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ABSTRACT

Methods of removing radioiodine from ^{237}Np-^{238}Pu dissolver solution and process off-gas were investigated. This program is part of a continuing effort to reduce releases of radionuclides from plant operations. The experimental data in this report show:

- Greater than 99.9% of the radioiodine in dissolver solution can be removed by precipitation, *in situ*, of manganese dioxide.
- Silver zeolite will sorb >99.9% of radioiodine in process off-gas.
- Other solid sorbents and nitric acid-mercuric nitrate scrubber solutions do not remove appreciable amounts of radioiodine from process off-gas, because radioiodine is present principally as relatively unreactive organic iodine compounds.

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INTRODUCTION

In the Savannah River Plant process[1,2] for the production of ^{238}Pu, irradiated ^{237}Np targets are dissolved and processed by anion exchange to remove fission products and nonradioactive impurities.[3] Radioiodine is one of the more volatile fission products and can be evolved during processing. The isotope of most concern for short-term exposure is ^{131}I with a 8.04-day half-life. Iodine-129 with a 1.59×10^7 y half-life is also of environmental interest, but its low specific activity moderates its population dose potential. Presently, release of short-lived radioiodine to the environment is minimized by processing only long-cooled ^{237}Np targets that contain little ^{131}I.

A program was undertaken to evaluate techniques that might be used should it be desired to further reduce ^{131}I releases. This report describes studies of (1) methods of removing radioiodine from dissolver solutions, (2) solid sorbents and aqueous scrub solutions for removal of radioiodine from process off-gas, and (3) the efficiency of the current process vessel vent scrubber system.

REMOVAL OF IODINE FROM DISSOLVER SOLUTION

Plant tests were conducted in 1967 to identify steps in ^{237}Np-^{238}Pu processing that are responsible for radioiodine releases. The irradiated ^{237}Np targets being processed contained approximately 1600 Ci of ^{131}I. Approximately 3 Ci of ^{131}I was released during dissolution, anion exchange, waste transfer, and waste recovery. Only 1% of the 3 Ci was released during dissolution; 99% was released during anion exchange and waste recovery. Based on these results, a removal factor (RF = ^{131}I input/^{131}I effluent) of 100 could be attained if iodine were removed from dissolver solution prior to anion exchange processing. This approach was evaluated with both simulated and actual plant dissolver solution. MnO_2 sorption, HgI_2 carrier precipitation, and CuI sorption were studied.

MnO_2 Sorption

Fission products such as ^{95}Zr and ^{95}Nb are removed from solution by sorption on MnO_2 during routine uranium separations processes. In plant tests, a 25-fold decrease in released ^{131}I was obtained by treating uranium dissolver solutions with 5×10^{-4}M Hg^{2+} and MnO_2.[4] Based on these results, tests were made to determine the efficiency of iodine sorption on MnO_2 at various conditions.

Thermodynamic calculations (Equations 1 through 5) indicate that ^{131}I is predominantly in the form of iodate in dissolver solutions that contain MnO_2 and Hg^{2+}. (In the current ^{237}Np process, Hg^{2+} is used to promote dissolution of aluminum, but MnO_2 is absent.)

	ΔG, kcal/mole	
$3MnO_2 + 6H^+ + I^- \rightarrow IO_3^- + 3H_2O + 3Mn^{2+}$	-20.1	(1)
$Hg^{2+} + I^- \rightarrow HgI^+$	-17.8	(2)
$2Hg^{2+} + I^- \rightarrow Hg_2I^{3+}$	-18.6	(3)

$$\frac{(IO_3^-)}{(HgI^+)} = \frac{47.8(H^+)^6}{(Mn^{2+})^3(Hg^{2+})} \quad (27°C) \qquad (4)$$

$$\frac{(IO_3^-)}{(Hg_2I^{3+})} = \frac{12.5(H^+)^6}{(Mn^{2+})^3(Hg^{2+})^2} \quad (27°C) \qquad (5)$$

Equations 4 and 5, derived from Equations 1-3, give the concentration ratios of iodate to HgI^+ and Hg_2I^{3+}. In typical dissolver solutions, the numerators in the right-hand sides of Equations 4 and 5 would be $\sim 10^5$, and the denominators would be less than unity. Removal of iodate from nitric acid solutions by MnO_2 is known, but the effect of Hg^{2+} was not determined.[5]

Neptunium-237 dissolver solution was simulated by dissolving an unirradiated $^{237}NpO_2$-Al compact in 9M HNO_3 containing small amounts of Hg^{2+} and F^-. The composition was:

^{237}Np	6.2 g/l
Al	1.2M
HNO_3	5.0M
Hg	0.004M
F^-	0.02M
I^-	10^{-6}M

KI was added after dissolution. This composition approximates that of actual dissolver solutions except that ^{238}Pu and fission products are absent.

At room temperature, MnO_2 was either added as a slurry or formed *in situ* in 100 ml of simulated dissolver solution by adding Mn^{2+} followed by MnO_4^-; the mixture was stirred 15 minutes and filtered. Filtrate, feed, and dissolved MnO_2 precipitate were analyzed for ^{131}I by high resolution Ge(Li) gamma spectroscopy. Material balance for ^{131}I was 100 ±10%. As shown in Table 1, ^{131}I removal was highest (greater than 99.9%) with 0.1M MnO_2 formed *in situ*. MnO_2 formed *in situ* was also more effective in removing ^{95}Zr and ^{95}Nb.

TABLE 1. ^{131}I Sorption on MnO_2

	^{131}I Removal Factor[a]	
MnO_2, M	MnO_2 Formed *in situ*	MnO_2 Added
0.01	10	50
0.05	260	340
0.10	>1170	510

---

a. Concentration ratio, ^{131}I initial/^{131}I after MnO_2 addition

Additional tests were made with 0.1M MnO_2 and simulated dissolver solution containing ^{238}Pu (0.69 g/l). Lower ^{131}I removal factors were obtained, probably because of radiolytic interactions. Removal of ^{131}I was again highest with 0.1M MnO_2 formed *in situ*, rather than added, with removal factors of 600 and 320, respectively. Heating the solution to 70°C reduced iodine removal factors to 350 and 100, respectively.

Sorption of iodine from two samples of actual dissolver solution was also investigated. The compositions of dissolver solutions were:

	(1)	(2)
^{237}Np, g/ℓ	1.8	2.6
^{238}Pu, g/ℓ	0.5	0.8
Al, M	1.2	1.2
H^+, M	3.1	5.3

Fission Products: (disintegrations per minute per milliter)	^{103}Ru, ^{95}Zr, ^{95}Nb:	10^{10}-10^{11}
	^{106}Ru, ^{144}Ce:	10^{9}-10^{10}
	^{137}Cs:	3-4 x 10^{8}

^{131}I was not present in measurable amounts since the irradiated ^{237}Np targets had been cooled more than 100 days. ^{131}I (as a dilute, alkaline KI solution) was added to 100 ml of dissolver solution and equilibrated for 60 hours. High levels of fission product activity precluded analyzing ^{131}I solutions directly, and ^{131}I was removed from test solutions by solvent extraction[6] with 30% tributyl phosphate (TBP) in *Ultrasene*.* The ^{131}I-containing extractant was then agitated with $AgNO_3$ crystals. $Ag^{131}I$ formed on the surface of the $AgNO_3$ crystals. After filtration, $AgNO_3$ and AgI were dissolved in aqueous KCN, and the solution was analyzed. (The accuracy of this analytical method was determined with simulated dissolver solution; about 90% of ^{131}I added was recovered.)

