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SUBJECT: DECONTAMINATION OF A HOMOGENEOUS REACTOR (Presented at American Nuclear Society Meeting, Pittsburgh, Pa., June 10-12, 1957)

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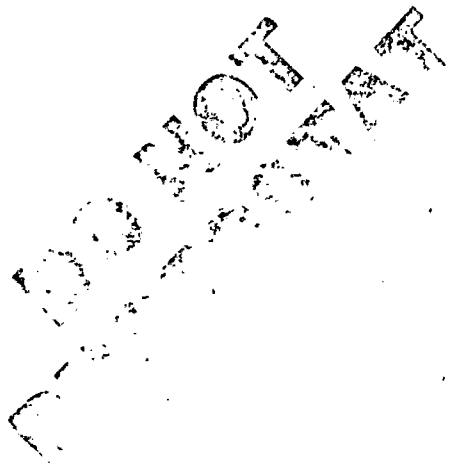

INTRODUCTION

A satisfactory method of decontaminating a homogeneous reactor has been developed using a chromous sulfate--sulfuric acid solution to dissolve and remove the oxide corrosion film deposited on stainless steel from uranyl sulfate solutions at 300°C. Investigations have shown that plutonium and fission products are incorporated in the oxide film and that descaling of the corrosion film is necessary for adequate decontamination. The 0.40 M $CrSO_4$--0.5 M H_2SO_4 solution has given excellent removal of the film by modifying and dissolving the oxides, together with excellent decontamination from plutonium and fission products in 2-4 hr at 80-90°C. The decontamination is a result of dissolution of the oxide film, so that the contaminants go into solution and are removed in the spent chromous sulfate solution.

It became evident during the decontamination of the first experimental homogeneous reactor (the "HRE") that conventional methods of decontaminating radiochemical plants are not adequate for a stainless steel reactor system which has been exposed to uranyl sulfate--fission product solutions at 300°C. Nitric acid alternated with an alkaline tartrate peroxide solution was not adequate for decontamination as the oxide was left intact. During one month of continuous decontamination of the HRE, the decontamination factor was ~23 and was due to both decay and removal of activity. Removal of the corrosion film would have given an additional decontamination factor of about 100.[1]

SCOUTING INVESTIGATIONS

Attempts to leach the contaminants from the oxide film with mineral and organic acids were unsuccessful. Descaling the oxide from the stainless steel required drastic treatment with solutions such as 1.0 M HCl--1.4 M H_2SO_4--0.2 M H_2O_2 with alkyl pyridines[2] or 20% HNO_3--3% HF at 60-80°C for periods of time from 3 to 24 hr. In the defilming operation with the

mineral acids the oxide film flaked off in large flakes and little or none of the oxide dissolved. Introduction of halides into the reactor system for descaling is undesirable owing to chloride stress corrosion of stainless steel at 250°C. The descaling was a result of interfacial corrosion between the oxide and the base metal, causing extensive intergranular and pitting corrosion of the structural metal. The oxide that flaked off contained about 95% of the total activity. Fission product analysis showed the contaminants in the oxide to be primarily Zr^{95}-Nb^{95}, with significant amounts of ruthenium, cesium, and rare earths.

CONDITIONS FOR DESCALING WITH CHROMOUS SULFATE

Since a chromous sulfate solution does not contaminate the reactor system with foreign ions and actually dissolves the oxide film, tests were made to determine the best operating conditions. The best solution for defilming stainless steel exposed to uranyl sulfate at 250-300°C was found to be 0.4 M $CrSO_4$--0.5 M H_2SO_4 at 75-85°C.

Chromous sulfate concentrations lower than 0.2 M removed the film very slowly. The maximum concentration is not critical, as the solution was effective up to 1.5 M. A chromium concentration of 0.4 M was chosen as this is the room temperature saturation concentration of the potassium chrome alum salt used as a starting material.

A minimum sulfuric acid concentration of 0.2 M was required for oxide dissolution, and 0.5 M appeared optimum where dissolution and corrosion were considered. The dissolution was more rapid in 1.0 M H_2SO_4, but the corrosion rate was also noticeably increased.

