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EQUIPMENT DECONTAMINATION METHODS FOR THE FUSED SALT--FLUORIDE VOLATILITY PROCESS

R. L. Jolley
R. D. Baybarz
D. O. Campbell
G. I. Cathers

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ORNL-2550

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section A

EQUIPMENT DECONTAMINATION METHODS FOR THE FUSED SALT--FLUORIDE VOLATILITY PROCESS

R. L. Jolley, R. D. Baybarz, D. O. Campbell, G. I. Cathers

DATE ISSUED

AUG 19 1958

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ABSTRACT

The decontamination methods studied included barren salt flushes, 0.5 M ammonium oxalate solution, 5 wt % nitric acid--5 wt % aluminum nitrate solution, and 10 wt % sodium hydroxide--2.5 wt % hydrogen peroxide--10 wt % sodium tartrate solution. Salt flushes were relatively ineffective for decontamination, their effect being mainly dilution of residual salt. Ammonium oxalate solutions at 90-100°C dissolved $NaF-ZrF_4$ (50-50 mole %) and removed much activity. The nitric acid--aluminum nitrate solution was required to remove a metallic scale formed in inconel equipment as the result of contact with HF, F_2, and UF_6 at 600°C. The alkaline-peroxide-tartrate solution was particularly effective in decontaminating descaled reactors and equipment exposed to gaseous reactants and products of the fluoride volatility process. Some application of the principles involved in the decontamination procedures appears possible in other fused salt projects, for example, in molten salt reactor technology.

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1.0 INTRODUCTION

There is increasing consideration of the use of fused salts in power reactor fuel processing and in high temperature nuclear power reactor systems. The fused salt volatility process being developed at Argonne National Laboratory and Oak Ridge National Laboratory made desirable some study of equipment decontamination methods for maintenance and repair purposes.[1,2] This paper describes exploratory work undertaken on this subject in the laboratory in support of the ORNL volatility pilot plant. The results, however, may have wider application as interest in fused salt projects develops, for example, in the molten salt reactor program.[3,4]

The work was conducted almost entirely with the $NaF-ZrF_4$ (approximately 50-50 mole %) system used in the ORNL volatility process. An excellent test of decontamination methods was made in disassembling laboratory fused salt equipment that had been in contact at 500-700°C with approximately 100 curies of mixed fission products during processing of irradiated natural uranium. The decontamination methods were developed principally for inconel used in this equipment to contain the fused $NaF-ZrF_4$ material. Supporting work was necessary for equipment of stainless steel, nickel, copper, and brass used to a large extent in the gas-phase section of the process equipment.

The authors express your appreciation for the assistance of C. J. Shipman in performing the actual decontamination work, and of G. W. Wilson, J. H. Cooper, and H. A. Parker of the Analytical Chemistry Division for the chemical and radiochemical analyses.

2.0 NONAQUEOUS DECONTAMINATION

2.1 Removal of $NaF-ZrF_4$ and Activity with Flush Salt

Various flush salts were studied in exploratory work to determine their effectiveness in reducing the residual radiation level in equipment that had been used for radiochemical processing by the fused fluoride method. These included KHF_2, KBF_4, $NaZrF_5$, and K_2ZrF_6. The first three materials gave a significant amount of decontamination, probably as a result of removing residual fused salt. The best material was $NaZrF_5$ from the viewpoint of compatibility and low corrosion. KHF_2 appeared a desirable material because of its low melting point (239°C), a low but finite corrosion rate, and the fact that K_2ZrF_6, a possible product, has a high aqueous solubility (approximately 250 g/liter at 100°C). However, an overpressure of HF is necessary to prevent decomposition of KHF_2 (Fig. 1), the overpressure being, moreover, highly dependent on the KF/HF mole ratio,[5] and the use of a low-melting salt requires removal of excess salt by a solids dissolution process. For this reason, more consideration was given to high-melting salts such as KBF_4 (529°C) and $NaZrF_5$ as flush salts. The 750°C melting point of K_2ZrF_6 is high compared to the temperature range 550-650°C usually used with the $NaF-ZrF_4$ system and thus eliminated its use as a flush salt despite aqueous compatibility.

