caustic cracking of the metal.

IV. SURVEY OF AVAILABLE DECONTAMINATION INFORMATION

Prior to undertaking an experimental program of screening tests of cleanup agents for possible use in the Yankee reactor, a survey of available decontamination information was conducted. One of the earliest documents examined was a comprehensive report concerning decontamination of stainless steel which was written at Oak Ridge National Laboratory by D. O. Campbell in March, 1955.¹ The most effective "non-corrosive" decontaminant suggested at that time was an alkaline tartrate peroxide solution. After the initial application of this reagent, its action is improved by a subsequent treatment of the contaminated surface with nitric acid. Several alternate treatments with nitric acid and alkaline tartrate-peroxide gave the best decontamination with negligible corrosion, however, these reagents are unable to dissolve the deposited oxide film, and only leach some of the activity from it with each successive application.

The most effective decontaminant reported was a 3% hydrofluoric acid - 20% nitric acid solution. This reagent has the ability to dissolve the oxide layer which forms on stainless steel when it is exposed to high temperature pressurized water during reactor operation, but it is found to severely corrode the base metal. The rate of decontamination is reported for sodium hydroxide, alkaline tartrate, alkaline tartrate-peroxide, nitric acid, and oxalic acid. These reagents are found to decontaminate rapidly at first, but the rate of activity removal drops off rapidly with time. As of 1955 apparently no reagent was known which had the ability to completely dissolve a crud layer without seriously damaging the base metal.

In October, 1956 a report was issued by the Hanford Atomic Products Operation, Richland, Washington, which gives additional information as to the corrosion rates to be expected should AISI 304L stainless steel be exposed to solutions of 20% nitric acid - 20% sodium dichromate, or 20% nitric - 3% hydrofluoric acid.² The results indicate that sensitized specimens of this particular austenitic stainless steel would be subject to corrosion rates of as high as 0.2 to 1.0 inches per year as a result of the application of these reagents. The report concludes that "both solutions are extremely corrosive". Certainly such treatments could not be used safely in the decontamination of components where close tolerances must be maintained.

In an attempt to protect materials of construction from undue attack, many mild cleaning agents have recently been proposed for use in removing radioactivity from crud covered components. One of the best known of these procedures is that developed at the Bettis Plant for the Shippingport Pressurized Water Reactor.^{3, 4, 5, 6} The suggested decontaminant for use on crud deposits is an aqueous solution in the pH range of 1.5 to 2.2 containing a pH adjusting reagent, a complexing or chelating reagent with corrosion inhibitor, and a reducing agent such as hydrazine or hypophosphite. Should the cleanup operation involve the removal of UO₂ and fission product contamination, an oxidizing agent such as hydrogen peroxide plus a stabilizer would be required. A typical list of the solution ingredients with their suggested concentrations is given in Table I.

TABLE I

Decontamination Solutions Suggested

For PWR Application^{4,5,6}

Ingredients	Description		
	Dilute Oxidizing	Concentrated Oxidizing	Concentrated Reducing
Hydrogen Peroxide (g/L)	0.3	1.5	
Acetanilide (g/L)	0.1	0.5	
Hydrazine (g/L)			5
Ethylenediamine Tetracetic Acid (g/L)	0.15	0.75	3.5
Sulfamic Acid (g/L)	0.25 - 0.5	2.5	25.
Hexamethylenetetramine (g/L)	0.1	0.5	1.
Temperature	250°F - 300°F	250°F - 300°F	200°F - 250°F
pH	1.8 - 2.3	1.5	1.5

Although the reducing solutions suggested by the Bettis Plant report do not completely dissolve the oxide film, they may loosen it to an extent where violent agitation results in the flaking off of a large portion of the oxide scale which can then be flushed away. However, it is difficult to achieve the needed agitation throughout the entire system; thus though this procedure is noninjurious to the base metal, the contaminating activity may not be removed to the desired extent. A summary of results achieved by the use of these solutions in decontamination trials that had been reported up to January, 1958 is contained in a "Literature Survey for Activity Build-Up on Reactor Primary System Components", edited by A. L. Medin and issued by Alco Products, Inc., of Schenectady, New York.⁷