The action of the chromous sulfate--sulfuric acid solution was also dependent on temperature. At room temperature the oxide film was modified and could be washed off in very fine particles after 12-24 hr contact, during which there was little oxide dissolution. At 70-90°C the solution

dissolved the oxide rapidly in 2 hr, giving excellent descaling. Above 110°C the chromous sulfate decomposed water, producing H_2 and O_2.

Since chromous sulfate is a powerful reducing agent it also is easily oxidized by air. Therefore an inert atmosphere, such as CO_2, N_2, or H_2, must be kept over the chromous sulfate solution to prevent oxidation to chromic sulfate.

CHROMOUS SULFATE DESCALING AND DECONTAMINATION

Metal Coupons

Contaminated stainless steel coupons were completely defilmed with chromous sulfate solution. The coupons were prepared by heating them for 100 hr at 250-300°C in 1.4 M UO_2SO_4 solution containing plutonium and fission products. They acquired a 5- to 10-mil-thick oxide film, which contained 2-15 μg of plutonium per square centimeter and 500-1000 mr/hr of beta and gamma activity. The descaling and decontaminating procedure consisted in contacting the samples with a 0.4 M $CrSO_4$--0.5 M H_2SO_4 solution at 85°C for 2 hr, after which they were washed and checked for plutonium and fission product contamination.

After the treatment the coupons all had a bright metallic luster. Plutonium removal in all cases was greater than 99% (Table I). Results were similar for plutonium contamination on titanium and zircaloy-2 samples. In all experimental work both adsorbed plutonium and PuO_2 crystals were dissolved as a result of reduction of Pu(IV) to Pu(III), which is soluble in the chromous sulfate solution.

The excellent fission product decontamination factors of 125 to 300 shown in Table II were primarily the result of dissolution of the oxide corrosion film, which enabled the occluded fission products to go into solution and be removed.

Table I

Removal of Adsorbed Plutonium from Stainless Steel with Chromous Sulfate

Contaminated stainless steel coupons contacted with 0.4 M $CrSO_4$--0.5 M H_2SO_4 at 85°C for 2 hr

Pu on Metal, $\mu g/cm^2$		Pu Removed (%)
Initial	Final	
2.64	0.0002	99.98
7.46	0.001	99.98
12.97	0.002	99.97
15.24	0.069	99.54

Table II

Removal of Fission Products from Stainless Steel with Chromous Sulfate

Contacted with 0.4 M $CrSO_4$--0.5 M H_2SO_4 at 85°C for 2 hr

Fission Product Activity, mr/hr		Decontamination Factor
Initial	Final	
1000	4	250
750	5	150
900	3	300
500	4	125

In-Pile Corrosion Loop

To check the decontamination of type 347 stainless steel which had large amounts of fission products in the oxide film, two sections of a loop that had been in the neutron flux during in-pile uranyl sulfate corrosion studies were treated with 0.4 M chromous sulfate--0.5 M H_2SO_4. The oxide film was completely removed and the decontamination factor was 20-30 (Table III). A sample that was not in the neutron flux was decontaminated by a factor of 143, and further treatment with alkaline tartrate peroxide gave an over-all decontamination factor of 5×10^3. The combination of the chromous sulfate and alkaline-tartrate-peroxide solutions gave the most satisfactory decontamination yet achieved with type 347 stainless steel that had been exposed to uranyl sulfate--fission product solutions at 300°C.

These loop specimens were decontaminated by contacting with the chromous sulfate sulfuric acid solution for 2 hr at 85°C, after which they were taken out of the solution and checked for activity. Samples that had been exposed to the neutron flux were decontaminated from 25 to ~1 r/hr. Essentially all the remaining activity was due to Fe^{59} and Cr^{51} induced by neutron activation. The third sample from the loop had not been in the neutron flux. After it had been in contact with the chromous sulfate solution for 2 hr, the activity had decreased from 30 to 0.2 r/hr. Analysis showed that the remaining activity was 99% Ru^{103} which had replated on the stainless steel from the chromous sulfate solution. Further contact of this specimen with alkaline-tartrate-peroxide solution for 4 hr reduced the activity to 6 mr/hr, giving an over-all decontamination factor of 5×10^3.