Iodine removal factors with actual dissolver solutions at 25°C were 3700 and 3250 when 0.1M MnO_2 was formed *in situ*, and 100 when 0.1M MnO_2 was added to the solution.

Tests were also made with freshly precipitated and aged MnO_2 in packed columns. Because of high pressure drop across the MnO_2 bed, a MnO_2-polysilicic acid sorbent containing 12 wt % MnO_2 (preparation given in the Appendix) was used in subsequent tests. A 50- to 100-mesh fraction of the MnO_2-polysilicic acid sorbent was used for ^{131}I removal tests with simulated and plant dissolver solution. The column bed was 1 cm in diameter x 19.5 cm long (15 cm^3 bed volume). Dissolver solutions containing ^{131}I were passed through the column at 2 ml/(min-cm^2) at 23°C. The iodine removal factor was 2.4 x 10^4 for simulated dissolver solution and greater than 1.5 x 10^4 for actual dissolver solution,

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* Tradename of a refined alkane C_{12} raffinate from Atlantic-Richfield Co., Philadelphia, Pa.

as determined by the solvent extraction technique. Although iodine removal was improved as compared to *in situ* tests, the sorbent is susceptible to osmotic shock* and must be conditioned with dilute (0.25M) and then increasingly concentrated nitric acid to the final acid concentration of the feed. Otherwise, fines are produced that cause high pressure drop across the bed.

CuI Sorption

Sorption of ^{131}I from dissolver solutions onto CuI was measured. In the tests, 0.01 mole of solid CuI added to 100 ml of simulated dissolver solution removed approximately 93% of the ^{131}I. This treatment is less efficient and more expensive than sorption with MnO_2.

HgI_2 Carrier Precipitation

Removal of ^{131}I from ^{237}Np dissolver solutions by carrier precipitation of HgI_2 was evaluated. The solubility of HgI_2 in 0 to 16M HNO_3 was determined by equilibrating acid solutions with excess solid HgI_2 (greater than 99.9% pure) at 30°C for 24 hours. The aqueous phases were isolated and analyzed for mercury by atomic absorption spectroscopy (Figure 1). Samples with $\geqslant$8M HNO_3 contained elemental iodine in solution after equilibration; samples with 14M and 16M HNO_3 contained both solid and dissolved elemental iodine. The solubility data indicate that 90% of the ^{131}I could be precipitated as HgI_2 from ^{237}Np dissolver solution (5M HNO_3).

Removal of ^{131}I was determined in tests with simulated dissolver solution. A solution containing up to 0.015M KI was added to precipitate HgI_2. At 0.005M KI, HgI_2 was formed but redissolved rapidly as I^- was oxidized to elemental iodine. Above 0.005M, HgI_2 did not redissolve, but elemental iodine also formed, and only 45 to 60% of the ^{131}I was removed. Addition of reductants such as sulfamic acid or sodium thiosulfate did not improve ^{131}I removal. Based on these results, this method was not considered suitable for plant operation.

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* Abrupt changes in concentration gradient cause increased pressure in sorbent particles as ions (molecules) diffuse into the matrix. This causes fracturing of the particles.

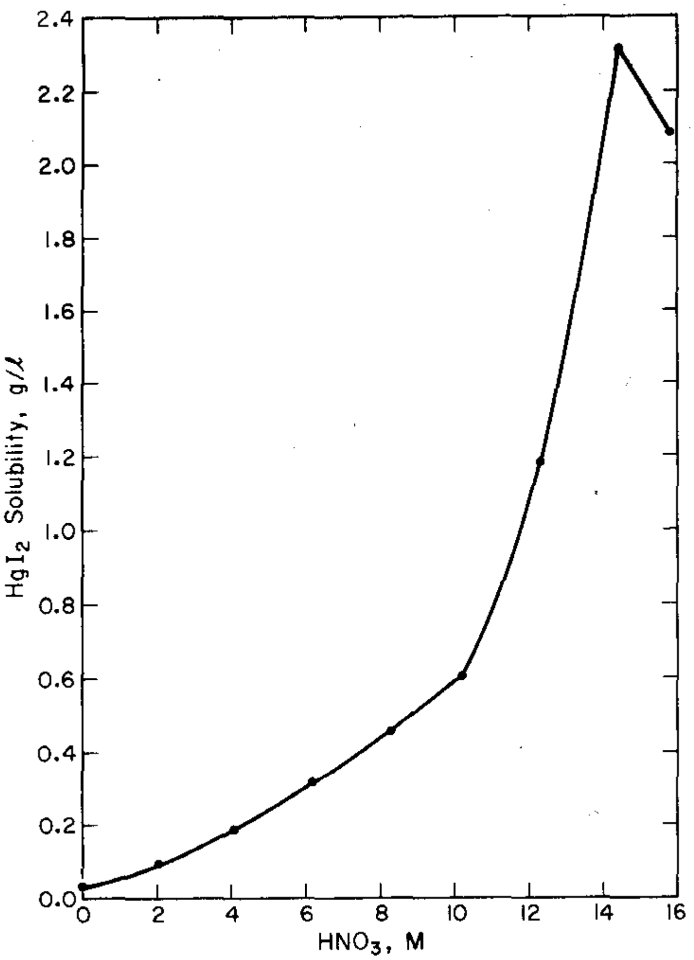

FIG. 1 SOLUBILITY OF HgI_2 IN HNO_3 SOLUTIONS AT 30°C

REMOVAL OF IODINE FROM PROCESS GASES

Scrub solutions and solid sorbents for ^{131}I were tested in the laboratory with simulated process gases. Promising sorbents and scrub solutions were evaluated in a test facility in the Plant.

Laboratory Tests

Preparation of $CH_3{}^{131}I$

Gaseous $CH_3{}^{131}I$ and $^{131}I_2$ were used in laboratory tests because they are representative of species in off-gases from nuclear fuel reprocessing.[7] $CH_3{}^{131}I$ was prepared in a stainless steel apparatus (Figure 2) by heating dimethyl sulfate, calcium carbonate, and $Na^{131}I$ to 90°C while slowly passing helium through the mixture.[8] The progress of the reaction was followed by monitoring the location of gamma activity in the system. Water vapor and unreacted dimethyl sulfate were condensed in a U-tube immersed in an ice bath. Trace amounts of elemental iodine which may have been produced were collected on a *Porapak Q** trap along with the product $CH_3{}^{131}I$. After the reaction was complete, the helium flow was increased to isolate the $CH_3{}^{131}I$ on a second *Porapak Q* trap.