Although the Bettis Plant procedure for the decontamination of primary coolant systems has been reported⁸ as being favorably considered for naval reactor and PWR application, a study has been made by R. D. Baybarz at Oak Ridge National Laboratory of an improved cleanup method for use in the Homogeneous Reactor Experiment. The new procedure developed by Baybarz involves the use of a 0.40 molar chromous sulfate - 0.5 molar sulfuric acid solution at 80 to 90°C for 2 to 4 hours in order to dissolve the oxide film.⁹ This is a very powerful reducing agent and must be used in an inert atmosphere in order to prevent a reaction with atmospheric oxygen.

The above procedure has been employed with satisfactory results in UO_2SO_4 dynamic loop cleanup operations, and has produced decontamination factors on contaminated stainless steel which were superior to those achieved with the milder reducing agents as developed at the Bettis Plant.^{9,7} Typical corrosion results obtained from the use of the chromous sulfate-sulfuric acid procedure on reactor primary system construction materials are given in Table II. Although most of the corrosion results listed in the table suggest that there was only very slight attack, the depth of penetration reported for AISI 304 stainless steel indicates that the chromous sulfate reagent is still potentially dangerous to a system containing sensitive elements fabricated of such a material.

Work with inhibited acid and detergent cleanup solution has been performed at the decontamination facility operated by the Fairchild Camera and Instrument Corporation of Syosset, Long Island, New York. WEDAK, a detergent containing highly inhibited phosphoric acid which is manufactured by the West Disinfectant Company of Long Island City, New York has been used¹⁰ quite successfully to decontaminate control rod drive mechanisms received for cleanup under contract with the Knolls Atomic Power Laboratory. Brush scrubbing is used in conjunction with exposure to the cleanup reagent in order to achieve the desired decontamination results.¹¹

In contrast with the acid detergent treatment in use at the Fairchild Decontamination Facility, and the acid reducing agent procedures recommended for crud removal by the Bettis Plant and the Oak Ridge National Laboratory, the United States Steel Corporation suggests a method for oxide scale removal from stainless steel which employs a strong oxidizing agent similar to those studied at the Hanford Atomic Products Operation.^{12,2} In this case however

TABLE II

Corrosion of Metals in 0.32 Molar Solution of CrSO_4 - 0.65

Molar Solution of H_2SO_4 at 85°C ⁹

(4.4 hr. contact time in dynamic loop)

Material	Depth of Penetration (mils)
(AISI) Stainless Steels	
347	0.13
321	0.06
318	0.02
316	0.02
304L	0.16
Stellites	
98M2	0.01
6	0.04
1	0.04
Zr Crystal Bar	0.01

a strong caustic environment is maintained during the first stage of the cleanup operation, and this is followed by a nitric acid wash. Table III indicates the actual chemical ingredients of the solutions employed in this procedure together with their suggested concentrations.

The use of ultrasonic energy for use in decontamination in conjunction with chemical procedures should also be mentioned. As early as 1955 extensive work was in progress both at the Hanford Atomic Products Operation¹³ and the Oak Ridge National Laboratory¹ concerning the application of ultrasonic equipment in the problem of reactor system decontamination. It was felt that the use of ultrasonics together with solutions less corrosive than nitric acid might provide better decontamination than had yet been achieved. High-intensity ultrasonic radiation was found to increase the rate of decontamination, but the problem of introducing ultrasonic radiation into large equipment was recognized as a formidable one. Work along this line is presently continuing at the General Electric Company, Schenectady, New York, where a recent study has been made to determine whether ultrasonic vibration would be effective in removing mixed radioactive deposits from the inside surface of steel pipes in a heat exchanger.¹⁴ It was found, as expected, that the effectiveness of the ultrasonic energy in enhancing the decontamination effect depends rather critically on the method of coupling to the work. Apparently the solution to the problem of perfecting practical ultrasonic decontamination still depends on the development of an efficient method for the introduction of the ultrasonic energy into the chambers to be cleaned.