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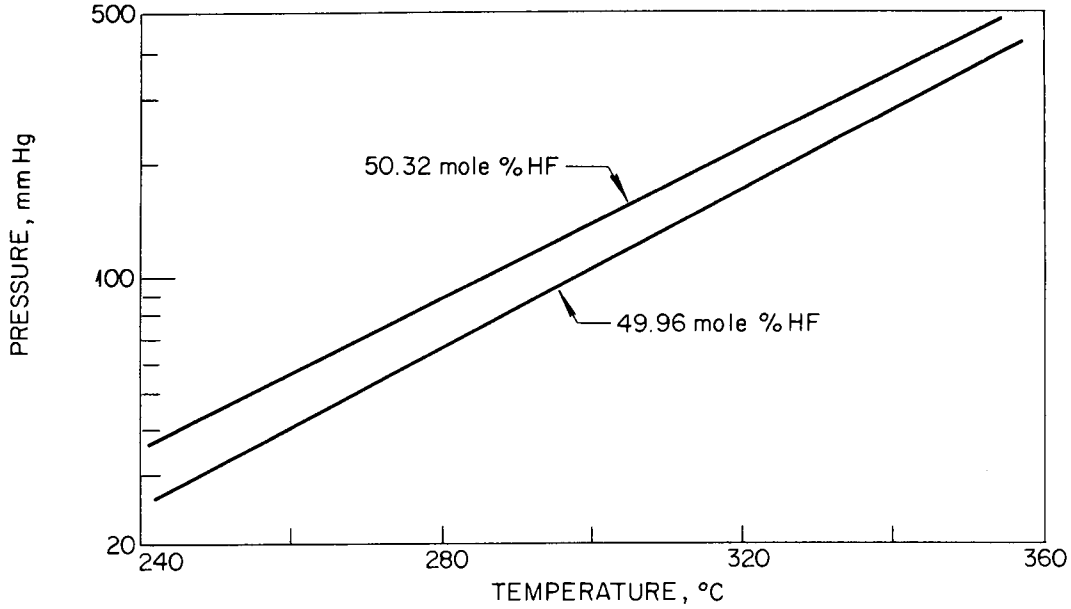

Fig. 1. Dependence of HF vapor pressure over KHF_2 on temperature.