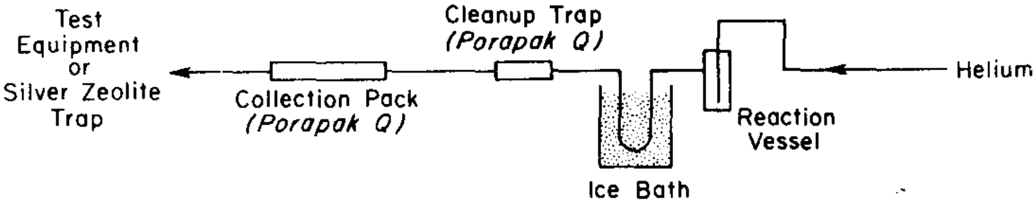

FIG. 2 APPARATUS FOR PREPARATION OF METHYL IODIDE

Preparation of $^{131}I_2$

$^{131}I_2$ was prepared[9] by fusing dried $Na^{131}I$ and potassium dichromate at 400°C in a glass tube contained in a stainless steel apparatus (Figure 3). The apparatus was cooled to ambient temperature to condense $^{131}I_2$.

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* Trademark of Waters Associates, Framingham, Massachusetts.

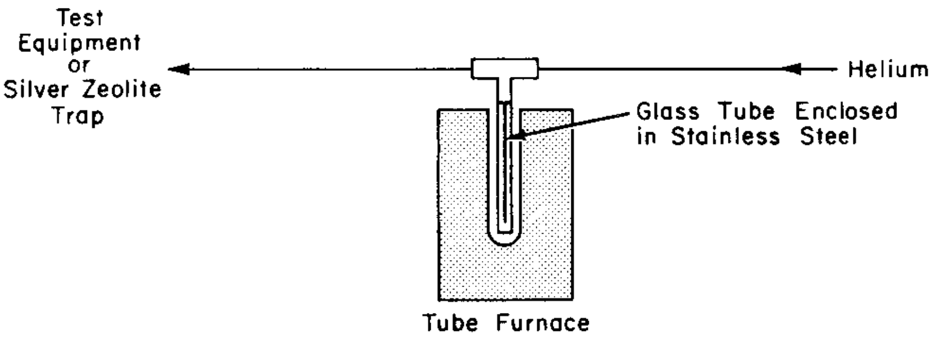

FIG. 3 APPARATUS FOR PREPARATION OF ELEMENTAL IODINE

Solid Sorbents

Solid sorbents tested were silver zeolite (AgZ), copper zeolite in the sulfide form (CuSZ), lead zeolite (PbZ), and CdI_2 on *Chromosorb P**. These sorbents were originally developed and evaluated by Idaho Nuclear Corporation.[10] Methods for preparing these sorbents are given in the Appendix.

A solid sorbent cartridge (Figure 4) was used to determine iodine retention efficiency of the sorbents. The cartridge contains, in succession, glass fiber filter paper to remove any particulate material, three packs of the sorbent to be tested (CdI_2 on *Chromosorb P*, CuSZ, PbZ, or AgZ), and a backup AgZ sorbent pack to remove all remaining iodine species. The cartridge was heated to 175°C for AgZ tests and 75°C for tests with other sorbents.

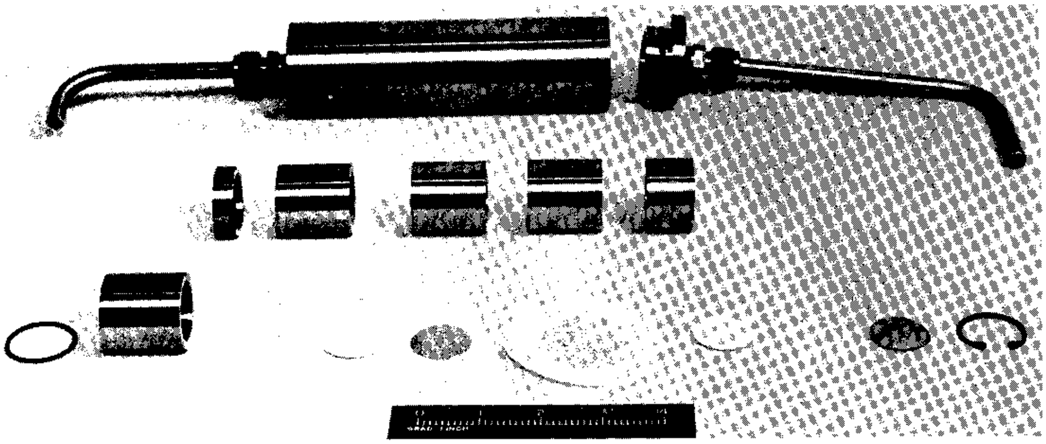

FIG. 4 SOLID SORBENT CARTRIDGE

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* Tradename of Johns-Manville Company, Denver, Colorado.

A $CH_3{}^{131}I$-helium stream or a $^{131}I_2$-helium stream was mixed with air and passed through the solid sorbent cartridge at 7.0 ℓ/min (45 ft/min linear velocity). $CH_3{}^{131}I$ concentration was adjusted by varying the helium flow to the *Porapak Q* tube; faster flow increases the removal rate of methyl iodide from *Porapak Q*. $^{131}I_2$ concentration was adjusted by varying helium flow and temperature of the I_2-generating apparatus. Total ^{131}I input was assumed to be the sum of that in the glass fiber filter papers and solid sorbents.

Test results are summarized in Table 2. At 75°C, ∿80% of the influent $^{131}I_2$ was sorbed by the filter paper; filter paper retention of elemental iodine at 175°C was negligible, as was CH_3I retention at either temperature.

TABLE 2. ^{131}I Retention by Solid Sorbents

Air Flow: 7.0 ℓ/min ^{131}I input: 10^{-10} g/ft^{3}[a]

	Sorption, %[b]	
Sorption Conditions	$^{131}I_2$	$CH_3{}^{131}I$
CdI_2/*Chromosorb P*, 75°C	90[b]	0.1
Copper zeolite (S^{2-}-form), 75°C	93[b]	0.3
Lead zeolite, 75°C	99.7[b]	45
Silver zeolite, 175°C	99.9	99.6

---

[a] The approximate total $^{127,129,131}I$ in process vessel vent air.

[b] Retention of elemental iodine that reached sorbents; up to 80% of the influent elemental iodine was retained by the glass fiber filter paper at 75°C.

$^{131}I_2$ sorbed by CdI_2/*Chromosorb P* and CuSZ was less than the published[10] 99+%. Small amounts of nonelemental iodine, e.g., HOI and organic iodides, form during preparation of elemental iodine by the dichromate-iodide method,[9] and the relative amount of nonelemental iodine increases at very low concentrations (<<10^{-8} g/ft^3).[11] The presence of nonelemental iodine may explain the test results, since ^{131}I input was 10^{-10} g/ft^3. Sorption with AgZ was excellent, even though the test temperature was less than the optimum 200°C. PbZ is also effective for $^{131}I_2$ and was chosen for further evaluation in the plant test facility.

