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**DECONTAMINATION OF BEAVER VALLEY
STEAM GENERATORS USING
THE CAN-DEREM PROCESS**

**DÉCONTAMINATION DES GÉNÉRATEURS DE VAPEUR DE LA
CENTRALE DE BEAVER VALLEY À L'AIDE DU PROCÉDÉ CAN-DEREM**

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THE CAN-DEREM PROCESS

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RÉSUMÉ

On a décontaminé trois fonds primaires de générateurs de vapeur de la Tranche 1 de la centrale de Beaver Valley, en septembre et octobre 1989, à l'aide du procédé CAN-DEREM. La décontamination d'un volume de 12 000 L par système de générateur de vapeur a représenté la première grande application du procédé CAN-DEREM suivant de près la décontamination réussie, en avril 1989, d'un échangeur de chaleur de recirculation d'un volume de 1 000 L du réacteur Indian Point-2. Le succès de ces applications a été le point culminant de plusieurs années d'études en laboratoire portant sur l'évaluation et la modification ultérieure de la technique CAN-DECON. On a entrepris ces études après que le procédé DAN-DECON a entraîné une corrosion intergranulaire de l'acier inoxydable 304 sensibilisé à la suite de la décontamination du refroidisseur d'eau de recirculation (RER) du réacteur Peach Bottom-2, au début de 1984. Le degré de corrosion était semblable à celui observé sur la tuyauterie de plusieurs des premiers réacteurs à eau bouillante: c'était le premier exemple de pièces fabriquées de réacteurs présentant une corrosion intergranulaire après une décontamination à l'aide du procédé CAN-DECON. Toutefois, les compagnies d'électricité ont hésité à se servir du procédé CAN-DECON après la décontamination du RER de Peach Bottom-2. Pour répondre aux inquiétudes des compagnies d'électricité, on a modifié la technique CAN-DECON pour réaliser la technique CAN-DEREM encore moins corrosive.

Dans le présent rapport, on résume brièvement les résultats des études de corrosion en laboratoire, ceux des évaluations de décontamination préalable à l'aide des échantillons de la centrale de Beaver Valley et ceux de la décontamination effective des générateurs de vapeur. Ces résultats montrent très nettement l'efficacité de la décontamination et la faible action corrosive du procédé CAN-DEREM. Du fait des études et démonstrations satisfaisantes, CAN-DEREM est en cours de qualification pour emploi dans des systèmes complets de caloportage de réacteurs à eau pressurisée dans le cadre d'un grand programme exécuté par Westinghouse aux États-Unis.

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ABSTRACT

Three steam generator channelheads at the Beaver Valley Unit 1 Power Station were decontaminated in September and October of 1989 using the CAN-DEREM process. With system volumes of about 12 000 L for each steam generator, this was the first major application of the CAN-DEREM process, following closely after the successful 1989 April CAN-DEREM decontamination of a 1000 L Indian Point-2 recirculating heat exchanger. The successful applications were the culmination of several years of laboratory study directed at assessing and subsequently altering the CAN-DECON formulation. The studies were initiated after the CAN-DECON process was implicated in causing intergranular attack in sensitized 304 stainless steel after the Peach Bottom-2 recirculating water cooling unit (RWCU) decontamination in early 1984. The degree of attack was similar to that observed on piping from several early Boiling Water Reactors, and this was the only instance of reactor artifacts revealing intergranular attack after a CAN-DECON decontamination. Nevertheless, utilities were reluctant to use CAN-DECON after the Peach Bottom-2 decontamination. In response to utility concerns, the CAN-DECON formulation was modified to produce the even-less-corrosive CAN-DEREM formulation.

In this report, the results of the laboratory corrosion study are briefly summarized along with the results of pre-decontamination assessments using Beaver Valley specimens, and the results of the actual steam generator decontaminations. The results show quite clearly the decontamination effectiveness and the low corrosiveness of the CAN-DEREM process. As a result of the successful laboratory program and demonstrations, the CAN-DEREM process is currently being qualified for use in full heat transport systems of Pressurized Water Reactors in a major program being carried out by Westinghouse in the United States.

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1. INTRODUCTION

The CAN-DECON decontamination process is a dilute regenerative process developed and patented by AECL in the early 1970s. The original solvent consisted of a mixture of citric acid, oxalic acid and EDTA used at a total concentration of 0.1-0.2 wt%. The solvent has been typically circulated in reactor systems at temperatures ranging from 85°C to 120°C for 24 h to 72 h where the solvent is continuously regenerated by removing Co-60 and other dissolved metals on ion-exchange resin. The CAN-DECON process has been used routinely in Canada, and, to date, 14 CANDU* reactor heat transport systems, including cores with fuel in place, have been decontaminated. In the United States, 19 Boiling Water Reactor (BWR) and 5 Pressurized Water Reactor (PWR) subsystems were decontaminated using CAN-DECON between 1979 and 1984; decontamination factors of about 5 to 10 were typically achieved. After the CAN-DECON decontamination of the recirculating water cooling unit (RWCU) system at Peach Bottom-2 in early 1984, a 6-inch-diameter pipe was removed and a weld was examined for localized corrosion attack. Shallow intergranular attack (IGA) to depths of 50 μm was observed in the weld. The degree of attack was similar to that observed on piping from several early BWRs, and this was the only instance of reactor artifacts revealing IGA after a CAN-DECON decontamination. Nevertheless, utilities were reluctant to use CAN-DECON after the Peach Bottom-2 decontamination, fearing that CAN-DECON would cause IGA in sensitized 304 stainless steel (SS), and perhaps increase the susceptibility of the SS to stress-corrosion cracking. In view of the concerns, an experimental study was undertaken at AECL's Chalk River Laboratories, to investigate the corrosiveness of mixtures of citric acid, oxalic acid and EDTA to severely sensitized 304SS and other reactor materials of construction, 304SS, 410SS, carbon steel (CS) 1010 and A508, and heat-treated Inconel-600. Results of the autoclave and loop experiments carried out under extreme conditions showed that the degree of general corrosion and localized attack in all solutions was minimal. The results of the tests also showed that of the three reagents considered, oxalic acid was most likely to cause IGA in sensitized 304SS [1-4]. The results also suggested that removal of oxalic acid from decontamination solutions would lower the corrosiveness of solutions to sensitized 304SS [1-3] and to other nuclear reactor materials, particularly 304SS and 410SS [4].

With particular reference to sensitized 304SS, pitting at grain boundaries and IGA to maximum depths of 85 μm were only observed under unrealistically severe conditions in sensitized 304SS exposed to solutions containing oxalic acid. As shown in Figure 1, although IGA can occur in citric-acid/oxalic-acid mixtures, IGA was more severe in specimens exposed to citric-acid/oxalic-acid/EDTA mixtures, while pitting predominated in specimens exposed to citric-acid/oxalic-acid mixtures. No localized attack was observed in any sensitized 304SS specimens exposed to citric-acid/EDTA mixtures in any autoclave or loop experiments. A benefit then could be obtained in terms of lowering corrosiveness by removing oxalic acid from decontamination solutions.

*CANDU: Canada Deuterium Uranium. Registered trademark.

sensitized 304SS specimens exposed to citric-acid/EDTA mixtures in any autoclave or loop experiments. A benefit then could be obtained in terms of lowering corrosiveness by removing oxalic acid from decontamination solutions.