V. EXPERIMENTAL PROGRAM

A. BENCH SCREENING TESTS

After examining the available decontamination information, a series of bench screening tests was performed in order to evaluate the effectiveness of various cleaning reagents in dissolving the type of film to be found on internal surfaces exposed to primary coolant in the Yankee reactor. Crud coated sample coupons of various materials to be used in the fabrication of the Yankee primary system components were prepared in dynamic loops under water chemistry conditions closely approaching those to be found during reactor operation.¹⁵

Clean sensitized specimens of AISI 304 stainless steel and other construction materials were also used in tests to determine the extent of the attack on base materials. As no radioactive specimens were available for these cleanup tests, all estimates as to the effectiveness of the solutions tested were made from weight loss data and on the basis of visual observations.

TABLE III

United States Steel Corporation Stainless Steel

Descaling Procedure¹²

Solution 1	5% Potassium Permanganate 20% Sodium Hydroxide 75% Water
To be used boiling hot (230°F) for 10 to 15 minutes.	

Solution 2	20% Nitric Acid
To be used 5 to 10 minutes, then rinse with hot water.	

The alkaline tartrate-peroxide solution and the three Bettis Plant solutions outlined in Table I were found to be ineffective in static attempts at dissolving Yankee type oxide films. Without violent agitation these solutions are apparently incapable of dissolving or even loosening such an oxide scale.

Tests using 3% hydrofluoric acid - 20% nitric acid solution effected removal of the deposited oxide film from stainless steel surfaces as expected, but resulted in very serious attack on the base metal (see Figure 1).

Experimentation with the chromous sulfate-sulfuric acid procedure as developed at the Oak Ridge National Laboratory⁹ yielded improved results, as the oxide layer could be dissolved with less severe attack on the base metal accompanying the cleaning operation. However, the reagent was difficult to prepare and apply since it reacts with oxygen, and there were still definite signs of intergranular attack visible in an examination of treated metal surfaces (see Figure 2). Tests conducted with WEDAK solution¹⁰ according to the procedure used by the Fairchild Camera and Instrument Corporation indicated that this reagent is capable of dissolving Yankee type oxide films, but that undue attack on stainless steel could still result if prolonged contact were allowed. Though this method appeared promising it was felt that a more adequate procedure could be found.

The results of cleanup tests using the basic permanganate-nitric acid procedure suggested by the United States Steel Corporation¹² proved most satisfactory. It was found that the oxide film could be dissolved completely without any significant attack on the stainless steel base metal. However, the danger remained that less corrosion resistant materials which might be present in the reactor system could be seriously damaged by the 20% nitric acid rinse solution.

In view of the potential hazard introduced by the use of nitric acid, a system substituting the use of a complexing agent (ammonium citrate) for the acid rinse was tested. This "Basic Permanganate-Citrate Method" provides an excellent solution to the acid attack problem as it completely avoids the use of strong acid which might be injurious to the system. The procedure employed and chemical ingredients used are given in Table IV.

The cleanup results produced by these reagents on sensitized specimens of AISI 304 stainless steel were found to be excellent. No signs of intergranular attack are evident and weight loss per unit area is negligible. (See Figure 3.)

After a comparison of the cleanup results produced by the various procedures tested, the basic permanganate-citrate method was chosen as the one showing the most promise for possible application in Yankee reactor decontamination.

Figure 1 Photomicrograph (400X) of Edge of Sensitized Specimen of AISI 304 Stainless Steel Tested with 3% HF-20% HNO_3 Decontamination Solution.