After the candidate sorbents had been evaluated individually, three were evaluated in the "modified Maypack" system.[10] This system comprises a pack of glass fiber filters containing (in order of flow) CdI_2 on *Chromosorb P*, CuSZ, AgZ, and a backup pack of AgZ. CdI_2 on *Chromosorb P* is reported to be selective for elemental iodine, CuSZ is selective for hypoiodous acid (HOI) but also sorbs elemental iodine, and AgZ traps all iodine species. The results are given in Table 3. These results show that only AgZ is effective in removing low concentrations of both $CH_3{}^{131}I$ and $^{131}I_2$ from off-gas. However, other solid sorbents could remove most of the elemental iodine and effectively reduce the iodine load on a subsequent AgZ column. The "modified Maypack" absorbed $CH_3{}^{131}I$; 99.6% of the organic iodide was sorbed by AgZ. The relatively poor results with $^{131}I_2$ on the "modified Maypack" may indicate the presence of nonelemental iodine as discussed above, poorer selectivity than reported,[10] or both.

TABLE 3. ^{131}I Retention by Modified Maypack

Air Flow: 7.0 ℓ/min Temp: 75°C ^{131}I Input: 10^{-10} g/ft^3

	Iodine Sorption, %			
Iodine Species	CdI_2/*Chromosorb P*	CuSZ	AgZ(1)	AgZ(2)
$CH_3{}^{131}I$	0.1	0.3	99.1	0.5
$^{131}I_2$	52.9	10.0	37.1	<0.1

Aqueous Scrubbers

Iodine retention efficiencies of various HNO_3-$Hg(NO_3)_2$ solutions were determined in the laboratory in an aqueous scrubbing system (Figure 5) similar to one used at Oak Ridge National Laboratory (ORNL).[12] The system comprised a glass column, 30 in. long by 1 in. diameter, filled with perforated stainless steel packing. Scrubber solution was pumped from the flask to the top of the column. $CH_3{}^{131}I$ or $^{131}I_2$ flowed countercurrently to liquid flow.

In each scrubber test, radioiodine was removed from the *Porapak Q* source by flowing helium, mixed with air, and passed into the scrubber at 10 ℓ/min (linear gas velocity of ∿1 ft/sec). Scrub solution was pumped at 100 ml/min (∿0.01 ft/sec). Both linear velocities approximate those of the process vessel vent scrubber.

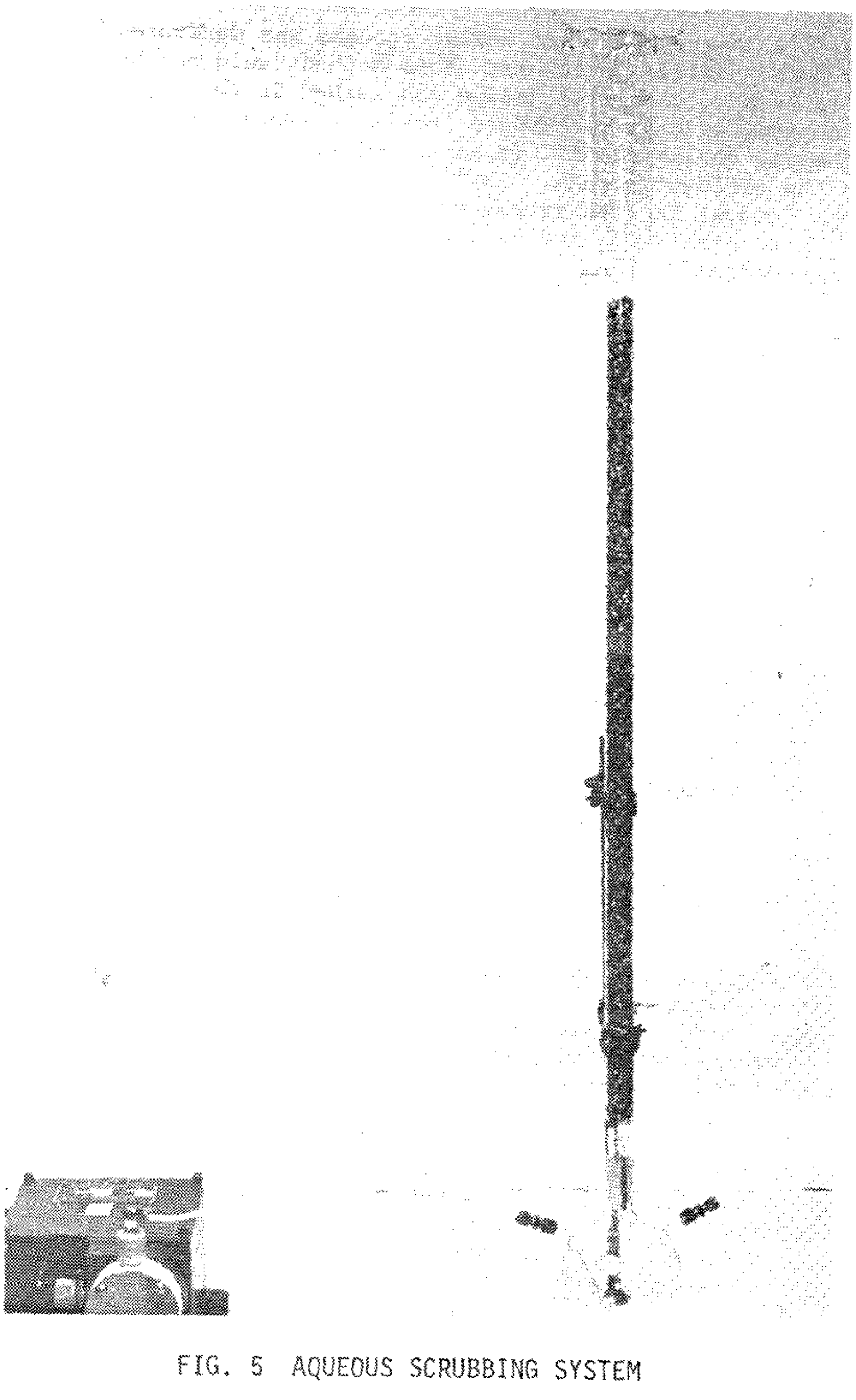

FIG. 5 AQUEOUS SCRUBBING SYSTEM

$CH_3{}^{131}I$ in the inlet and outlet streams was monitored with two 3 x 3-in. NaI(Tl) detectors. This method could not be used for ${}^{131}I_2$ because elemental iodine was sorbed in the *Teflon** loop and produced high background levels. Removal factors were determined by analyzing ${}^{131}I$ in scrub solution and silver zeolite beds in the effluent stream. $CH_3{}^{131}I$ tests are summarized in Table 4. Removal factors increased with increasing nitric acid and Hg^{2+} concentrations, and decreased with increasing methyl iodide concentration.

TABLE 4. Removal of $Ch_3{}^{131}I$ from Air Streams Using Mercury Solutions

	Iodine Removal Factors			
	At 0.2M Hg$^+$		At 0.4M Hg$^+$	
HNO_3, M	10^{-7}[a]	10^{-10}[a,b]	10^{-7}[a]	10^{-10}[a,b]
6	2.7	8.9	2.5	9.0
8	2.0	7.0	4.0	8.0
10	6	10	14	40
12	20	60	180	350
14	500	2200	10^4	$>10^4$[c]

[a] Initial methyl iodide concentration, Ch_3I, in g/ft^3.