To assess whether removal of oxalic acid from solvents would affect decontamination effectiveness, experiments were carried out using actual radioactive specimens from two boiling water reactors (BWRs) and two pressurized water reactors (PWRs). In loop experiments [5], radioactive specimens were suspended in solutions of single acids or in mixtures of reagents at total reagent concentrations of less than 0.1 wt% under conditions similar to those used to decontaminate reactor systems in the field. Rate constants for dissolution of oxides and decontamination factors were measured. Based on the corrosion and decontamination experiments, it was concluded that effective decontaminations of BWR and PWR systems could be achieved with mixtures of citric acid and EDTA (the formulation used in the CAN-DEREM process) with minimum risk of causing IGA or other localized attack in sensitized 304SS. This was considered particularly true at temperatures above 100°C where the possibility of localized attack is highest. At temperatures below 100°C, use of mixtures of citric acid, oxalic acid and EDTA (the formulation used in the CAN-DECON process) could be considered since the risk of localized attack is minimized. A CAN-DECON formulation is currently used during decontamination of CANDU heat transport systems.

In September and October of 1989, three steam generator channelheads at the Beaver Valley Unit 1 Power Station were decontaminated using the CAN-DEREM process. Results of pre-decontamination assessments using Beaver Valley specimens and of the steam generator decontaminations are described in turn below.

2. PRE-DECONTAMINATION ASSESSMENTS

Pre-decontamination experiments were carried out to characterize the oxide on a manway cover insert obtained from a Beaver Valley steam generator, and to assess the extent of oxide removal in the selected alkaline permanganate (AP) and CAN-DEREM solutions. During the AP pretreatment, the chromium-rich oxides on the 304 stainless steel and Inconel-600 surfaces of the steam generator are conditioned (by oxidizing chromium in the oxide from +3 to +6) to dissolve during the subsequent CAN-DEREM applications. Since the oxidizing pretreatment only penetrates the oxide film to a limited depth, the objective of the pre-decontamination experiments was to predict the number of AP/CAN-DEREM applications that would be required to effectively clean the steam generator channelheads. One experiment was carried out using an AP/CAN-DECON process for comparison with AP/CAN-DEREM results.

To assess the possibility of shortening critical path time by shortening the length of the AP step, and to assess the possibility of improved decontamination effectiveness, some experiments were carried out using

higher concentrations of potassium permanganate and/or shorter times than the 12 h normally used.

Results of the oxide characterization and process optimization are described in turn below.

2.1 Characterization of Oxide on a Manway Cover Insert

Specimens of the manway cover insert were gamma counted then examined by scanning electron microscope (SEM) and oxides were analyzed by X-ray techniques (EDX). Only Co-60, in surface concentrations of about 11-12 $\mu\text{Ci}/\text{cm}^2$, was observed on the specimens. SEM micrographs and results of EDX analyses are given in Figure 2 and Table 1, respectively. As shown in Figure 2, the oxide consisted of bands of crystallites covering an amorphous underlying oxide. As given in Table 1, the crystals were enriched in chromium and nickel and appear to be a mixture of substituted spinels such as nickel ferrites and chromites. The inner oxide was also enriched in chromium and nickel to maximums of 36 wt% and 20 wt% in some locations. As given in Table 1, such concentrations of chromium and particularly nickel are relatively high compared with oxides which have been characterized from other reactors [6]. As verified by the decontamination experiments described in the next section, the oxides were difficult to dissolve. Similar oxides, particularly those which are enriched in Ni, have proven particularly difficult to dissolve in previous experiments [7].

2.2 Decontamination Effectiveness

Pre-decontamination assessments were carried out to ensure that optimized reagent concentrations and times were used during the actual steam generator application. Of note is the fact that 304 stainless steel specimens from a manway cover insert were used in the assessments. During the channelhead decontaminations, the decontamination solutions were expected to be in contact with 30 m² of stainless steel compared with about 500 m² of I-600 steam generator tubes. While assessments based on the only available artifact (a 304SS manway cover insert) were considered useful, results were used, in most part, for comparisons of effectiveness of process changes.

Specimens of 304SS were exposed in beakers to solutions of alkaline permanganate (KMnO_4 , adjusted to pH = 10.5 with NaOH) at KMnO_4 concentrations ranging from 0.1 wt% to 0.3 wt% at 85°C for times ranging from 6 h to 12 h. Specimens were then exposed to CAN-DEREM or CAN-DECON solutions at 115°C for 24 h in separate loop experiments. Experiment conditions are summarized in Table 2. In the case of specimens exposed to 0.1 wt% AP for 12 h and CAN-DEREM for 24 h, a second cycle of AP/CAN-DEREM was carried out. To assess the effectiveness of the decontamination processes, decontamination profiles were measured during the loop runs using on-line gamma counting. Decontamination factors were calculated using the on-line results and by gamma counting specimens before and after decontamination using an off-line counter. Results are summarized in Table 2 and in Figures 3-5. As given in Table 2 and illustrated in Figure 3 (after pretreating specimens with

0.1 wt% AP for 12 h), both CAN-DEREM and CAN-DECON processes removed about one-third of the Co-60, and hence oxide, originally on the 304SS specimens. SEM micrographs of the specimen exposed to AP/CAN-DEREM showed that partial dissolution of the fixed oxide (Figure 6a) and of the loose crystallites (Figure 6b) occurred. As illustrated in Figure 4, a second application of an AP/CAN-DEREM step removed another third of the oxide from the specimen. As shown in Figure 7, removal of the fixed oxide was more significant and dissolution of the loose crystallites was essentially complete. These results suggested that at least two applications of AP/CAN-DEREM solutions and possibly three would be required to achieve a significant reduction in fields in the Beaver Valley steam generator channelheads.

To assess the possibility of improving the decontamination effectiveness of the AP/CAN-DEREM process, a specimen was exposed to a 0.2 wt% KMnO_4 solution for 12 h before CAN-DEREM decontamination. As illustrated in Figure 5, the process was unexpectedly less effective than a 0.1 wt% KMnO_4 exposure. In fact, subsequent pretreatments of specimens with 0.2 wt% KMnO_4 and 0.3 wt% KMnO_4 solutions (directed at assessing whether the AP step could be shortened) confirmed this result. One possibility is that the 304SS specimens were coated with more MnO_2 in the solutions containing more KMnO_4 , and the MnO_2 could have prevented MnO_4^- in solution from conditioning the oxide. These results suggested that a 0.1 wt% KMnO_4 solution should be used in the Beaver Valley decontaminations.

2.3 Plan for Steam Generator Decontaminations

Based on assessments described in Section 2.2 and in refs. [5,8,9], a minimum of two applications of the AP/CAN-DEREM process (0.1 wt% AP, 95°C, 12h; 0.1 wt% CAN-DEREM, 120°C, 6h to 24 h) was recommended for decontamination of the Beaver Valley channelheads. Based, in part, on time constraints, a decision was made to decontaminate the first steam generator B using two applications. Since decontamination of the second steam generator A was to be done off critical path, three applications were to be carried out. Based on a comparison of results obtained from steam generators B and A, a decision was to be made whether to use two or three applications for the decontamination of steam generator C.