Dynamic Corrosion Loops

Four closed loop systems (Fig. 1) that had been operated more than 22,000 hr at 200-300°C with uranyl sulfate solution containing no fission products were completely descaled in 4 hr by circulating 0.4 M $CrSO_4$--

Table III

Decontamination of In-pile Loop Sections under Static Conditions

Section	Decontaminating Solution	Activity of Loop Section, r/hr		Decontamination Factor
		Initial	Final	
In neutron flux	0.4 M $CrSO_4$--0.5 M H_2SO_4 at 85°C for 2 hr	25	1.2[a]	21
In neutron flux	Same	26	0.9[a]	29
Not in neutron flux	Same	30	0.21[b]	143
	Alkaline-tartrate-peroxide for 4 hr at 30°C	0.21	0.006	35
				5000

[a] Fe^{59} and Cr^{51}.

[b] 99% Ru^{103}.

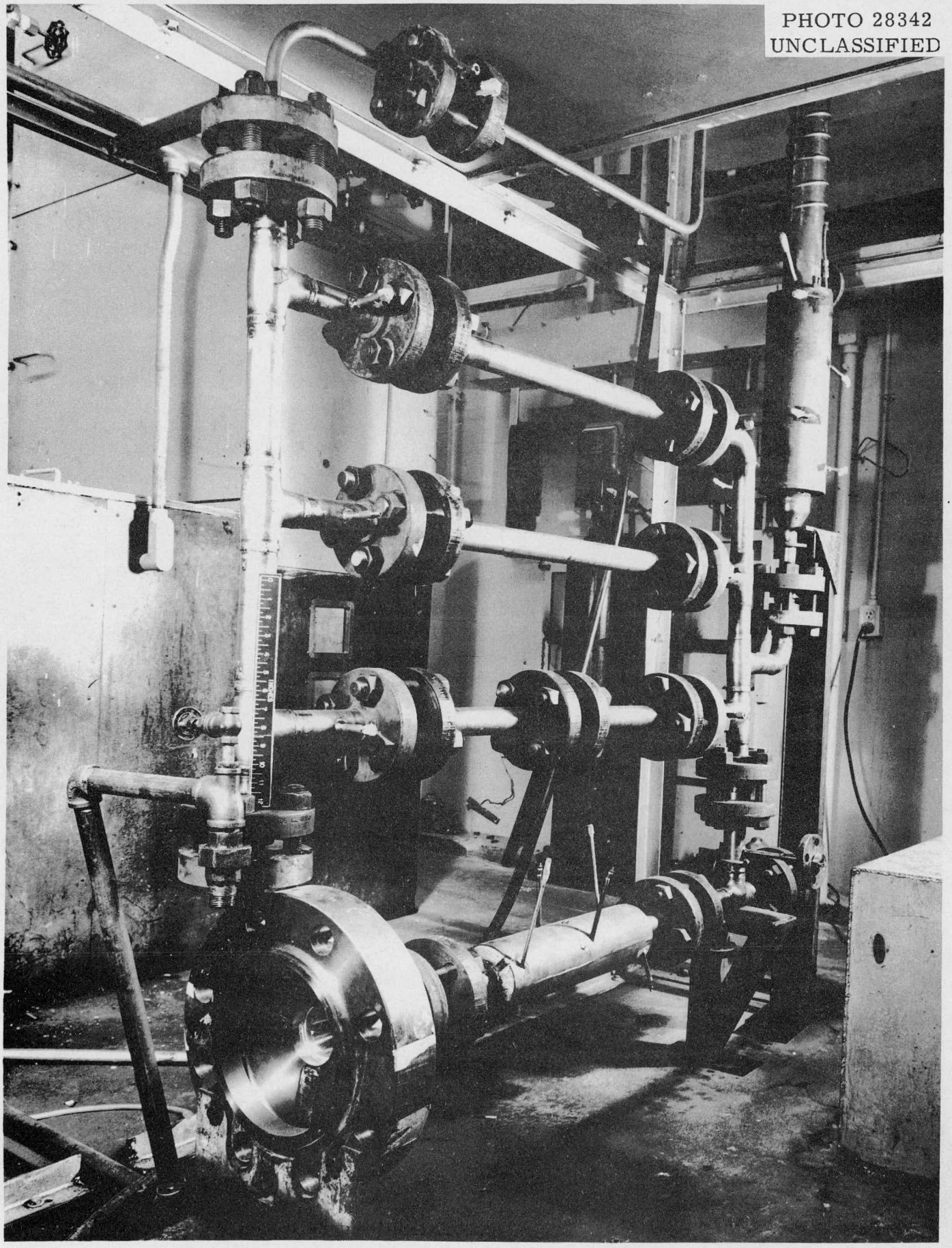

Fig. 1 Out-of-Pile Dynamic Loop

0.5 M H_2SO_4 solution at 85°C. Each loop had a capacity of 22 liters. Initially the corrosion film was so thick that during the thermal cycling tests for which the loop had been used, large flakes of corrosion products had frequently entered the circulating stream and clogged by-pass lines. At the end of the decontamination runs, the interior of the loop was free of all clinging oxide and the metal surface was bright and shiny. The corrosion products had dissolved during the descaling operation. A section of out-of-pile corrosion loop is shown in Fig. 2. The pipe was cut apart, and Section B was submitted to the descaling procedure. As is seen in the photograph, Section A has a