[b] The approximate total iodine (${}^{127,129,131}I$) concentration initially present in PVV air.

[c] High background prevented accurate determination.

Elemental iodine scrub tests are summarized in Table 5. As with methyl iodide, the removal factor was high and increased with increasing nitric acid and Hg^{2+} concentrations. However, the removal factor increased with increasing iodine concentration, in contrast to the reverse effect with $CH_3{}^{131}I$. This effect, also observed at ORNL,[13] may have been caused by reaction of an intermediate in the oxidation of elemental iodine with organic impurities in the scrub solution or air, with subsequent volatilization of organic iodides. Increasing the elemental iodine concentration increased the I_2/impurity ratio, and thus increased the RF for elemental iodine. Tests at ORNL[14] showed that elemental iodine and organic impurities, particularly aromatics, can react rapidly in nitric acid, and that the products are destroyed slowly in the presence of Hg^{2+}.

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* Trade name for polytetrafluoroethylene (E. I. du Pont de Nemours and Company, Wilmington, Delaware).

TABLE 5. Removal of $^{131}I_2$ from Air Streams Using Mercury Solutions

Air Flow: 10ℓ/min Scrub Flow: 100 ml/min

	^{131}I Removal Factors			
HNO_3	10^{-8} [a]	10^{-10} [a,b]	10^{-8} [a]	10^{-10} [a,b]
6M	170	-	120	-
8	175	-	140	-
10	200	-	450	-
12	290	70	4120	540
14	3910	460	8400	2260

---

[a] Initial I_2 concentration, g/ft^3.

[b] The approximate total iodine ($^{127,129,131}I$) concentration initially present in PVV air.

Tests were also made to determine whether iodine volatilization from scrubber solutions or solution entrainment in off-gas could cause low iodine removal (Table 6). A 14M HNO_3-0.4M Hg^{2+} scrub test lasting 6 hours gave an RF of 3600, indicating no significant volatilization. In another test, 10^9 dis/min ^{131}I (as I^-) was added to the scrub solution. The scrub system was then purged with air at 10 ℓ/min. Less than 0.002% of the added ^{131}I was volatilized during this 5-hour purging test. Tests with 14M HNO_3 (no Hg^{2+}) determined the effects of possible organic impurities in nitric acid or the laboratory air supply. The removal factor (RF) was 820 with as-received acid; removal was only slightly more efficient (RF = 970) with acid treated with ozone to destroy possible organic impurities. Because iodine input varied by a factor of 100 in the two tests, no conclusions can be made except that the effect of ozonization, if any, is small. Volatilization and solution entrainment were not significant factors. Organic contaminants in as-received acid and laboratory air are either absent or stable to ozonization.

TABLE 6. Iodine Volatilization From Scrub Solutions

Air Flow: 10ℓ/min Scrub Flow: 100 ml/min

Solution Conditions	Iodine Input	Removal Factor
14M HNO_3/0.4M Hg^{2+}	7.2×10^{-11} g/ft^3	3600
14M HNO_3/0.4M Hg^{2+}	10^9 dis/min total ^{131}I[a]	5.7×10^4[a]
14M HNO_3	7.2×10^{-8} g/ft^3	820
Ozonized 14M HNO_3	2.8×10^{-10} g/ft^3	970

---

[a] ^{131}I (as iodide) was added directly to the scrub solution; no iodine was detected in the air stream. The removal factor represents radioiodine entrained, sparged, or volatilized from solution.

Plant Tests

Solvent extraction and anion exchange process vessels are vented to canyon air in the separations facility and are maintained at negative pressure with respect to the canyon by pumping off-gas through the Process Vessel Vent (PVV) system to a scrubber containing 0.01M $Hg(NO_3)_2$ in 1M HNO_3.

Process off-gas from the PVV system was drawn into an iodine test facility located in Section 7 of the H-Area Hot Gang Valve Corridor. Samples from upstream and downstream (points 1 and 2, respectively, in Figure 6) of the scrubber were collected in identical, independent sampling stations in the test facility. This enabled the determination of the PVV scrubber system efficiency and testing of proposed solid or liquid sorbers with actual plant off-gas.

Equipment

The iodine test equipment was installed in two stainless steel glove boxes. Samples of process gas were drawn by air jets through particulate filters [rated for 100% removal of small diameter (>1 μm) particulates] in Box 1 (Figure 7) and then through radioiodine sampling and testing equipment in Box 2 (Figure 8). Box 2 contained two identical, independent iodine sampling systems; one for process off-gas was located upstream of the PVV scrubber, the other was located downstream of the PVV scrubber. Each system comprised a shielded ^{131}I monitoring loop followed by a cold trap, aqueous scrubber, solid sorbent bed, flowmeter, and air jet.