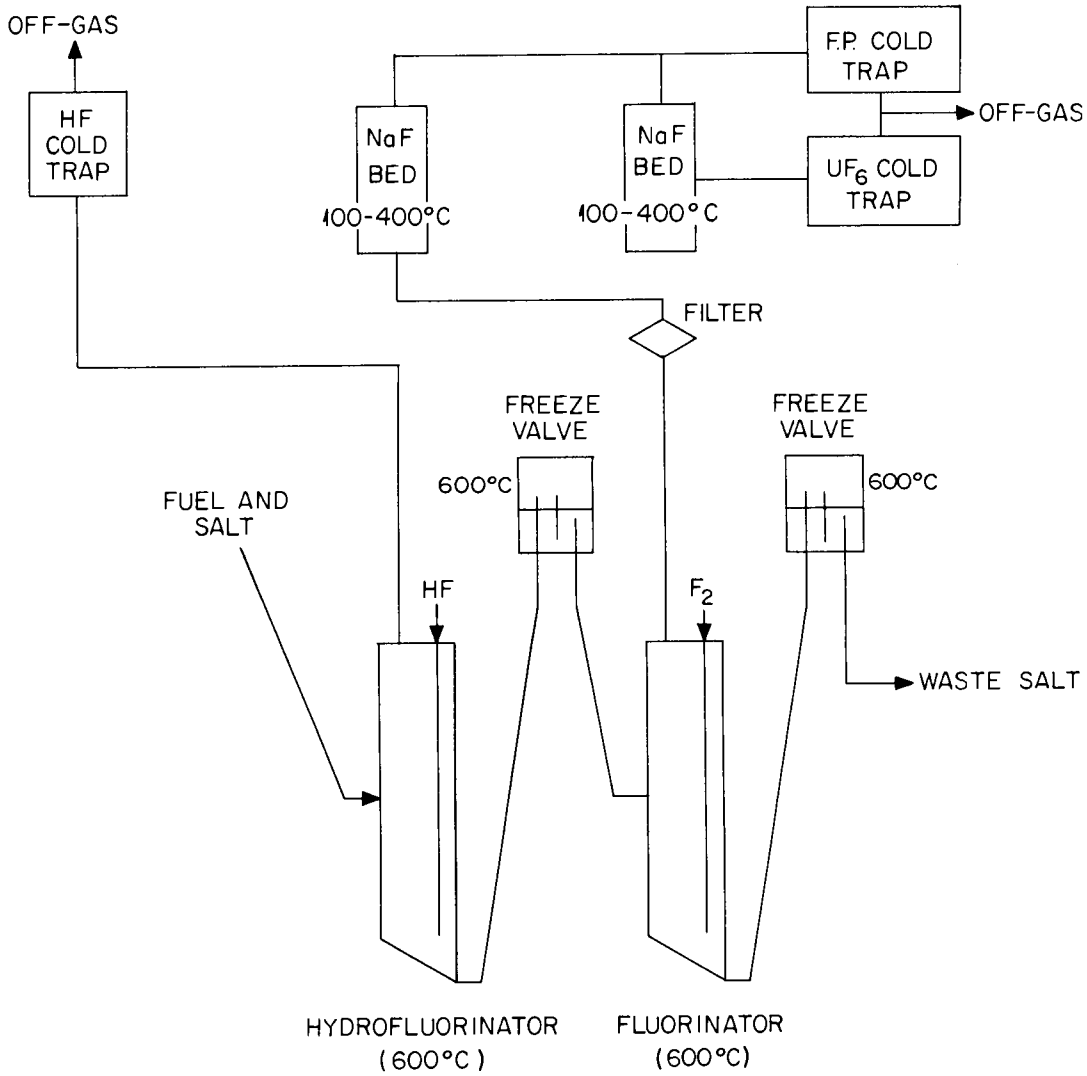

Fig. 2. Fused Salt – Fluoride Volatility process equipment.

Nickel and inconel coupons (1 by 3 cm) were prepared for testing by exposure at 650°C to fused $NaZrF_5$ containing mixed fission products; radiation readings were 0.1-10 r/hr at about 1 in., depending on the amount of clinging salt. The radiation level did not appear particularly dependent on the length of exposure time. Exposure of these coupons for 15 min to either KHF_2 at 275°C, KBF_4 at 550°C, or mechanical removal of the residual salt reduced the radiation to approximately 65 mr/hr. Longer submersion in the fused salt resulted in somewhat greater decontamination. In one test the contamination of a nickel coupon was decreased from 350 mr/hr to 10 mr/hr by exposure to KHF_2 at 250°C for 10 min. An additional 4 hr in the KHF_2 lowered the activity to about 1 mr/hr.

The efficiency of decontamination (after removal of residual salt) is believed related to some extent to corrosion. KHF_2 at 250°C gave gravimetric static corrosion rates of approximately 40, 25, and 13 mpy on inconel, nickel, and monel, respectively. The inconel was visually pitted.

$NaF-ZrF_4$ (50-50 mole %) was tested for decontaminating fused salt laboratory equipment that had been used over a period of one year with irradiated uranium.[2] The design of the equipment system, and particularly of the freeze valves, made it difficult to blow the system for eventual passage of aqueous decontaminating solutions. The inconel laboratory system, consisting of a hydrofluorinator, fluorinator, freeze valves and transfer lines (Figs. 2 and 3), was flushed three times with the standard $NaF-ZrF_4$ salt loading of 440 g. The total heel in the entire system was approximately 250 g, making a dilution ratio of ~1/3 for each salt pass. The effect of the three salt passes was to reduce the activity in the residual salt by factors of 40, 24, 7, 55, 60, and 51 for gross β, gross γ, Ru γ, Zr γ, Nb γ, and total rare earth β activities, respectively. This was in fair agreement with the expected total dilution factor of 27. The exception was ruthenium, which is suspected of having plated out in parts of the system. Further work with salt flushing was not pursued since activity deposited in the upper portion (gas region) of the reactors was not being removed, and the radiation level was still high (10-100 r/hr).

3.0 AQUEOUS DECONTAMINATION

Several approaches have possible application in the aqueous dissolution or removal of radioactive fused fluoride salts. The use of aluminum nitrate or boric acid to complex fluoride is feasible, but usually in combination with corrosive mineral acids. In the case of $NaF-ZrF_4$ salt, oxalate complexing of the zirconium is attractive. The use of ammonium oxalate is desirable because it is nearly neutral and is not highly corrosive, and because one reaction product, ammonium fluoride, has a high aqueous solubility. Tartrate in combination with alkaline peroxide was particularly applicable in the decontamination of activity from fused salt equipment as well as from gas phase equipment used in the volatility process. Chemical descaling and controlled corrosion, as typified by use of a dilute nitric acid--aluminum nitrate solution, is another method investigated briefly.