3. RESULTS OF STEAM GENERATOR DECONTAMINATIONS

The Beaver Valley steam generator B was decontaminated 1989 September 15-18, using a four-step decontamination process consisting of alternating applications of:

- (1) an oxidizing alkaline permanganate (AP) solution circulated through the steam generator at 95°C for 12 h; and
- (2) a reducing CAN-DEREM solution circulated at 120°C for 8 h.

In total, then, the decontamination sequence consisted of AP/CAN-DEREM/AP/CAN-DEREM steps applied using the decontamination circuit illustrated in Figure 8. It consisted of pumps, heaters and ion-exchange columns connected using 3 in. hoses. A reverse flow skid was used to ensure that adequate flow and reagent contact was achieved on both sides of the steam generator. The equipment was centrally located so that only hoses had to be rerouted to decontaminate steam generators A and C. Steam generator A was decontaminated using a six-step process September 24-29. Steam generator C was decontaminated using a four-step process October 6-8.

As described previously, during the AP pretreatment, the chromium-rich oxides on the 304SS and I-600 surfaces (of the steam generator) were conditioned to dissolve during the subsequent CAN-DEREM applications. As the oxide dissolved in the CAN-DEREM solution, the radionuclides trapped within the oxide were released into the decontamination solution and were then removed on ion-exchange resin.

The amounts of activity and metals removed during each AP/CAN-DEREM application are summarized in Tables 3 and 4, respectively. Decontamination factors (DFs calculated by dividing initial fields by final fields) for each steam generator are given in Table 5. Detailed breakdowns of radionuclides and metals removed are given in Appendices 1, 2 and 3. A description of the chemistry parameters and efficiencies of the AP and CAN-DEREM steps are given in turn below.

3.1 Process Chemistry

The ranges of process parameters measured during the decontaminations are summarized in Tables 6 and 7 for steam generators B and A, respectively. Process parameters for the steam generator C decontamination were similar. The parameters were generally within specifications outlined in procedures. In some cases, parameters were initially outside of specifications; for example, when EDTA absorbs on ion-exchange (a condition which is known to occur and has been observed previously). In these cases, chemical additions were made to bring reagent concentrations to within specified values. At no time did conditions become excessively corrosive or was the process operating in a region that was inefficient from a decontamination effectiveness point of view. In fact, dissolution of AP conditioned oxides was so rapid in CAN-DEREM solutions that CAN-DEREM steps were terminated after only 8 h. The rapid dissolution is illustrated in Figure 3 using laboratory data; as illustrated, most oxide that dissolves does so within 1 h. The rapid dissolution is illustrated in Figure 9 for the first CAN-DEREM application to steam generator B (plot shows $\mu\text{Ci/ml}$ of activity in CAN-DEREM solution versus time). As shown, after the first 2 h the amounts of activity in solution decrease with the purification half-life of the ion-exchange cleanup system suggesting that no oxide is dissolving after 2 h. In some cases, a second peak in activity was observed between the fourth and sixth hours, as illustrated in Figure 9. As shown in Figure 3, this effect was also observed in laboratory experiments and probably represents dissolution

of nickel ferrites (and other relatively easy-to-dissolve oxides) embedded in the chromium-rich oxide.

Note that at the end of each decontamination step, all chemicals and residues were removed from the steam generators on mixed bed ion-exchange resin.

3.2 Process Effectiveness

The amounts of activity and metals removed during steam generator B, A, and C decontaminations are given in Tables 3 and 4. Decontamination factors obtained for the three steam generators are given in Table 5. As shown in Table 5, overall DFs (average of hot leg and cold leg DFs) ranged from 6.2 and 6.5 for steam generators B and A, respectively, to 4.8 for steam generator C. Since a four-step process was used on generator B, a six-step process on A and a four-step process on C, a higher DF should have been obtained for generator A, compared with generators B and C (assuming that the oxides in all generators were similar). As described below, the oxide in generator B was probably easier to dissolve than oxides in generators A and C (explaining why the DF for generator B with only four steps was as high as the DF for generator A with six steps). As shown in Table 3, approximately 42 Ci were removed from generator B compared with 33 Ci from generator A and 36 Ci from generator C for the same number of steps. After six steps, a total of 42 Ci were removed from steam generator A. Examination of radionuclides removed from steam generators B, A and C (see Appendices 1-3) shows that 96% of the activity removed from both generators was Co-58 and Co-60. A breakdown of the amounts removed with each AP/CAN-DEREM process application is given in Tables 8 and 9. As shown in Table 8 for steam generator A, the amounts of Co-60 removed with each AP/CAN-DEREM step were approximately equal, suggesting an equal effectiveness of each AP/CAN-DEREM application. These results are consistent with the laboratory results, illustrated in Figure 3, showing that approximately one-third of the oxide (from a Beaver Valley manway cover) was dissolved during each AP/CAN-DEREM application.

As shown in Table 9, the amounts of Co-58 removed from steam generator A decreased from 12.4 Ci during the first AP/CAN-DEREM, to 5.9 Ci and 3.2 Ci during the second and third applications. This is an expected result in that (with an 80-day half-life) the Co-58 in the inner oxide has decayed since being incorporated into the growing oxide several years ago. The net effect of the decay of short-lived isotopes is that there is a diminishing return to each AP/CAN-DEREM application. Using steam generator A as an example, about 50% of the total curies removed were removed during the first AP/CAN-DEREM application, while 30% and 20% of the total curies removed, were removed during the second and third applications, respectively.

Examination of Tables 8 and 9 shows clearly that more Co-60 (38% more) and Co-58 (66% more) were removed during the first application of AP/CAN-DEREM to steam generator B compared with steam generators A and C. Amounts of

Co-58 and Co-60 removed from steam generators A and B during the second AP/CAN-DEREM application were comparable. Interestingly, more Co-60 and Co-58 were removed during the second application of AP/CAN-DEREM to steam generator C, compared with generators B and A. Significantly more oxide (as evidenced by metal-removal, Table 4) was removed from generator B compared with generators A and C during both AP/CAN-DEREM applications. Since the chemistries of all AP/CAN-DEREM applications were similar, it is unlikely that differences in oxide and Co-60 removal were associated with differences in process efficiencies. It is likely, though, that the oxide inventory in steam generator B was higher than in generators A and C, and that the oxides in generator B dissolved more readily than the oxide in generators A and C. It is possible, then, that most of the radionuclide inventory in steam generator B was removed during the first two AP/CAN-DEREM applications.

The suggestion that the oxide in steam generator B was easier to dissolve is supported by data on oxide composition. Oxide compositions can be approximated from data on amounts of metals removed assuming that minimal amounts of corrosion occurred during the decontamination (corrosion rates measured by coupons were in fact close to detection limits, i.e. $< 0.005 \mu\text{m/h}$); the ratios of chromium to the total of iron and nickel are given in Table 10. As shown, the average chromium content of oxides in steam generator B was about 9%, significantly lower than the 14% observed for steam generator A and 16% for generator C. A probable explanation is that steam generator B contained a significant amount of low chrome oxide, perhaps nickel ferrite (which dissolves in CAN-DEREM solutions even without an AP pretreatment) in addition to a chromium-rich inner oxide. As given in Table 1, such low chromium, nickel-rich oxides were observed in pre-decontamination examination of a Beaver Valley manway cover insert. A more detailed examination of operating features of the three steam generators might suggest why oxides in the steam generators were different. A comparison of the average compositions of oxides based on metals removed and on EDX analyses of the manway cover is given in Table 11. As suggested by the relatively high Ni concentration in estimates 1-3, a significant amount of oxide on the steam generator tubes dissolved.