heavy black oxide film on it while Section B is free of the film after the descaling procedure. The corrosion in the pipe (in section labeled C) is due to the 22,000 hr of operating with various uranyl sulfate solutions at 200-300°C and not to the chromous sulfate.

This was the first time that descaling of a loop was satisfactory. All previous attempts at descaling the dynamic corrosion loops were made with solutions which merely loosened the scale by dissolving the steel from under the oxide, and little if any of the oxide dissolved. Flushing the loose oxide from the piping system was difficult, and often resulted in plugging of the smaller pipes.

Corrosion with Chromous Sulfate

Corrosion data were obtained from sample pins inserted in the loop while the descaling operation was carried out. Corrosion of stainless steels in the 0.4 M $CrSO_4$--0.5 M H_2SO_4 solution at 85°C was 200-500 mils/year, and was not affected by the velocity of the solution in the range 10-80 ft/sec. Corrosion rates were higher, 800-1000 mils/year, in one run when the sulfuric acid concentration was 1.0 M, indicating the importance of limiting the acid concentration to 0.5 M. Although the corrosion rate was high, the actual depth of penetration per defilming operation was small since only 4 hr was required for complete oxide dissolution and removal. The penetration of 0.1-0.2 mil (Table IV) is not considered a serious drawback to use of the solution.