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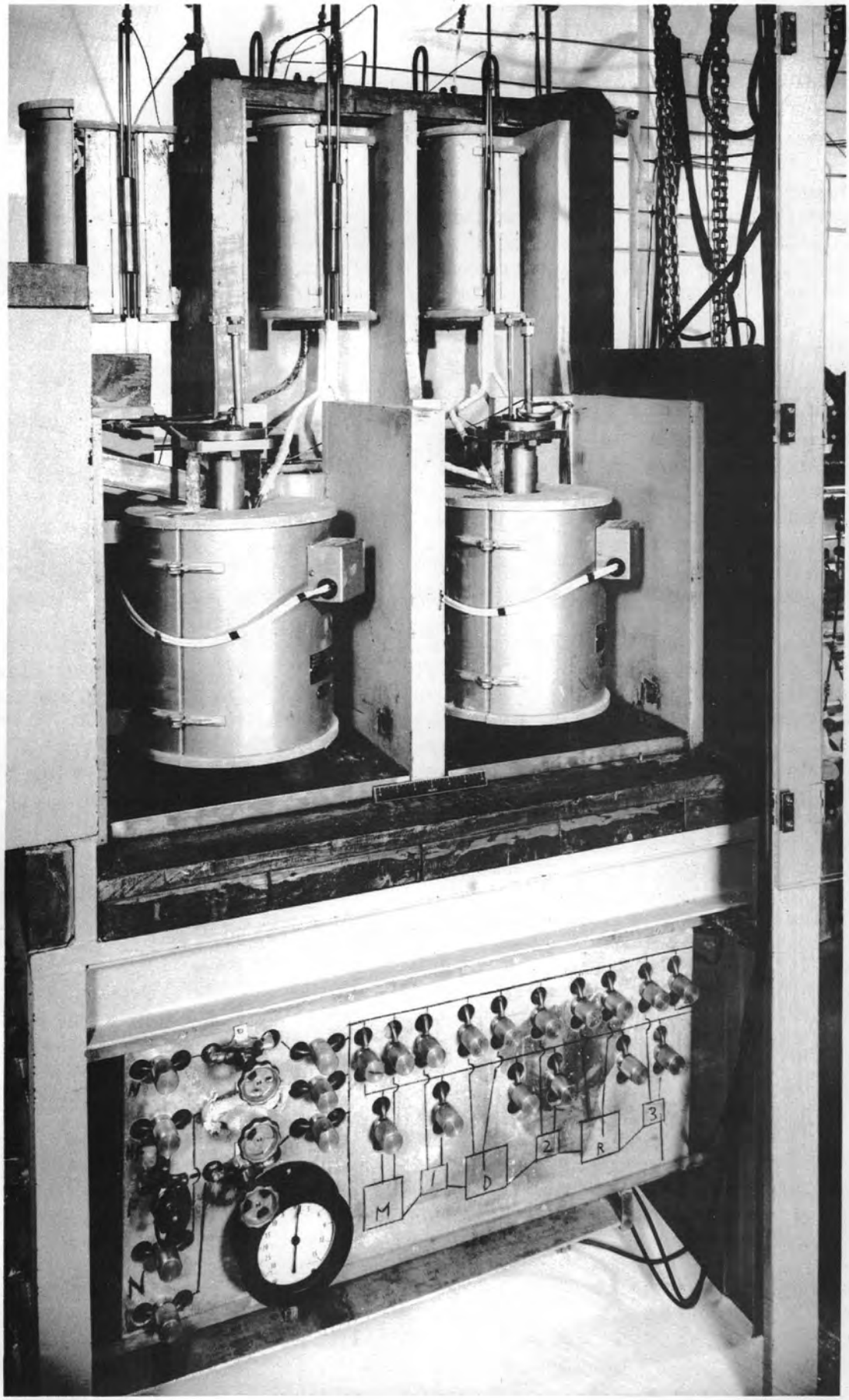

Fig. 3. Shielded section of fused salt volatility process development equipment.

3.1 Ammonium Oxalate

Ammonium oxalate solutions were studied in relation to the solubility of ammonium oxalate in water, the solubility and solution rate of $NaF-ZrF_4$ (50-50 mole %) in oxalate solution, and the corrosion rates of inconel and nickel in oxalate solution. Increasing the ratio of oxalic acid to ammonium oxalate improved solubility, but corrosion was greater at the lower pH.