3.3 Corrosion Results

During the decontamination of each steam generator, a set of corrosion coupons consisting of 304SS, sensitized 304SS, 316SS and I-600 was placed in an autoclave of the decontamination circuit. After each steam generator decontamination, the coupons were removed for weight loss and SEM examination. As given in Table 12, corrosion rates for all materials were low, i.e., close to detection limits in most cases, and comparable to laboratory results [1-4]. As shown in Figure 8, SEM micrographs of the coupons showed no localized attack and little, if any, evidence of general corrosion.

4. SUMMARY

Three steam generator channelheads at the Beaver Valley Unit 1 Power Station were decontaminated in September and October of 1989 using the CAN-DEREM process. The chemistry associated with the decontaminations was well-behaved, decontamination factors were high, ranging from 4 to 9, and negligible amounts of corrosion were observed. This was the first major application of the CAN-DEREM process, following closely after the successful CAN-DEREM decontamination of an Indian Point-2 recirculating heat exchanger. The successful applications were the culmination of several years of laboratory study directed at assessing and subsequently altering the CAN-DECON formulation. As a result of the successful laboratory program and demonstrations, the CAN-DEREM process is currently being qualified for use in full heat transport systems of PWRs in a major program being carried out by Westinghouse in the United States.

5. ACKNOWLEDGEMENTS

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TABLE 1. Results of EDX Analysis of Oxide on Manway Insert.

ANALYSIS LOCATION	COMPOSITION (wt%)		
	Cr	Ni	Fe
1. <u>Loose Oxide</u>			
(a) large crystal 1	19	9	69
(b) large crystal 2	5	32	60
(c) band of crystals	29	23	44
(d) other reactors*	14	9	75
2. <u>Fixed Oxide</u>			
(a) machining mark	36	20	41
(b) flat surface	19	8	71
(c) other reactors**	39	15	45
3. <u>Metal</u>			
304SS	18	9	73
I-600	16	72	8

* Average of three other reactors (B, D, Ringhals 2) reported in ref.[6].

** Average of five other reactors (B, D, Surry 2, Ringhals 2 and Loviisa 2) reported in ref.[6]. Standard deviations were approximately ± 3 .

TABLE 2. Summary of Decontamination Results Obtained Using Beaver Valley Manway Insert Specimens.

PRETREATMENT		DECONTAMINATION SOLUTION		DECONTAMINATION FACTOR**
[AP] (wt%)*	Time (h)	Solution	Time (h)	
0.1	12	CR	24	1.40 ± 0.10 [†]
0.2	12	CR	24	1.37 ± 0.06
0.2	6	CR	6	1.29 ± 0.04
0.3	6	CR	6	1.23 ± 0.06
0.1	12	CD	24	1.80 ± 0.20

AP - alkaline permanganate

CR - CAN-DEREM

CD - CAN-DECON

* Concentration of KMnO_4 is listed.

** Decontamination Factor = $\frac{\text{final activity}}{\text{initial activity}}$; results are the average of off-line and on-line gamma counting results.

[†] Experiment carried out in duplicate.

TABLE 3. Comparison of Curies Removed During Decontamination of Beaver Valley SGs (Ci).

SG	1st AP/CR	2nd AP/CR	3rd AP/CR	CUMULATIVE	
				1st & 2nd AP/CR	1, 2 & 3 AP/CR
B	29.0	13.5	-	42.5	-
A	20.1	12.8	8.72	32.9	41.6
C	17.4	18.7	-	36.1	-

TABLE 4. Comparison of Total Metals (Fe, Ni, Cr) Removed During Decontamination of Beaver Valley SGs (kg).

SG	1st AP/CR	2nd AP/CR	3rd AP/CR	CUMULATIVE	
				1st & 2nd AP/CR	1, 2 & 3 AP/CR
B	2.9	1.8	-	4.7	-
A	1.3	0.6	0.8	1.9	2.7
C	1.5	0.9	-	2.4	-

TABLE 5. Decontamination Factors Obtained by Decontaminating Beaver Valley SGs with AP/CAN-DEREM.

STEAM GENERATOR	AVERAGE OF HOT AND COLD LEG DFs	HOT LEG					COLD LEG				
		Average Hot Leg DFs	Rad. Survey	TLD			Average Cold Leg DFs	Rad. Survey	TLD		
				Average Whole Body	Front Torso	Back of Head			Average Whole Body	Front Torso	Back of Head
B	6.2	4.6	5.3	4.1	4.8	4.3	7.8	7.7	7.5	8.0	7.9
A	6.5 (6.8*)	4.2 (4.8*)	6.2	3.5	4.6	2.5	8.8	7.9	9.6	7.7	10.0
C	4.8	3.6	3.3	3.6	3.4	4.2	6.0	5.5	6.6	5.1	6.8

*Excluding 2.5 (Back of Head TLD) measurement as anomalously low.

TABLE 6. Process Parameters During Steam Generator B Decontamination.

PARAMETER	STEP			
	1st AP	1st CR	2nd AP	2nd CR
pH	10.8-11.3	2.6-3.0	9.5-10.1	2.6-2.9
[KMnO ₄], ppm	850-1250	-	850-1150	-
[EDTA], ppm	-	200-600	-	500-700
Conductivity (μhos/cm)	1300-1800	600-1200	1400-2400	850-1400

TABLE 7. Process Parameters During Steam Generator A Decontamination.

PARAMETER	STEP					
	1st AP	1st CR	2nd AP	2nd CR	3rd AP	3rd CR
pH	10.4-11.0	2.6-3.0	10.2-11.5	2.6-3.0	9.6-10.5	2.7-3.0
[KMnO ₄], ppm	800-1100	-	825-1180	-	800-1210	-
[EDTA], ppm	-	300-700	-	370-750	-	540-750
Conductivity (μhos/cm)	1250-1800	850-1100	1300-2050	800-1000	1100-2200	720-1100

TABLE 8. Comparison of Co-60 Removed During Decontamination of Beaver Valley SGs (Ci).

SG	1st AP/CR	2nd AP/CR	3rd AP/CR	CUMULATIVE	
				1st & 2nd AP/CR	1, 2 & 3 AP/CR
B	9.4	6.5	-	15.9	-
A	6.9	6.6	5.2	13.5	18.7
C	6.7	9.8	-	16.5	-

TABLE 9. Comparison of Co-58 Removed During Decontamination of Beaver Valley SGs (Ci).

SG	1st AP/CR	2nd AP/CR	3rd AP/CR	CUMULATIVE	
				1st & 2nd AP/CR	1, 2 & 3 AP/CR
B	18.7	6.5	-	25.2	-
A	12.4	5.9	3.2	18.3	21.5
C	10.0	8.5	-	18.5	-

TABLE 10. Ratios of Chromium to Total of Iron and Nickel.

STEAM GENERATOR	AMOUNT REMOVED (g)			RATIO $\frac{Cr}{Fe+Ni}$
	Fe	Ni	Cr	
B	2642	1714	375	0.09
A	1531	793	332	0.14
C	1499	518	334	0.16

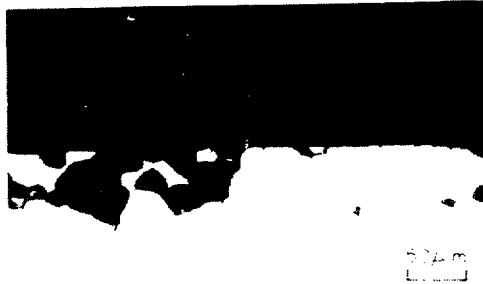
TABLE 11. Estimates of Average Composition of Oxide.