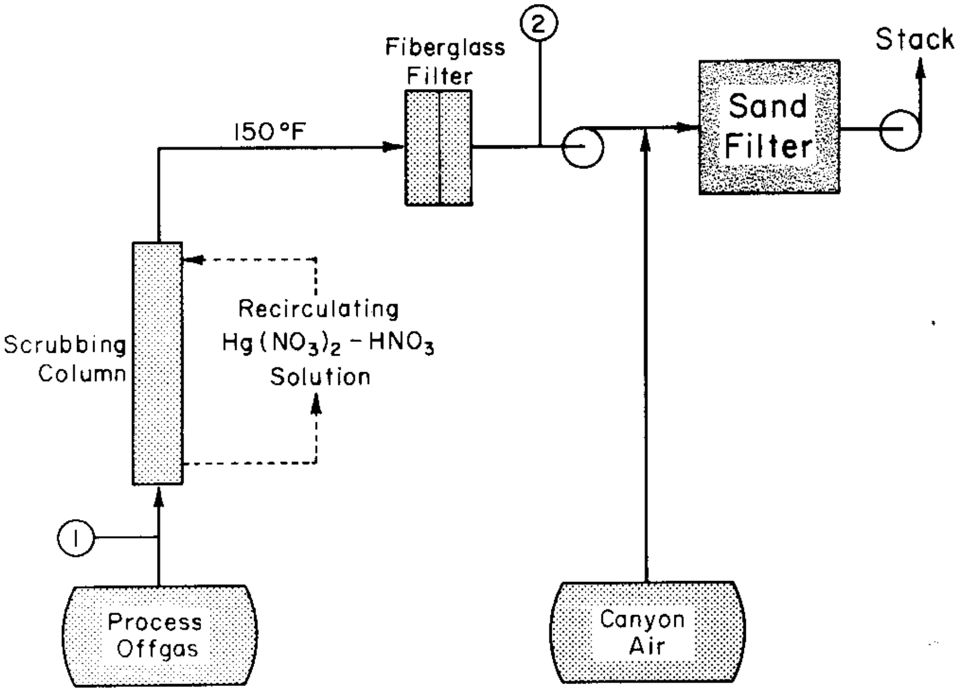

FIG. 6 EXISTING SCRUBBER FOR H AREA OFFGAS

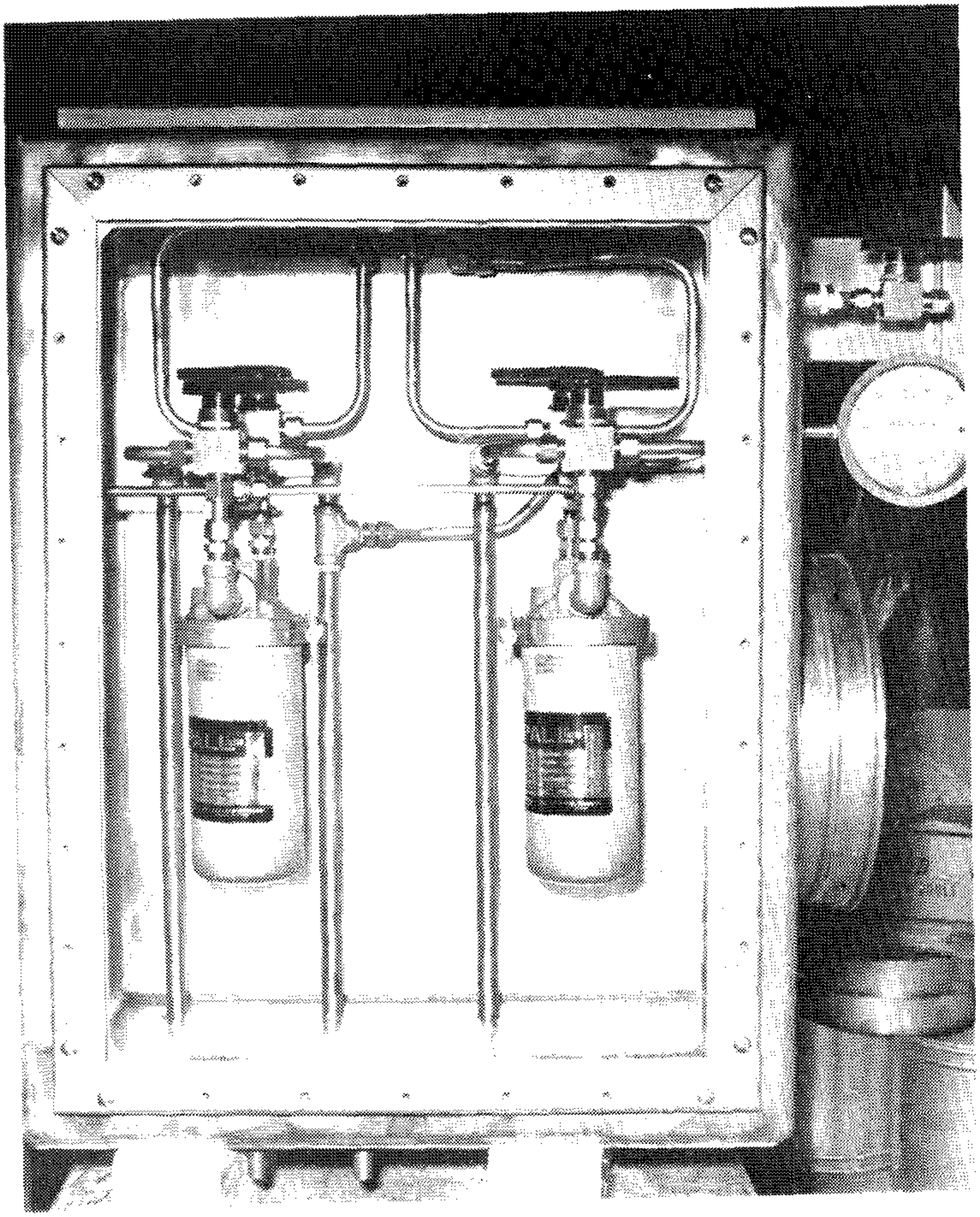

FIG. 7 PARTICULATE FILTERS (BOX 1)

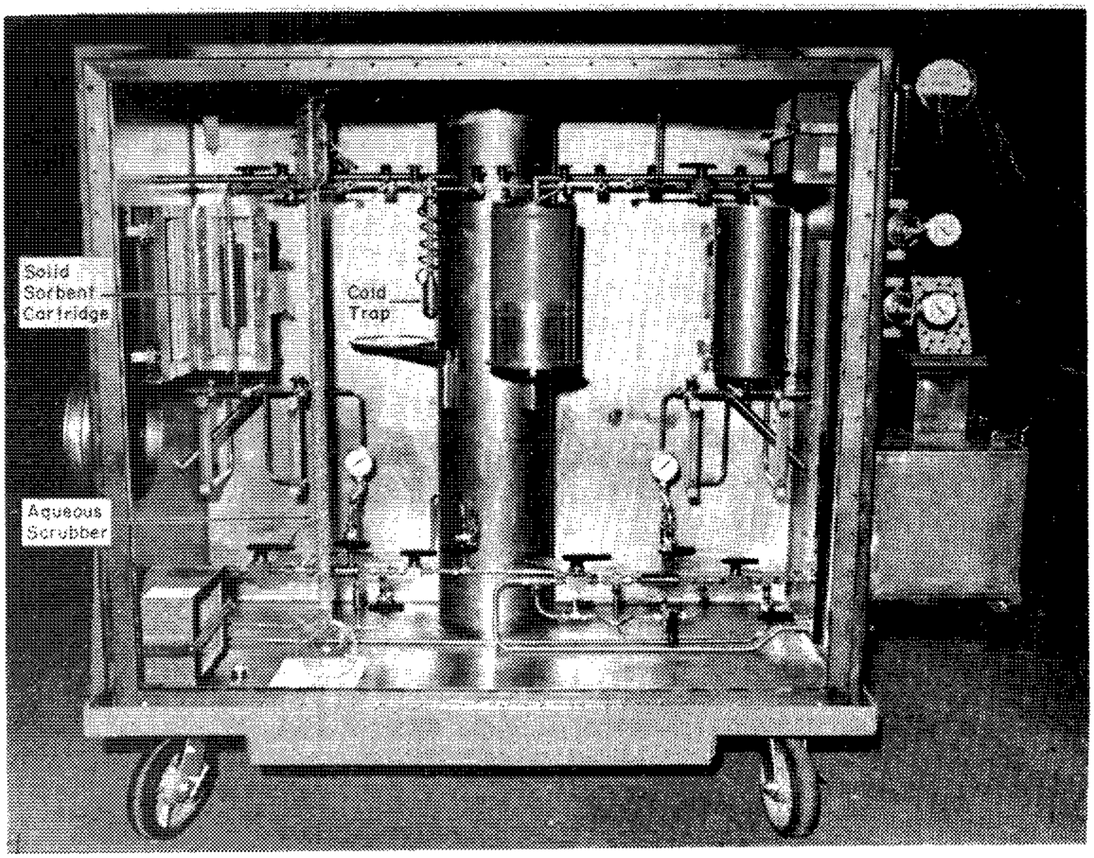

FIG. 8 SAMPLING AND TESTING EQUIPMENT (BOX 2)

Solid Sorbents

The solid sorbent cartridge and sorbents used in sampling plant off-gas were the same as for the laboratory tests. Sorbent cartridges were installed online with vacuum fittings, and the system was leak-tested prior to sorption tests. Cartridges were heated with insulated clam-shell heaters, which were regulated by thermocouple-activated controllers. Tests were run either singly or concurrently, i.e., the independent systems were sampled from both upstream and downstream of the PVV scrubber system simultaneously.