The solubility of ammonium oxalate is very dependent on temperature. At 25°C, the solubility of ammonium oxalate is slightly less than 0.4 M, with a pH about 6. At 90°C, the solubility is in excess of 1 M. The capacity of 0.5 M ammonium oxalate was approximately 80-100 g of $NaF-ZrF_4$ per liter of solution, corresponding to a zirconium/oxalate mole ratio of about 1/1. Solutions containing about 0.5 M ammonium oxalate and 0.5 M zirconium were stable at room temperature and capable of dissolving more ammonium oxalate, up to a total of 1 M, without precipitation, i.e., with a zirconium/oxalate mole ratio of about 1/2. Such a solution was capable of dissolving more $NaF-ZrF_4$, but the 80-100 g/liter capacity of 0.5 M ammonium oxalate solution was believed adequate for decontamination work.

The solution rate of $NaF-ZrF_4$ in 0.5 M ammonium oxalate was very dependent on temperature. At 80-90°C a rate of about 0.2 mm/hr was measured, a rate apparently independent of the amount of salt dissolved. No quantitative measurements were made at reflux, but the rate appeared larger by at least an order of magnitude, possibly 1 cm/hr. Dissolution of large masses of salt is feasible in short periods if the temperature is near the reflux point.

The corrosion rate of inconel in 0.5 M ammonium oxalate solution at reflux temperature was studied as a function of the amount of $NaF-ZrF_4$ salt dissolved (Fig. 4). These corrosion rates were determined by measurement of weight losses, and therefore do not accurately reflect the amount of intergranular corrosion attack. The time required for $NaF-ZrF_4$ salt dissolution in these corrosion tests was usually short (a few minutes) compared to the total corrosion test time ($\sim$24 hr). The various amounts of $NaF-ZrF_4$ dissolved did not affect the initial pH of 6 to any extent. The highest corrosion rate of 6×10^{-4} mil/hr was obtained with no fused salt present. It is interesting to note that as $NaF-ZrF_4$ is added the corrosion rate is inhibited somewhat, probably because of the utilization of the oxalate in complexing the zirconium. In other tests the corrosion attack on inconel was approximately 2×10^{-3} mil/hr at a pH of 2-3.

The corrosion rate of nickel in 0.5 M ammonium oxalate at pH 6 was comparable to that of inconel. With no $NaF-ZrF_4$ present, the corrosion rate was 4.5×10^{-4} mil/hr at reflux temperature. With 4 g of $NaF-ZrF_4$/100 ml solution, the corrosion rate was lowered to 8.8×10^{-5} mil/hr at reflux. At higher pH's the corrosion rate with no $NaF-ZrF_4$ present was essentially the same. The corrosion rate at pH 2 with 4 g of $NaF-ZrF_4$/100 ml solution was 1.67×10^{-3} mil/hr.

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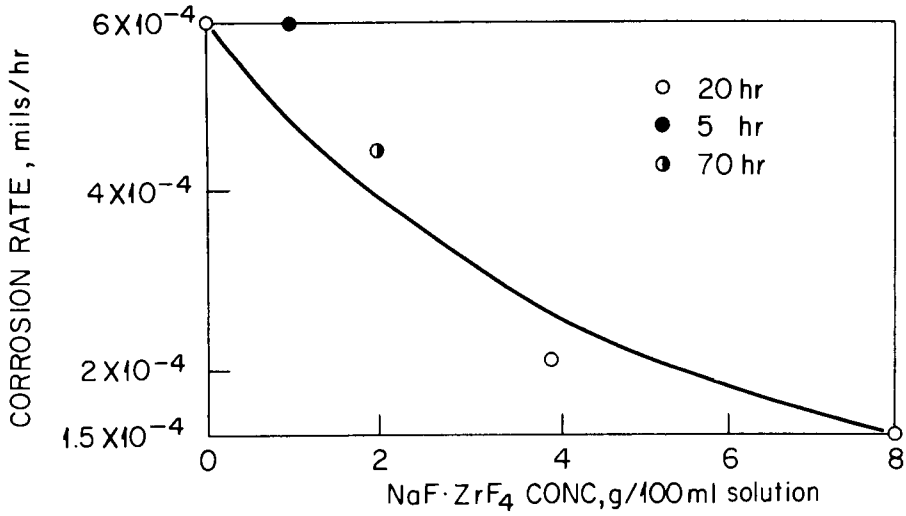

Fig. 4. Corrosion rate of inconel in 0.5 *M* $(NH_4)_2C_2O_4$ at reflux temperature.