METHOD	OXIDE COMPOSITION (wt%)		
	Cr	Ni	Fe
EDX, 304SS - loose oxide	29	23	44
EDX, 304SS - fixed oxide	19-36	8-20	41-71
B - metals removed	8	36	56
A - metals removed	12	30	58
C - metals removed	14	22	64
304SS	18	9	73
I-600	16	72	8

TABLE 12. Summary of Corrosion Rates.

MATERIAL	CORROSION RATES ($\mu\text{m}/\text{h}$)*		
	S/G B	S/G A	S/G C
304SS	0.003	0.005	<0.001
Sensitized 304SS	0.006	0.005	0.004
316SS	0.002	0.005	0.001
I-600	0.005	0.005	0.013

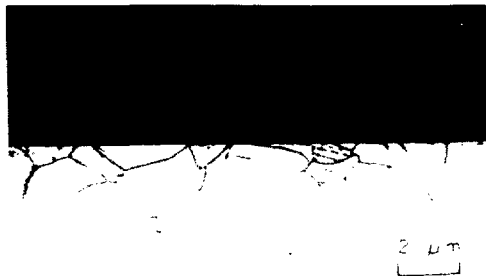
*calculations based on exposure time to the CAN-DEREM solution.



(a) 270 mg/kg CA, 210 mg/kg OA and 400 mg/kg EDTA

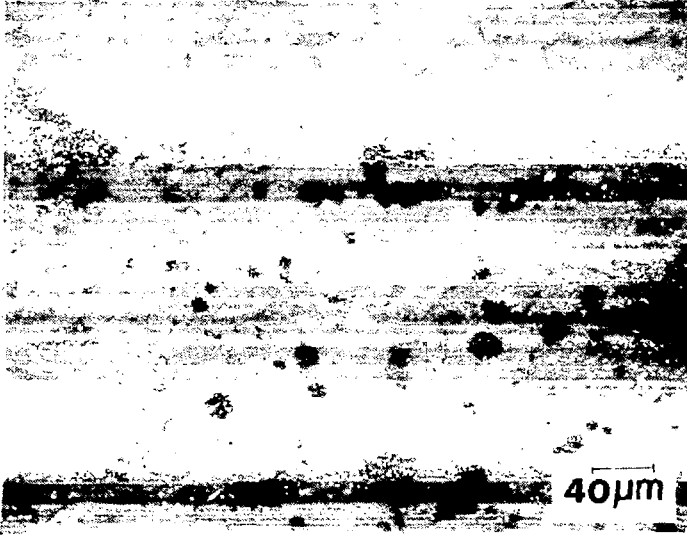


(b) 270 mg/kg CA and 355 mg/kg OA

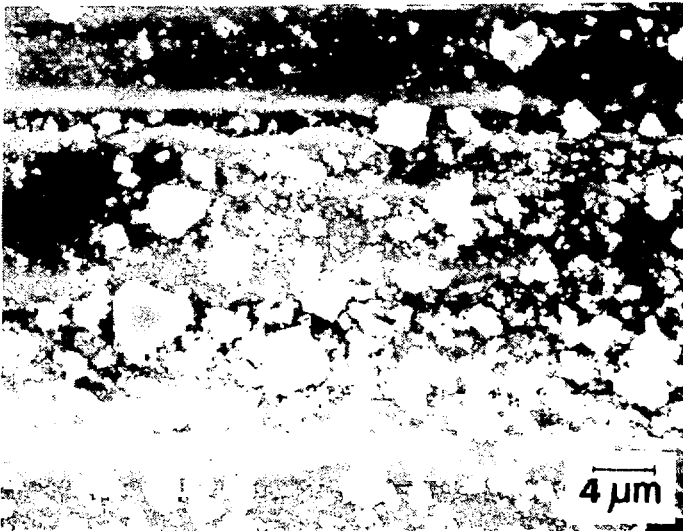


(c) 270 mg/kg CA and 700 mg/kg EDTA

FIGURE 1. Metallographs of severely sensitized 304SS specimens exposed to mixtures of citric acid (CA), oxalic acid (OA) and EDTA at 125°C for 22 h (from ref.1).



(a) Bands of nickel- and chrome-rich crystals on chrome-rich inner-oxide.



(b) Nickel- and chrome-rich crystals.

FIGURE 2. SEM micrographs of manway cover insert removed from Beaver Valley steam generator.

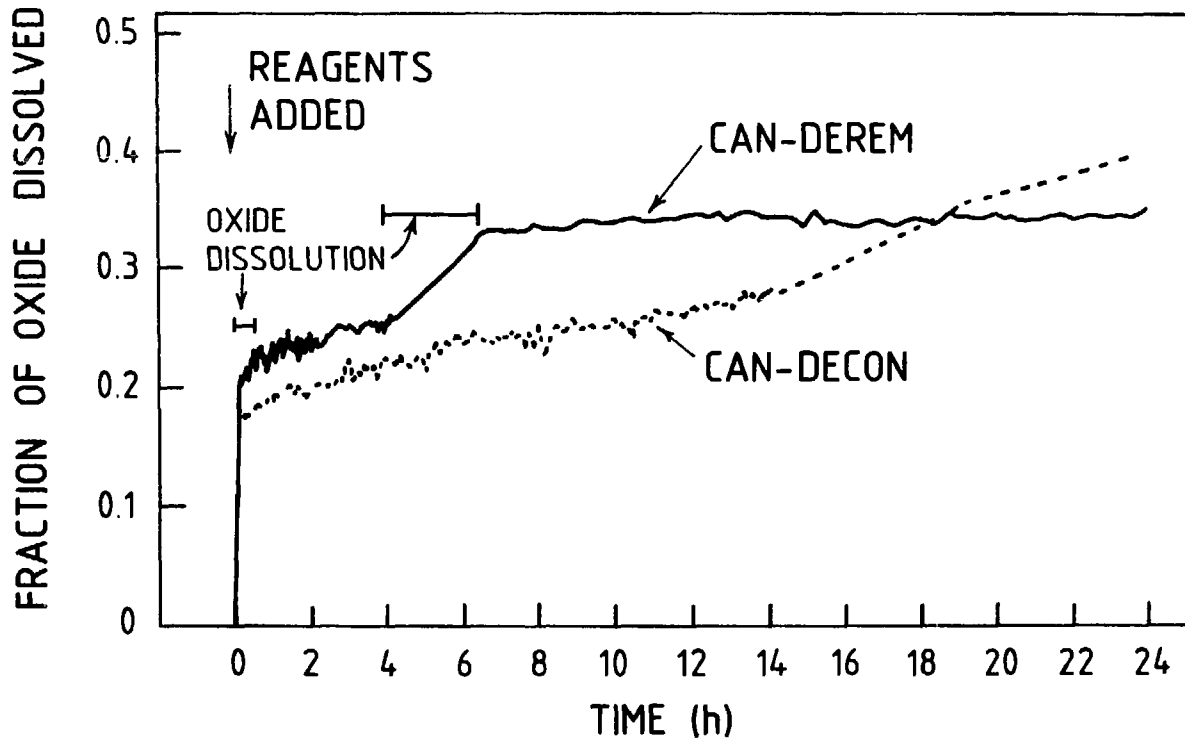


FIGURE 3. Laboratory comparison of the effectiveness of CAN-DEREM and CAN-DECON using specimens from a Beaver Valley manway cover insert.