Silver Zeolite

Silver Zeolite (AgZ) was found to be the most effective sorbent for radioiodine in PVV off-gases. The first two cartridge packs contained 40 to 60 mesh AgZ; the second two, 20 to 40 mesh AgZ. On concurrent sorption tests at 200°C and 6 ℓ/min air flow for 12 hours, ⩾99.9% of influent iodine was removed from both upstream and downstream off-gas (RF $\geqslant 10^3$); 5.35×10^{-6} μg ^{131}I was collected upstream, 2.24×10^{-6} μg ^{131}I was collected downstream of the PVV scrubber system. AgZ was also used as a backup for other solid sorber and scrub tests.

Lead Zeolite

In another concurrent test, cartridges of lead zeolite (PbZ) were heated to 75°C and PVV off-gas was drawn into the cartridges at 7 ℓ/min (linear velocity = 45 ft/min). Packs 1 and 2 were loaded with 40 to 60 mesh PbZ, Pack 3 with 20 to 40 mesh PbZ, and Pack 4 with 40 to 60 mesh AgZ. PbZ sorbed 80% of total influent ^{131}I (1.47×10^{-6} μg ^{131}I) and 70% of total influent ^{131}I (0.65×10^{-6} μg ^{131}I) upstream and downstream of the PVV scrubber, respectively. PbZ sorbed >99% of influent elemental iodine and ∿55% of influent methyl iodide in laboratory tests. These results suggest that considerable organic iodine is present in the PVV system.

Modified Maypack

Concurrent tests and upstream tests with the modified Maypack demonstrated that iodine in PVV gases is principally organic. All tests were made at 75°C and 7 ℓ/min (45 ft/min linear velocity). Test results are given in Table 7. As described for the laboratory tests, CdI$_2$ on *Chromosorb P* and CuSZ are reported to be selective for elemental iodine and HOI, respectively, although CuSZ also is reported to sorb 99+% elemental iodine.[10]

TABLE 7. Retention of ^{131}I by the Modified Maypack in the PVV Scrubber System

Temperature: 75°C   Flow Rate: 7 ℓ/min   Linear Velocity: 45 ft/min

Test	Sorption Time, hr	Total ^{131}I Sorbed, pg[a]	Iodine on Individual Sorbents, %			
			CdI_2	CuSZ	AgZ(1)	AgZ(2)
1[b]	6	1.32	6.1	6.8	87.1	<0.1
2[b]	12	0.49	8.6	15.2	76.2	<0.1
3[c]	12	1.19	1.9	5.3	92.8	<0.1
4[b]	6	1.46	2.0	15.7	82.3	<0.1
5[d]	6	0.46	1.4	1.5	97.1	<0.1

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[a] Weight in picograms.
[b] Tests 1, 2, and 4: Upstream of PVV scrubber system.
[c] Test 3: Downstream of PVV scrubber system; concurrent with Test 2.
[d] Test 5: Downstream of PVV scrubber system; concurrent with Test 4.

Because of these uncertainties, the variation in results for these two sorbents (Table 7) cannot be considered significant. However, total iodine sorbed by both materials does indicate the amount of inorganic iodine present; CdI_2 on *Chromosorb P* and CuSZ sorbed only 0.1% and 0.3% influent methyl iodide, respectively, in laboratory tests. Thus, the % ^{131}I sorbed in AgZ Pack 1 (Table 7) gives an upper limit for organic iodides present in PVV gases. The effectiveness of AgZ for radioiodine sorption is demonstrated again by the negligible amount of iodine on AgZ Pack 2.

Although there is variation in the data shown in Table 7, it appears that 75-97% of ^{131}I in the PVV system is organic. These data also show that AgZ is an effective sorbent for ^{131}I in the PVV gas stream.

Aqueous Scrubbers

Iodine retention efficiencies of HNO_3-$Hg(NO_3)_2$ solutions were determined in an aqueous scrubbing system identical to that used in laboratory tests (Figure 5). Two identical systems were used in the plant facility to sample off-gas from upstream and downstream of the PVV scrubber system. Solid sorbent cartridges loaded with AgZ were used to sorb iodine not removed by the scrubber. Results are shown in Table 8.

TABLE 8. Decontamination of PVV Air With Mercury Scrub Solutions

Liquid Rate: 100 ml/min Temp: Ambient

Test	Scrub Solution	Air Flow, ℓ/min	Time, hr	^{131}I Input pg[a]	Effluent ^{131}I pg[a]	RF
1[b]	14M HNO_3-0.4M Hg^{2+}	7.4	12	5.70	2.23	2.6
2[b]	14M HNO_3-0.4M Hg^{2+}	7.4	7	0.44	0.02	22
3[b]	10M HNO_3-0.4M Hg^{2+}	7.4	10.5	2.01	0.64	3.1
4[b]	14M HNO_3-0.4M Hg^{2+}	8.5	5	3.49	0.15	23
5[b]	14M HNO_3-0.4M Hg^{2+}	7.4	14	6.70	0.23	29
6[b]	14M HNO_3-0.4M Hg^{2+}	6	14	7.12	0.56	13
7[c]	14M HNO_3-0.4M Hg^{2+}	6	14	6.73	0.73	9.1

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[a] Weight in picograms.

[b] Offgas from upstream of PVV scrubber system

[c] Offgas from downstream of PVV scrubber system; concurrent with Test 6.

14M HNO_3-0.4M $Hg(NO_3)_2$ was chosen for off-gas testing since this solution gave removal factors greater than 10,000 and 1000 for $CH_3{}^{131}I$ and $^{131}I_2$, respectively, in laboratory tests. Flow rates in the scrubbing system were reduced because of pressure drop across the AgZ backup cartridge and limited air jet capacity. Decreased air flow should have increased scrubber efficiency by increasing gas residence time in the scrub column. However, removal factors attained were low compared to values obtained in laboratory tests. Similar low removal factors during scrub tests on radioactive process off-gas at ORNL have been attributed to easily iodinated organic species resistant to oxidation by nitric acid; the species have not yet been identified.[15] Workers at ORNL found that 10M HNO_3 improved iodine removal if organic contaminants were present;[15] however, 10M HNO_3 (Test 3) was ineffective in our tests. Off-gas flow was increased in Test 4 (by using 20 to 40 mesh AgZ throughout the sorbent cartridge to reduce pressure drop) and was decreased in Test 6. No meaningful improvements in RF were measured. There was no difference in iodine sorption from upstream and downstream samples.