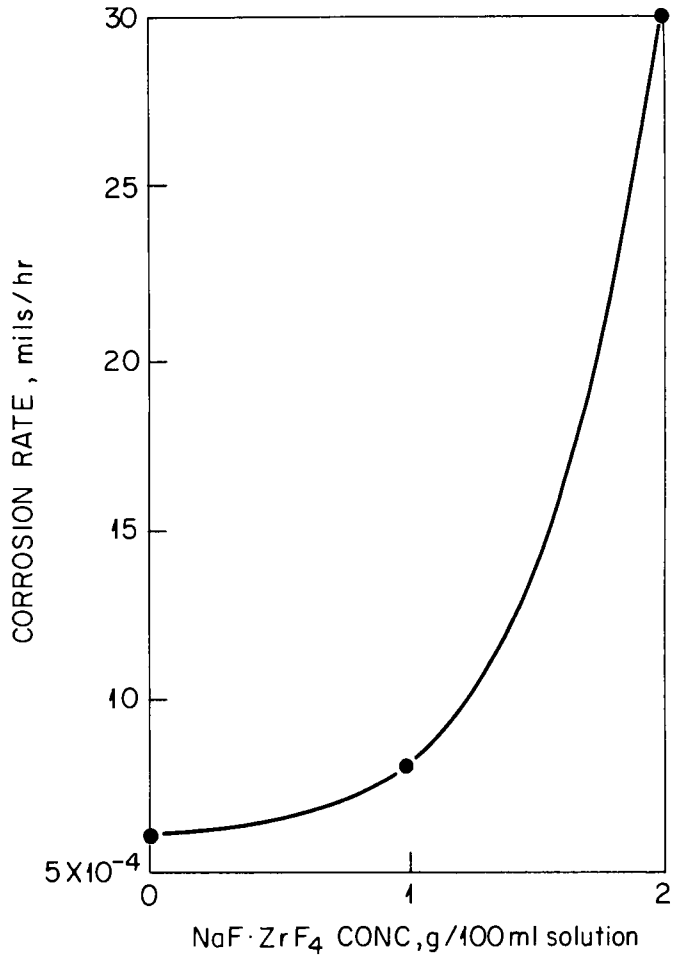

Fig. 5. Corrosion rate of inconel in 5 wt% HNO_3 -- 5 wt % $Al(NO_3)_3$ at reflux temperature.

3.2 Nitric Acid-Aluminum Nitrate Solution

A 5 wt % HNO_3--5 wt % $Al(NO_3)_3$ solution was developed for and effective in dissolving a scale (predominantly nickel metal) that had deposited inside of the inconel reactors wherever there was contact with salt. It was a particularly effective decontaminating agent in this case owing to the large amount of activity (mainly ruthenium) in the scale. The action of the nitric acid--aluminum nitrate solution is an example of controlled corrosion by a buffered acidic solution.

The 5 wt % HNO_3--5 wt % $Al(NO_3)_3$ solution was highly corrosive to nickel but much less so to inconel, particularly in the absence of fluoride. The inconel corrosion rate at reflux temperature was 6×10^{-4} mil/hr. The corrosion rate was studied in the presence of $NaF\text{-}ZrF_5$ as a slurry in order to determine the effect of fluoride salt presence (Fig. 5). As the amount of $NaF\text{-}ZrF_4$ present increased, the corrosion rate rose rapidly. The corrosion was measured by weight loss and therefore did not show if intergranular penetration or pitting occurred.

3.3 Alkaline-Peroxide-Tartrate Solution

During operation of volatility equipment in the laboratory an alkaline--peroxide-tartrate solution (10 wt % NaOH-2.5 wt % H_2O_2-10 wt % Na tartrate) at room temperature proved efficient for the decontamination of equipment exposed to gaseous and entrained fission products in either the hydrofluorination or fluorination step. It appeared particularly good for ruthenium although originally developed to remove zirconium and niobium.[6] The corrosion rate on inconel by itself or with a 2-4 g $NaF\text{-}ZrF_4$/100 ml slurry was 5.8×10^{-5} mil/hr. There was no increase with $NaF\text{-}ZrF_4$ present. The corrosion rate of nickel was 2.3×10^{-5} mil/hr under the same conditions.

The first evidence of the efficiency of alkaline-peroxide-tartrate reagent was obtained in the case of stainless steel traps used for volatile fission product fluorides in the volatility process, and therefore contaminated primarily with ruthenium activity.[2] Hot 8 M HNO_3 containing some fluoride was only partially effective in reducing the radiation level by a factor of 5. Two 250-ml rinses with alkaline-peroxide-tartrate reagent reduced the radiation reading from 600 to 20 mr/hr, with most of the reduction occurring with the first rinse. The removed activity was determined to be more than 99% ruthenium.