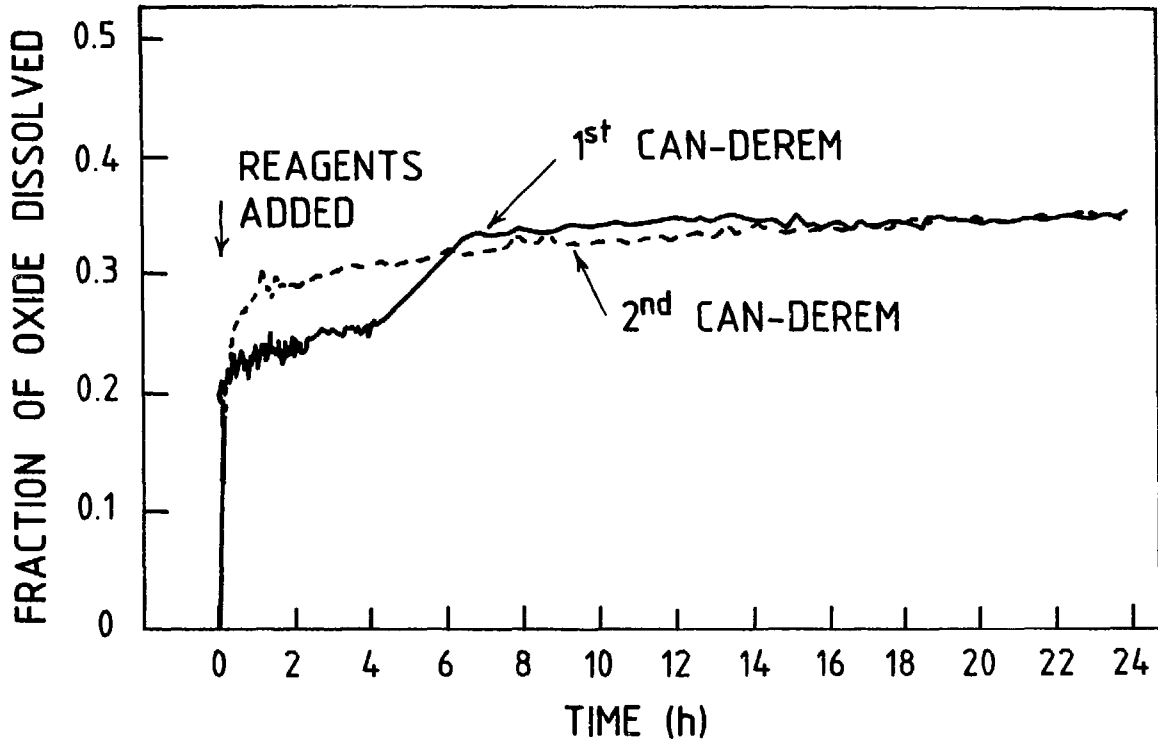


FIGURE 4. Fraction of oxide dissolved with time for the first and second applications of AP/CAN-DEREM solutions to a Beaver Valley manway cover insert specimen.

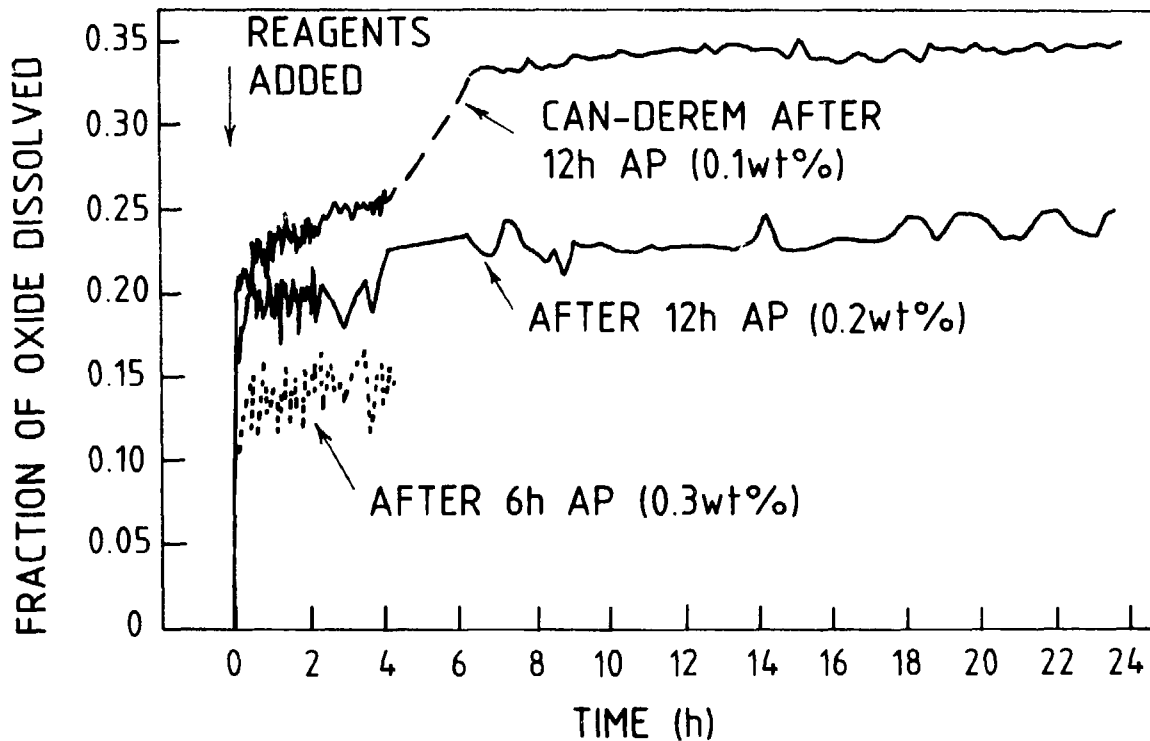
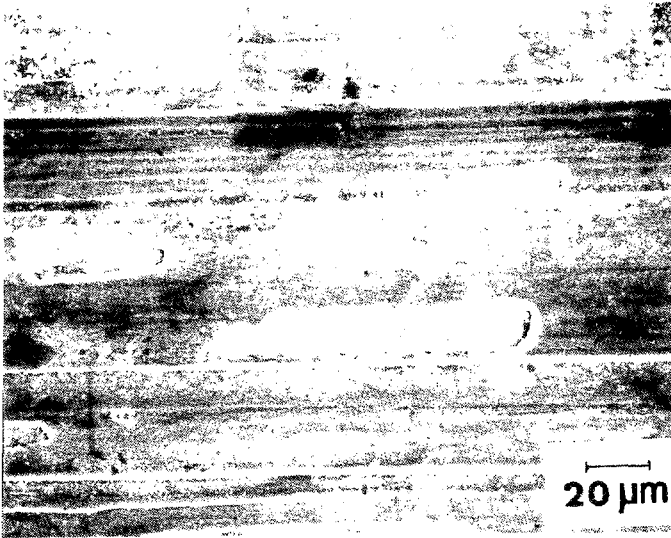
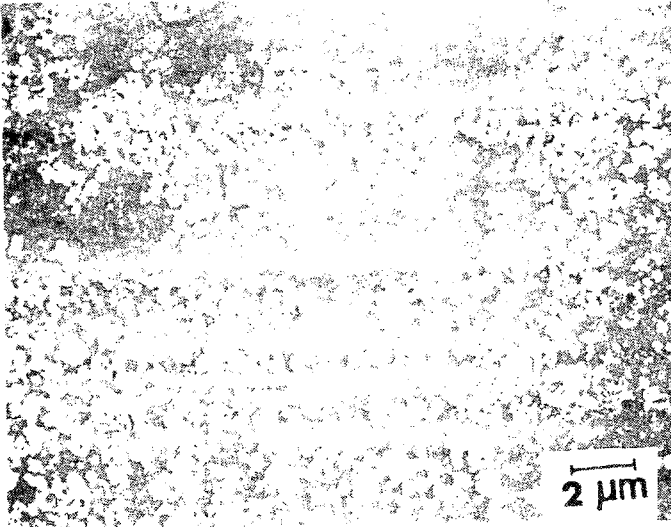