Figure 2 Photomicrograph (400X) of Edge of Sensitized Specimen of AISI 304 Stainless Steel Tested According to the Chromous Sulfate-Sulfuric Acid Decontamination Procedure.

Figure 3 Photomicrograph (400X) of Edge of Sensitized Specimen of AISI 304 Stainless Steel Tested According to the Basic Permanganate-Citrate Decontamination Method.

TABLE IV

Basic Permanganate-Citrate Decontamination Procedure

Chemical Ingredients of Cleanup Solutions	Contact Time Minutes	Temperature Degrees C
1. 18 Percent NaOH 3 Percent KMnO_4 Hot water Rinse (65-95°C), then	30	105
2. 10 Percent Ammonium Citrate	15	100

B. DETAILED TESTING OF SELECTED PROCEDURE

An extensive series of tests was conducted using the 3% KMnO_4 - 18% NaOH "basic permanganate" solution and the 10% ammonium citrate reagent under various conditions and in contact with assorted reactor materials. The standard treatment times and temperatures, as cited in Table IV, were used in all tests unless otherwise stated.

The relation of exposure time to weight loss for AISI 304 stainless steel at 105°C in the basic permanganate solution is shown in Figure 4. Note that time is shown on a log scale, and that the attack is seen to drop off exponentially with time. As an average penetration of 1/1000 of a mil is equivalent to a weight loss of approximately 2 mg per dm^2 for this material, this graph shows that after an exposure of 120 minutes, the average penetration is still less than 3/1000 of a mil.

The relations of exposure time to weight loss for AISI 304 stainless steel in contact with 10% ammonium citrate solution at 100°C is shown in Figure 5. Here again the weight loss drops off rapidly with time. After 54 hours the total attack on the base metal resulting from the use of this solution was still quite negligible.

The relation of exposure time to change in surface finish during basic permanganate decontamination of AISI 304 stainless steel is illustrated in Figure 6. After an initial increase in surface roughness there is very little change during a prolonged exposure. This test was conducted for a total of 3-1/2 days starting with highly polished coupons, the standard 15 minute citrate treatment being used after each exposure to the basic permanganate solution. One of the stainless steel specimens used in the surface finish test after 88 hours of exposure to the basic permanganate solution is shown in Figure 7. It is of interest to note that the reflection of the caption is clearly visible on the coupon's surface as it has retained its original polished appearance.

In order to achieve a high ratio of surface area to mass for accurate weight loss determinations AISI 304 stainless steel wire mesh coils were used as test specimens in many of these decontamination studies. Two such samples, one after cleanup and one still coated with an oxide layer formed during exposure in a static autoclave, are shown in Figure 8.

An AISI 304 stainless steel clad Yankee fuel rod section exposed for 708 hours to boronated water in a dynamic loop at 600°F and 1850 psi is shown in Figure 9. The right half of this rod section was cleaned according to the basic permanganate citrate procedure. It is interesting to note that this method may be considered for use in cleaning individual fuel rods after autoclave leak testing, but prior to brazing into fuel bundles. The light scale formed in the autoclave tests must be removed before the brazing operation. This procedure may offer a simple solution to the problem.

RELATION OF EXPOSURE TIME TO WEIGHT LOSS IN BASIC PERMANGANATE-CITRATE DECONTAMINATION OF AISI 304 STAINLESS STEEL

FIGURE 4

RELATION OF EXPOSURE TIME TO WEIGHT LOSS FOR AISI 304 STAINLESS STEEL IN CONTACT WITH 10% AMMONIUM CITRATE SOLUTION AT 100° C

FIGURE 5

RELATION OF EXPOSURE TIME TO CHANGE IN SURFACE FINISH DURING
BASIC PERMANGANATE-CITRATE DECONTAMINATION OF AISI 304 STAINLESS STEEL

FIGURE 6

Figure 7 Note Reflection of the Caption on the Test Coupon's Surface Which Has Retained its Original Polished Appearance,

Figure 8 (Each of the Wire Mesh Coils Shown Above Have Surface Areas of Over 33 dm².)