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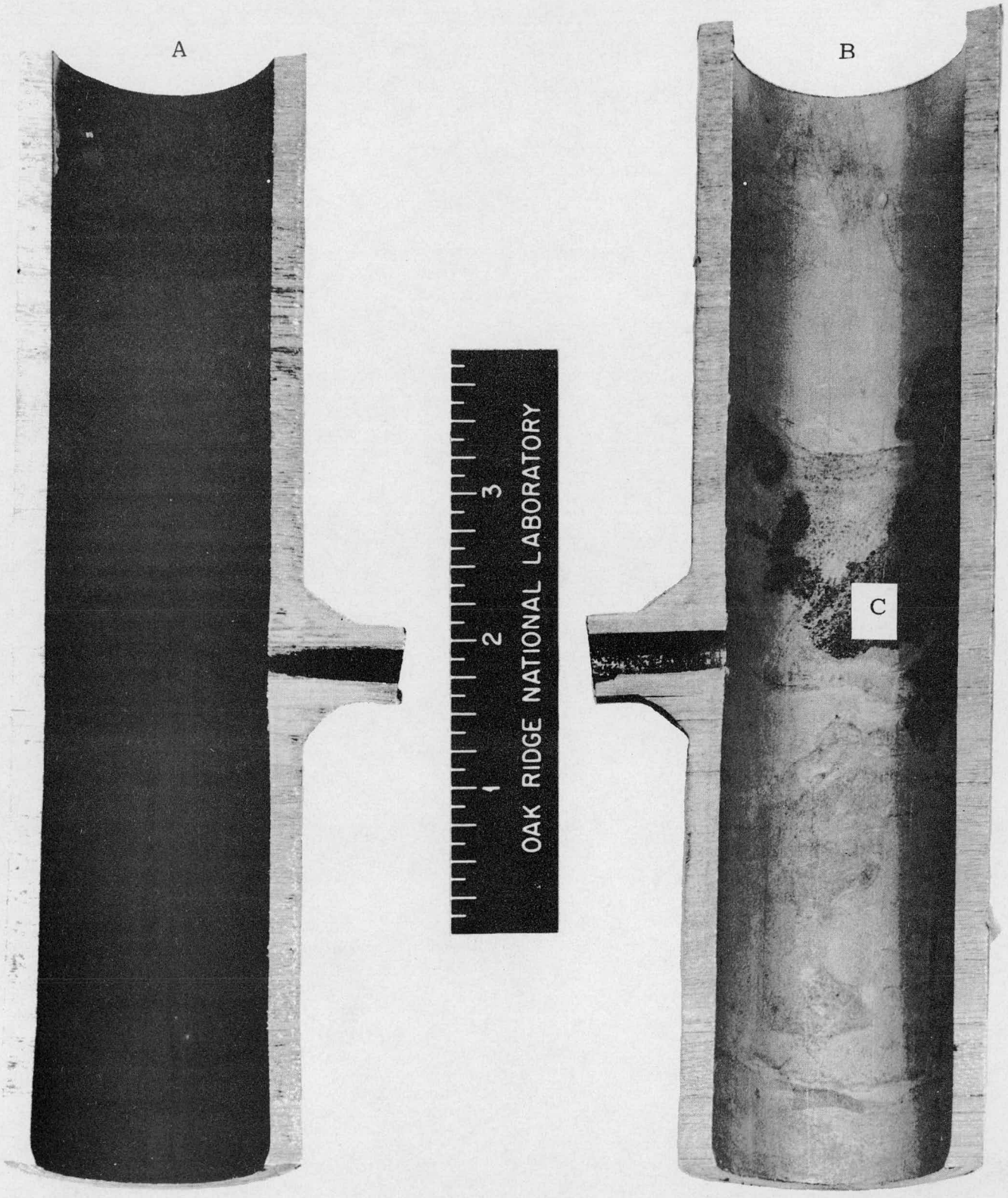

A. Before descaling
B. After descaling
C. Corrosion due to UO_2SO_4 at 250°C

Fig. 2 Section of Out-of-Pile Solution Loop

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Table IV

Corrosion of Metals in 0.32 M $CrSO_4$--0.65 M H_2SO_4 at 85°C

4.4 hr contact time in a dynamic loop

Material	Corrosion Rate (mils/year)	Depth of Penetration (mils)
Stainless Steels		
347	250	0.13
321	120	0.06
318	31	0.02
316	46	0.02
304L	320	0.16
Stellites		
98M2	23	0.01
6	77	0.04
1	69	0.04
Ti RC-55	56	0.03
Zr crystal bar	14	0.01

PREPARATION OF CHROMOUS SULFATE

Chromous sulfate solution was prepared from chromic sulfate by reduction with a metal, e.g., zinc, or by electrolytic reduction. Owing to several factors, such as ease of preparation, economics, and handling, the electrolytic method seems to be the most applicable for preparing large volumes of solution.

In the reduction with zinc, a potassium chrome alum--sulfuric acid solution is contacted with granular zinc under an inert atmosphere until the solution is reduced, and the acid is then adjusted to 0.5 M.

For the electrolytic method a cell shown (Fig. 3) was constructed. This cell consisted of alternating anode and cathode compartments separated by anion-exchange membranes to prevent the chromous ion from being oxidized back to the chromic state at the anode. Lead foil electrodes were used, and the reduction was carried out at a current density of 0.25 amp/in^2 with a nitrogen or carbon dioxide atmosphere in the cell. The chromic sulfate solution was pumped through the cell in such a way that the chromium in the solution emerging from the cell was almost completely reduced.

Chromous sulfate solution may also be made from sodium or potassium dichromate, which is considerably cheaper than chromic sulfate. The dichromate is reduced to a chromic solution by bubbling SO_2 through the solution, and this chromic sulfate solution is reduced to the chromous, as discussed above.

CONCLUSIONS

In the laboratory, chromous sulfate solution has given decontamination of stainless steel much superior to other reagents. It should be seriously considered for use in decontaminating homogeneous reactors since the method gives rapid descaling and decontamination with minimum expense and time, and with no introduction of a foreign ion into the reactor system which would hinder future operation.