FIGURE 5. Comparison of the fraction of oxide dissolved with time in CAN-DEREM solutions for 304SS specimens pretreated with different concentrations of KMnO_4 .



(a) Chrome-rich oxide partially dissolved.

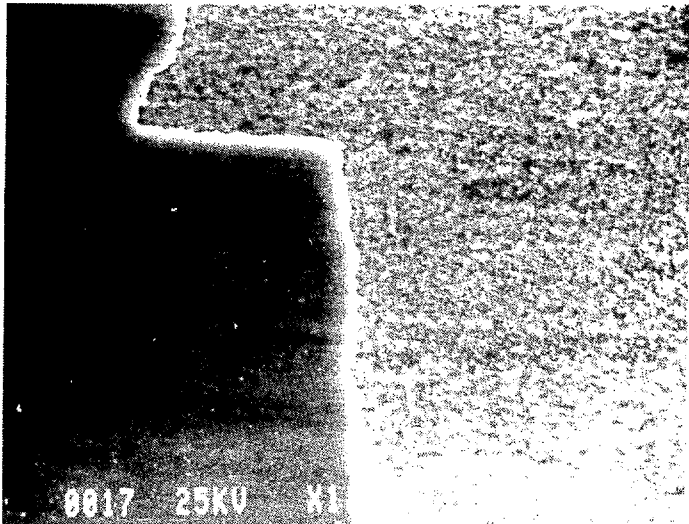


(b) Nickel- and chrome-rich crystals partially dissolved.

FIGURE 6. SEM micrographs of manway cover insert specimen after AP/CAN-DEREM decontamination.



(a) Chrome-rich fixed-oxide partially dissolved.



(b) Nickel- and chrome-rich crystals completely dissolved.

FIGURE 7. SEM micrographs of manway cover insert specimen after AP/CAN-DEREM/AP/CAN-DEREM decontamination.

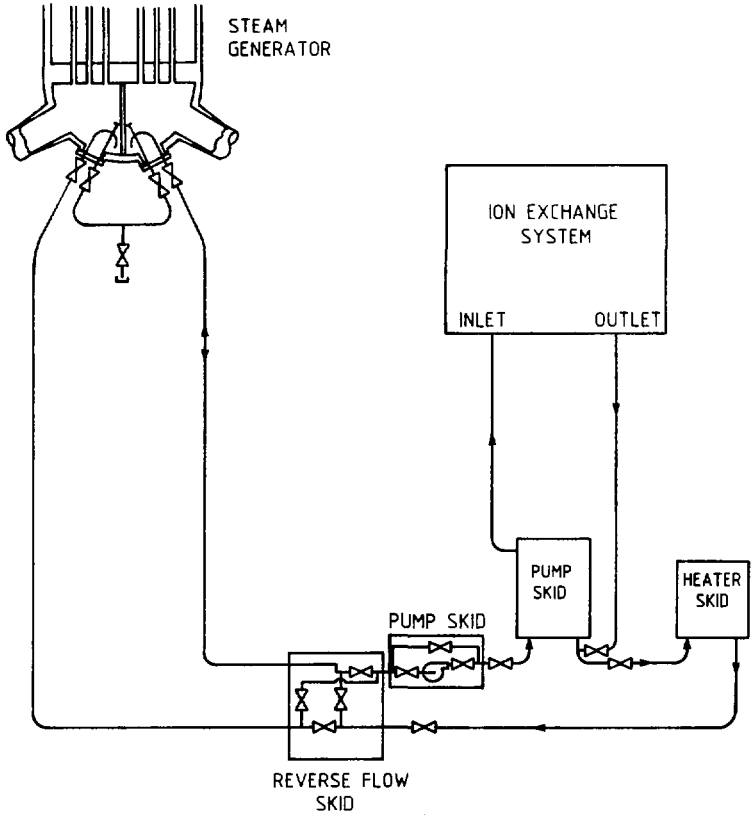


FIGURE 8. Simplified diagram of steam generator decontamination circuit.