TYPE 304 STAINLESS STEEL FUEL ROD
SECTION EXPOSED FOR 708 HOURS TO
BORONATED WATER AT 600 DEGREES F.
& 1850 PSI. RIGHT HALF CLEANED VIA
EXPOSURE TO THE BASIC PERMANGANATE
CITRATE DECONTAMINATION REAGENTS.

Figure 9 AISI 304 Stainless Steel Yankee Fuel
Rod Section Exposed for 708 Hours to
Boronated Water at 600°F and 1850 psi.
Right Half Cleaned by Exposure to the
Basic Permanganate - Citrate Decontam-
ination Reagents.

The results of corrosion tests performed with a variety of materials proposed for use in the Yankee reactor primary coolant system are summarized in Table V. Although the corrosion rates may appear high in some cases, the actual depth of penetration per defilming operation is small since less than an hour is required for complete oxide dissolution and removal. The results of the bench scale tests have indicated that an overall decontamination factor of at least 10 (i.e., 90% activity removal) can be achieved through the use of this procedure and it is anticipated that much larger D.F. values may be obtained. Quantitative measurement of such values can not be made, however, without the use of radioactive test specimens.

VI. BASIC PERMANGANATE AND CAUSTIC EMBRITTLEMENT

The most serious objection raised concerning the use of the basic permanganate-citrate decontamination procedure has been the possibility of caustic embrittlement of stainless steel resulting from contact with the hot sodium hydroxide solution which is used as the primary reagent in this procedure. In an effort to determine the possibility of the occurrence of such attack, a literature survey on the subject of caustic embrittlement of steel was conducted and a series of fatigue tests and cold bend tests followed by metallographic analysis was carried out.

A. LITERATURE SURVEY

The literature search on the subject of caustic embrittlement of steel in general was made by the use of the "Bibliographic Survey of Corrosion" published annually by the National Association of Corrosion Engineers. Particular attention was paid to all references to this phenomena occurring in ferrous alloys containing nickel and chromium. The following abstracts present the most significant information obtained with regard to the problem of possible embrittlement of stainless steel resulting from exposure to the basic permanganate reagent.

Uhlig, in his classical "Corrosion Handbook"¹⁶, mentions caustic embrittlement in carbon steel boilers and gives several examples of the occurrence of this phenomenon together with photomicrographs of the intercrystalline cracks which are typical of this type of attack. (See Figure 10.) No mention is made concerning embrittlement of stainless steel. He states, however, that the minimum NaOH concentration necessary to cause caustic embrittlement in a carbon steel boiler is 10%. (A long exposure period at high temperature and pressure is assumed in a discussion of boiler corrosion.)

TABLE V

Corrosion of Yankee Reactor Primary Coolant System

Materials of Construction During Basic Permanganate-

Citrate Decontamination

Material	Wt. Loss mg/cm ² /30 min.	Average Penetration mils
AISI 304 s/s	0.035	0.0017
AISI 316 s/s	0.033	0.0016
AISI 347 s/s	0.032	0.0016
AISI 410 s/s	0.34	0.018
Microbrazed-50	0.56	0.032
Inconel	0.02	0.001
80% Ag-15% In-5% Cd	2.28	0.090
Control Rod Alloy		
Graphitar-14*	0.67	0.132

*A "back flushing" procedure is suggested for preventing the decontaminants from contacting Graphitar pump bearings during cleanup operations of an existing loop or reactor. The corrosion values listed for Graphitar could be considerably reduced through the application of such a technique.

Figure 10 Photomicrographs (200X) of Stressed Boiler Steel Subject to Corrosion by Alkaline Solution¹⁶. Note Honeycomb of Fine Cracks Which Do Not Cut Across Grains of the Metal But Follow the Grain Boundaries.