The alkaline-peroxide-tartrate solution was used frequently in decontaminating laboratory equipment used in development of the volatility process, including copper UF_6 process lines, stainless steel cold traps, and nickel micrometallic filters. Contact radiation readings of several hundred milliroentgens per hour were generally reduced to < 10 mr/hr with this solution at room temperature. For example, a stainless steel trap used for condensed HF from the process was decontaminated by overnight solution contact from an initial reading of 400 mr/hr down to background.

4.0 AQUEOUS DECONTAMINATION OF HIGH-LEVEL LABORATORY PROCESS EQUIPMENT

Use of the three aqueous methods described in the previous sections led to completely satisfactory decontamination of the inconel system (hydrofluorinator, fluorinator, freeze valves, and salt lines) used more than a year with fused salts for high-level activity volatility process testing (Figs. 2 and 3). This was carried out to a large extent with the equipment in situ behind 4 in. of lead shielding as used in process testing. Complete decontamination without some disassembly was not possible because of the equipment not having been designed with this in mind. Sufficient decontamination of the equipment was carried out with the shielding in place before the final disassembly and decontamination. Decontamination of this equipment appears to have been justified from the interesting results obtained in final examination of the equipment, particularly in relation to the process corrosion and activity behavior after use over a year. Discussion of the status of the equipment, corrosion-wise, will be made the subject of a separate report after metallurgical examination is complete.

The three types of aqueous decontamination solution were circulated through separate parts of the process system by means of a finger pump (Sigmamotor). The high level of residual activity in the equipment, even after barren salt flushing, necessitated use of a large number of separate solutions to minimize personnel exposure. In a properly designed system convenient crossover of the nonaqueous process system to an aqueous condition would be provided.

The total amounts of salt and activities removed in the aqueous treatment of the two main process vessels are summarized in Table 1. The first solution used was 0.5 M ammonium oxalate at approximately 95°C. This removed most of the salt heel along with some scale and sludge. The presence of some nickel fluoride was expected, and seemed confirmed by the fact that at least 20 g of nickel was removed by the oxalate treatment from each reactor. Smaller amounts of chromium and iron were removed. The oxalate treatment was highly effective in removing gamma activity from the fluorinator (largely niobium), but was less effective in the case of the hydrofluorinator because of ruthenium.

After further alternate treatments with oxalate and tartrate solutions failed to lead to the expected reduction of the gamma field, partial disassembly of the equipment revealed an adherent metal scale on all the reactor surfaces. It was heavier in the part in contact with fused salt. Dilute nitric acid--aluminum nitrate decontamination reagent successfully removed the scale and reduced the radiation to the point where total disassembly of the equipment was possible. The equipment was further decontaminated with alternate use of the different decontamination reagents.

The extent to which decontamination was carried is illustrated by a schematic (Fig. 6). In the fluorinator, radiation in the zone in contact with liquid salt was reduced to lower readings (1-16 mr/hr) than that in the gas zone just above the liquid salt zone. This may have been due to the local high concentration of activity (ruthenium and niobium) as volatilized from the salt during the fluorination.

Table 1. Removal of Residual Salt, Scale and Associated Activity from Process Equipment by Aqueous Decontamination Procedure

Salt and Scale	Fluorinator				Hydrofluorinator			
	Total, g	% of Total			Total, g	% of Total		
		By Oxalate	By Acid	By Tartrate		By Oxalate	By Acid	By Tartrate
$NaZrF_5$ salt	109.4	94.7	0.4	4.9	138.3	98.8	---	1.2
Nickel	20.2	49.4	49.1	1.5	43.5[a]	28.4	68.5[a]	3.1
Iron	1.8	64.3	11.2	24.5	2.6	80.4	6.9	12.7
Chromium	2.3	69.1	17.2	13.7	1.0	84.8	8.6	6.6
Activity	(c/m)				(c/m)			
Gross β	5.4×10^9	22	62	16	8.5×10^{10}	26	55	19
Gross γ	4.2×10^{10}	78	19	2.6	7.5×10^{10}	28	51	21
Ru γ	5.1×10^9	39	49	12	6.2×10^{10}	24	53	23
Zr γ	4.2×10^8	98	0.6	1.8	5.0×10^8	97	1.3	1.7
Nb γ	2.4×10^{10}	98	0.5	1.2	2.4×10^9	68	15	17
Cs γ	2.8×10^9	97	0.1	2.5	3.4×10^8	92	4.3	3.5
Ce β	4.0×10^9	98	---	1.7	3.0×10^8	33	1.4	66
TRE β	5.1×10^9	98	0.1	1.5	4.6×10^8	43	7	50
Pu α	7.4×10^8	99	---	0.4	9.9×10^6	86	5	9

[a]High because of some corrosion of the nickel chute that was attached to the inconel hydrofluorinator vessel.