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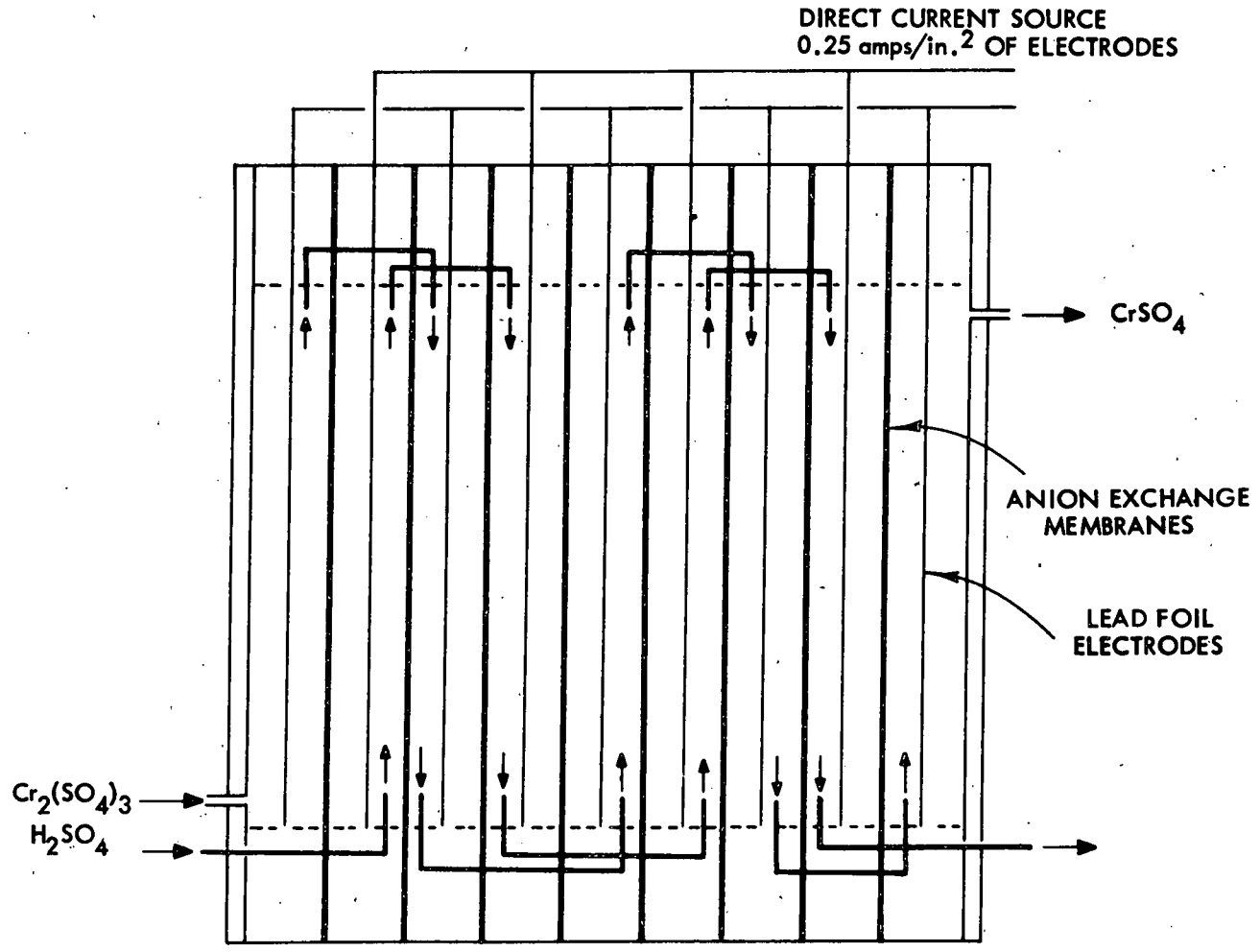

Fig. 3 Electrolytic Chromous Sulfate Reduction Cell

The reactor system can be decontaminated of virtually all the fission products, the decontamination being limited only by the induced activity in the structural material.

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