A paper by Schmidt, Gegner, Heinemann, Pogacar, and Wyche,¹⁷ reports on the results of a survey involving a large number of actual applications of metals in service handling caustic solutions. Figure 11 is a plot of the data obtained for mild steel. Regions of concentration and temperature above the curve in this figure represents areas where cracking is likely to occur.

Berk and Waldeck, in a comprehensive paper¹⁸ describe the results of embrittlement tests with caustic solutions, and give what they call a "caustic danger zone" on a temperature-concentration plot, above which failure is likely to occur. They used stressed mild steel specimens with test durations varying from six to sixty-two days. Their data are reproduced in Figure 12. It is of interest to note that the "caustic danger zone" is located at a higher temperature than the "limiting temperature curve" as given by Schmidt et.al. (see Figure 11), indicating that the latter curve may be conservative. On the other hand, it is significant that the laboratory tests were run for a maximum of only sixty-two days, whereas the field data include reference to cases of many years of service.

An article by Fontana¹⁹ presents an excellent discussion on the action of materials of construction. He states that generally the caustic corrosion resistance of a material is almost proportional to the nickel content. The chief metals and alloys used for caustic services, listed roughly in order of corrosion resistance, are given as follows: Inconel, Monel, cupronickel, austenitic stainless steel and alloys, austenitic cast iron such as Ni-Resist, 9% nickel steel, low nickel alloy cast irons and steels, and ordinary steel and cast iron. Thus AISI 300 series stainless steel ranks considerably above carbon steel in its resistance to possible caustic attack. Four factors are listed as being significantly involved in the tendency for caustic cracking in steel. These are caustic concentration, temperature, exposure time, and stress.

Only two examples of caustic cracking of austenitic stainless steel were located in this survey. These are reported by Galibourg²⁰ and by Edeleanu-Snowden.²¹ In the former case the occurrence of alkaline embrittlement is reputed to have produced cracks in 22% nickel, 2% chromium steel in the presence of superheated steam. The latter work describes a case in which caustic cracking was observed in austenitic stainless steel after sample specimens were coated by being dipped in molten caustic and then exposed to highly superheated steam (310°C, 150 lb/in²). Needless to say, these conditions are significantly more rigorous than any to be anticipated in a reactor decontamination operation using the basic permanganate procedure.

Figure 11 Effects of Temperature and Concentration on Cracking of Mild Steel in Sodium Hydroxide (Based on Actual Service Experience and Reported in a Paper by Schmidt et al.¹⁷).

Figure 12 Caustic Danger Zone Resulting From the Use of Caustic Solutions on Mild Steel Specimens as Reported by Berk and Waldeck⁶.

B. LABORATORY EVALUATION

1. Fatigue Tests.- Standard 1/8 inch thick specimens of AISI 304 stainless steel were prepared and fatigue tested on a Sonntag testing machine model SF-1-U. Two series of experiments were performed, each with a different loading in order to modify the breaking point of the specimens. The "pretreated specimens" were exposed for 20 hours to a 20% NaOH, 3% KMnO_4 solution at 105°C prior to testing. As illustrated in Figure 13, the results obtained in the two test series varied widely and no significant relationship was apparent between break point and whether or not the specimen had been pretreated with the basic permanganate solution (see Figure 14).
2. Cold Bend Test.- A series of cold bend tests was performed on specimens of pretreated and untreated AISI 304 stainless steel in an effort to determine whether or not the exposure to the basic permanganate solution has produced embrittlement of the metal. One specimen which had originally been prepared for fatigue testing (see previous section) was pretreated for 20 hours as before. Another was exposed for 48 hours to a 70% solution of NaOH maintained at approximately 150°C, while a third specimen was used as a control. All three were bent 180° using a 2 inch diameter pipe as a guide. (This pipe diameter was equal to twice the width of the specimens at the point of bending.) Examination of the bend areas of the three specimens under 45X magnification did not reveal signs of caustic cracking. (See Figure 15 and 16.)
3. Metallographic Examination.- After microscopic examination, the cold bend test specimens were sectioned, mounted, polished, and etched prior to re-examination under 400X magnification (see Figure 17). There appeared to be little or no difference between the structure of the control "blank" and the sample pretreated for 20 hours with the basic permanganate reagent. No significant attack had taken place. The specimen that was subject to the most rigorous treatment (48 hours contact with 70% NaOH at 150°C) appeared to have suffered slight intergranular attack. Even in this case, however, the maximum depth of grain boundary penetrations seemed negligible (less than 0.5 mil), and there was no evidence of "caustic cracking" or embrittlement. (See Figures 17, 18, and 19.)