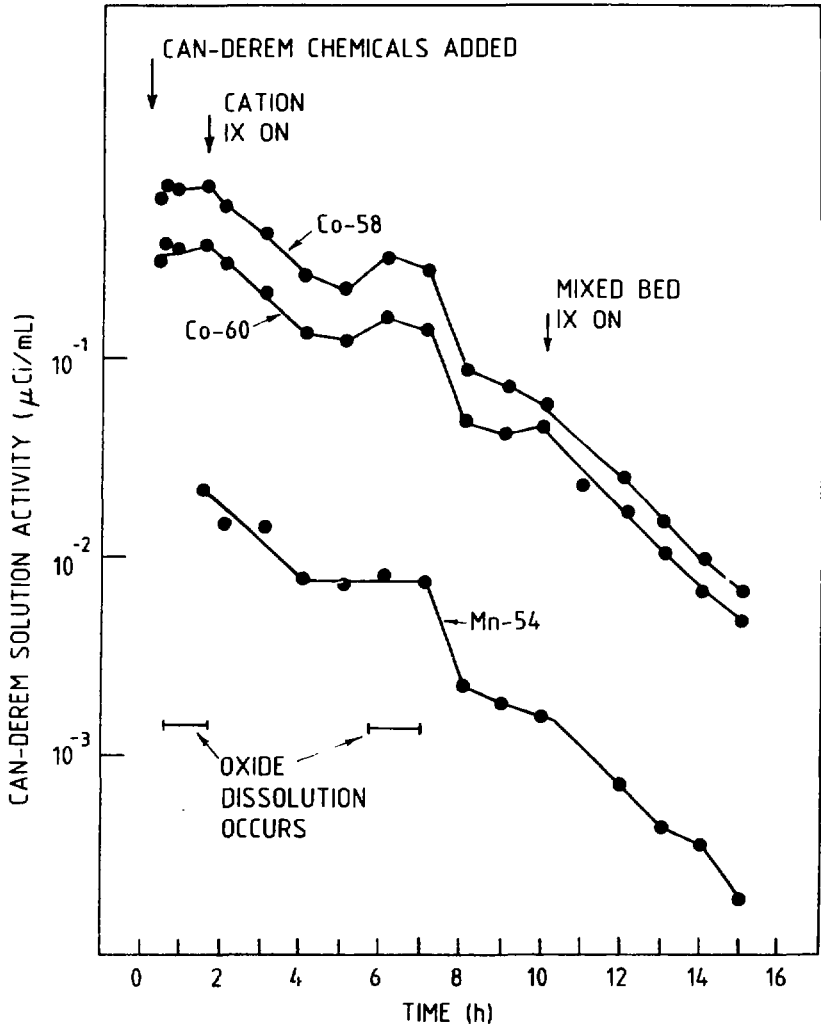
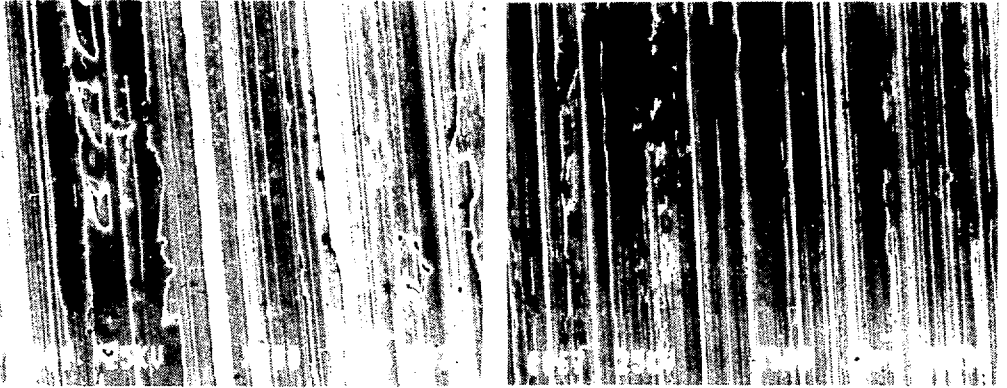
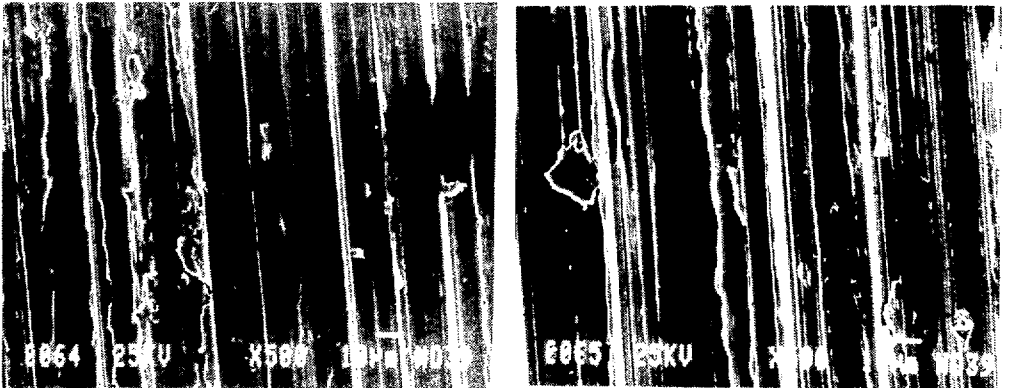


FIGURE 9. Plot of solution activity versus time during first CAN-DEREM decontamination of steam generator B.



(a) 304SS

(b) sensitized 304SS



(c) 316SS

(d) I-600

FIGURE 10. SEM micrographs of corrosion specimens exposed to AP/CAN-DEREM/AP/CAN-DEREM solutions during decontamination of steam generator B.

A P P E N D I X 1

DECONTAMINATION SUMMARY FOR STEAM GENERATOR B

A. METALS REMOVED

METAL REMOVED (g)	1st AP	1st CD	2nd AP	2nd CD	ALL STEPS
Iron	0	1520	56	1066	2642
Nickel	0	1270	104	340	1714
Chromium	45	120	170	40	375
Manganese	N/A	600*	N/A	228*	828
Copper	0	0	0	0	0
TOTAL	45	2910	330	1446	4731

N/A - not analyzed

*From residual MnO_2 - not included in totals

B. ACTIVITY REMOVED

ACTIVITY REMOVED (Ci)	1st AP	1st CD	2nd AP	2nd CD	ALL STEPS
Co-60	0.05	9.31	3.00	3.51	15.87
Cr-51	0.05	0.17	0.07	0.05	0.34
Mn-54	0.01	0.50	0.10	0.21	0.82
Co-58	0.23	18.42	2.60	3.90	25.15
Fe-59	0	0.15	0	0	0.15
Zn-65	0	0	0	0	0
Ru-103	0.02	0.05	0.02	0.02	0.11
TOTAL	0.36	28.60	5.79	7.69	42.44

A P P E N D I X 2

DECONTAMINATION SUMMARY FOR STEAM GENERATOR A

A. METALS REMOVED

METAL REMOVED (g)	1st AP	1st CD	2nd AP	2nd CD	3rd AP	3rd CD	ALL STEPS
Iron	0	674	18	317	20	502	1531
Nickel	10	467	36	120	20	140	793
Chromium	72	44	89	21	84	12	322
Manganese	N/A	218*	N/A	296*	N/A	378*	892*
Copper	0	0	0	0	0	0	0
TOTAL	82	1185	143	458	124	654	2646

N/A = not analyzed

*From residual MnO_2 - not included in totals.

B. ACTIVITY REMOVED

ACTIVITY REMOVED (Ci)	1st AP	1st CD	2nd AP	2nd CD	3rd AP	3rd CD	ALL STEPS
Co-60	0.76	6.09	2.81	3.75	2.00	3.24	18.65
Cr-51	0.09	0.10	0.04	0.02	0.04	0.01	0.30
Mn-54	0.04	0.30	0.09	0.10	0.05	0.09	0.67
Co-58	1.4	11.00	2.39	3.50	1.00	2.20	21.49
Fe-59	0	0.24	0	0.04	0	0.06	0.34
Zn-65	0	0	0	0	0	0	0
Ru-103	0.02	0.04	0.02	0.02	0.02	0.01	0.13
TOTAL	2.3	17.8	5.35	7.43	3.11	5.61	41.58

A P P E N D I X 3

DECONTAMINATION SUMMARY FOR STEAM GENERATOR C

A. METALS REMOVED

METAL REMOVED (g)	1st AP	1st CD	2nd AP	2nd CD	ALL STEPS
Iron	52	785	26	636	1499
Nickel	50	429	23	16	518
Chromium	100	72	138	24	334
Manganese	N/A	107*	N/A	208*	315
TOTAL	202	1286	187	676	2351

N/A - not analyzed

*From residual MnO₂ - not included in totals

B. ACTIVITY REMOVED

ACTIVITY REMOVED (Ci)	1st AP	1st CD	2nd AP	2nd CD	ALL STEPS
Co-60	2.58	4.13	3.04	6.75	16.50
Cr-51	0.13	0.07	0.05	0.05	0.30
Mn-54	0.12	0.18	0.12	0.17	0.59
Co-58	3.76	6.26	2.71	5.78	18.51
Fe-59	0	0.04	0	0	0.04
Zn-65	0	0	0	0	0
Ru-103	0.09	0.02	0.01	0.01	0.13
TOTAL	6.68	10.70	5.93	12.76	36.07

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