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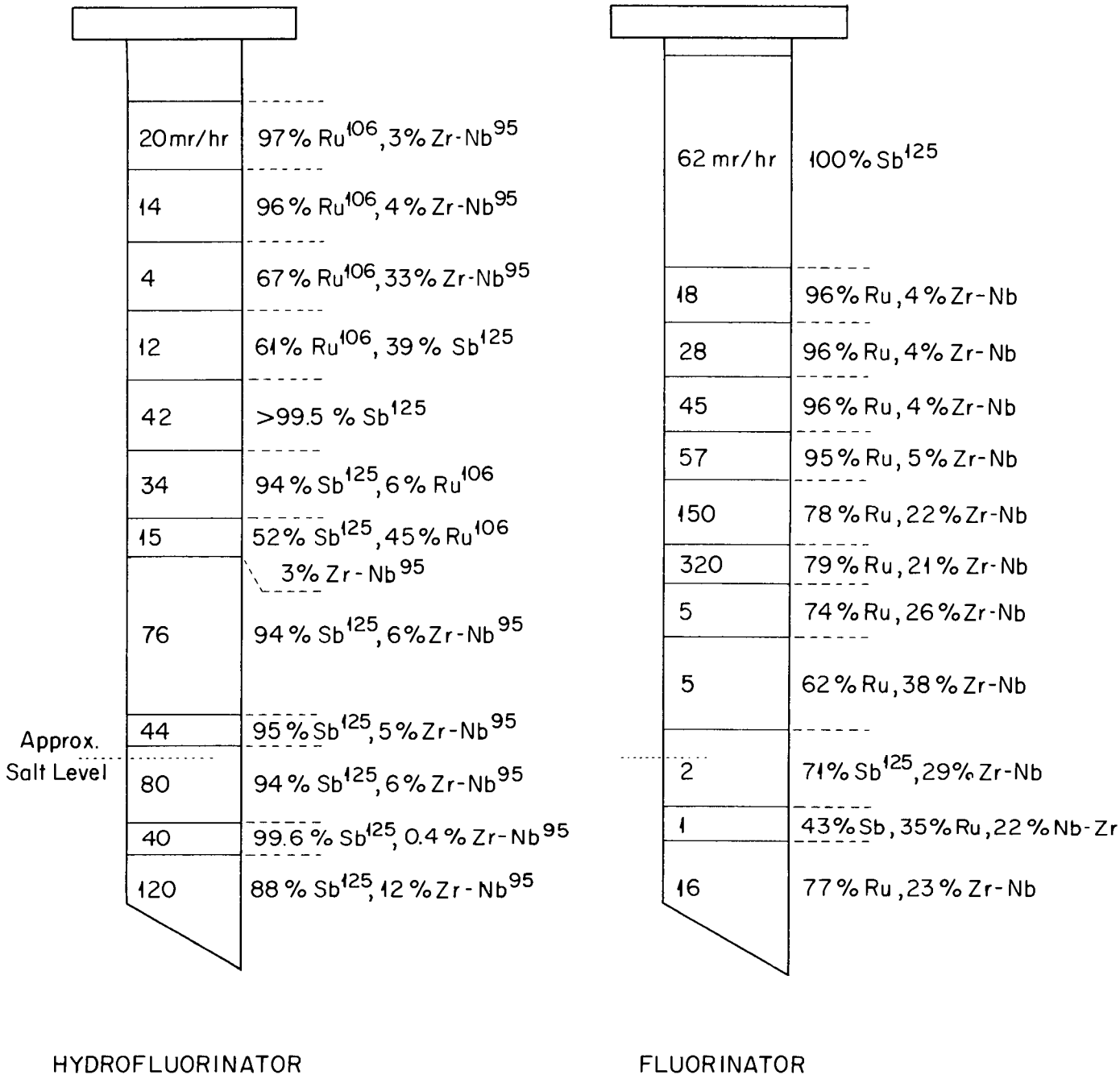

Fig. 6. Activity distribution in vessels after decontamination (radiation readings at 0.5 in.)

The activities remaining in the fluorinator and hydrofluorinator vessels were determined by scanning with a gamma spectrometer, and by radiochemical analysis of dissolved metal samples taken from the sectioned reactors. The distribution of activities reflects partially the behavior of fission product fluorides in the volatility process.

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