VII. FUTURE OUTLOOK

With the completion of this first phase of the Yankee Research and Development Program Decontamination Project the foundation has been laid for future large scale testing of the selected decontamination procedure. In an attempt to gain experience with the application of the basic permanganate-citrate procedure in situations more closely approaching the actual reactor

AISI 304 STAINLESS STEEL FATIGUE TEST RESULTS

FIGURE 13

Figure 14 AISI 304 Stainless Steel Fatigue Test Specimens after Failure. Top Untreated, Bottom Pretreated with the Basic Permanganate Decontamination Reagent.

(a)

(b)

(c)

Figure 15 Bend Area Surface of AISI 304 Stainless Steel Cold Bend Test Specimens 30X, (a) Untreated, (b) Pretreated 20 Hours With Basic Permanganate Reagent at 105°C, (c) Pretreated 48 Hours With 70% NaOH at 150°C.

Figure 16 Cold Bend Test Specimens of AISI 304 Stainless Steel Showing Sections Removed for Metallographic Analysis. Left to Right, Untreated, Pretreated 20 Hours With Basic Permanganate Reagent at 105°C, Pretreated 48 Hours With 70% NaOH at 150°C.

(a)

(b)

Figure 17 Photomicrographs (400X) of Edge of AISI 304 Stainless Steel Cold Bend Test Specimen, Pretreated for 20 Hours at 100°C to the Basic Permanganate Decontamination Reagent. (a) Outside of Bend, (b) Inside of Bend.

(a)

(b)

Figure 18 Photomicrographs (400X) of Edge of AISI 304 Stainless Steel Cold Bend Test Specimen, Pretreated for 48 Hours at 150°C with 70% NaOH. (a) Outside of Bend, (b) Inside of Bend.

(a)

(b)

Figure 19 Photomicrographs (400X) of Edge of AISI 304 Stainless Steel Cold Bend Test Specimen Blank - Not Exposed to Basic Permanganate Reagent. (a) Outside of Bend, (b) Inside of Bend.

application, dynamic autoclave system cleanup trials and large loop decontamination tests will be conducted. This procedure, which has proven to be effective in small "bench scale" experimentation will be refined to the point where 15 gallon batches of the reagents may be handled easily and employed efficiently in the cleanup of circulating systems.

It has been proposed that the second phase of the Decontamination Project be concluded with the cleanup of the Yankee In-Pile Test Loop at the MTR site. This could be performed at the completion of the Yankee fuel element irradiation damage test program. The opportunity to conduct a cleanup of this contaminated system (which will have been operated for 12 months under conditions of water chemistry and neutron flux approaching as closely as possible those anticipated for the actual primary coolant system), would offer additional evidence as to the feasibility of applying the basic permanganate-citrate procedure in actual Yankee reactor system decontamination. The quantitative decontamination factors obtained in this test would be extremely valuable in estimating the degree of cleanup to be achieved in actual plant usage of this method and would provide practical proof of the effectiveness of the procedure.

The third and final phase of the Decontamination Project will involve an organization of all information known concerning the state of the cleanup art as it pertains to the Yankee plant, and the writing of a detailed "Decontamination Guide" for the application of the selected chemical procedure in actual primary coolant system decontamination.

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