These test results indicate that HNO_3-$Hg(NO_3)_2$ scrubber solutions tested are not highly efficient for ^{131}I removal from the PVV gas stream. Reasons for the smaller removal factors, as compared to laboratory tests (Tables 4 and 5), are not known.

Efficiency of Process Vessel Vent Scrubber System

Concurrent sampling from upstream and downstream of the existing PVV scrubber system, which uses dilute HNO_3-Hg^{2+} scrub solution, permits calculation of iodine removal factors for that system. Amounts of iodine collected in concurrent tests and removal factors are shown in Table 9. The tests show that iodine removal across the PVV scrubber system is poor. This was expected, based on poor iodine removal in laboratory tests with dilute HNO_3-Hg^{2+} scrub solutions, even without the presence of organic contaminants.

TABLE 9. Iodine Removal Efficiency of the PVV Scrubber System

Test	Upstream ^{131}I Input, picograms	Downstream ^{131}I Input, picograms	RF
Modified Maypack	1.46	0.46	3.2
14M HNO_3-0.4M Hg^{2+} scrub	7.12	6.73	1.1
Silver Zeolite	5.35	2.24	2.4
Lead Zeolite (AgZ Backup)	1.47	0.65	2.3

Analysis of Process Off-gas

The cold trap (Figure 9) used in the SRP tests consists of two valves and tantalum bulb and tubing, connected to the sample line by vacuum fittings. The trap was cooled to -77°C in a dry ice-trifluoroethylene mixture. Process off-gas from upstream or downstream of the PVV scrubber system was drawn into the trap by air jet.

At ambient temperature, the sample comprised a gas phase and a liquid phase; the liquid was mainly water condensed from the PVV air. Total inorganic or organic iodine in both phases could not be determined quantitatively because the composition of the sample was unstable.

Elemental iodine was present in the condensate. The gas contained concentrations of organic iodides in the order butyl > methyl >> ethyl; subsequent analysis showed decreasing amounts of methyl iodide, which may account for the previously reported absence of methyl iodide in exhaust air at SRP.[16] Similar analysis of off-gas during dissolution of irradiated fuel targets at other sites showed organic iodide concentration in the order methyl > ethyl > propyl > butyl.[17] If dissolver solution is processed by solvent extraction with TBP, and if process off-gases are mixed, butyl iodide can be formed by reaction of a butyl radiolysis product (probably butanol) and iodine.[18]

Other radionuclides found in the residual cold trap liquid were: 10^3 dis/(min-ml) each of ^{103}Ru, ^{106}Ru, ^{144}Ce, ^{95}Zr, ^{95}Nb and 10^5 dis/(min-ml) of ^{238}Pu.

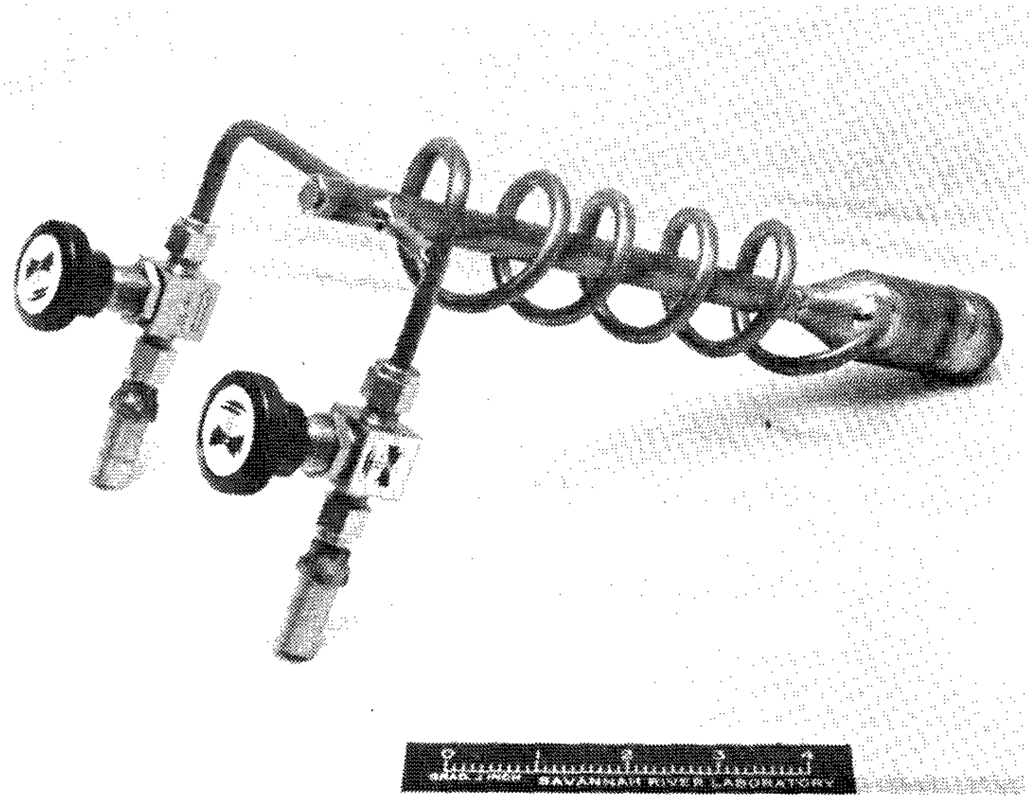

FIG. 9 COLD TRAP

CONCLUSIONS

In situ formation of MnO_2 can remove greater than 99.9% of radioiodine from simulated and actual SRP dissolver solutions. MnO_2 should remove iodine from dissolver solutions even at very low iodine concentrations. Semiworks testing has shown that centrifugation would be required for MnO_2 removal.

Iodine evolved from process solutions is primarily a mixture of organic compounds. A relatively large amount of butyl iodide may result from reaction of iodine with radiolytic degradation products of TBP. Part of the iodinated organic degradation products then passes unchanged through the existing PVV scrubber system.

Silver zeolite adequately removes all iodine species from PVV effluent (by factors of about 1000). Removal factors with silver zeolite are expected to be high through a wide range of iodine concentrations. Low removal factors for other solid sorbents may result from the presence of relatively unreactive organic iodine compounds.

Low radioiodine removal factors for HNO_3-$Hg(NO_3)_2$ solutions may also be caused by relatively unreactive organic iodine compounds.

The present PVV scrubber system removes at most 50 to 75% of the radioiodine present.

If radioiodine retention equipment is to be installed in the plant process PVV system, leakage of effluent from the system into the canyon air should first be minimized to realize maximum radioiodine retention. Also, the long-term stability and ultimate capacity of silver zeolite for radioiodine in the PVV environment must be determined.

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APPENDIX: SORBENT PREPARATION

Sorbents prepared for this study included a MnO_2-polysilicic acid material for removal of iodine from dissolver solution; CdI_2 on *Chromosorb P*, copper zeolite in the sulfide form, silver zeolite, and lead zeolite were tested for iodine removal from process off-gas.

MnO_2-Polysilicic Acid

Manganous nitrate solution and potassium permanganate were reacted to give 10 g of MnO_2. The product was slurried in 2 ℓ of water, and 300 ml of Na_2SiO_3 solution (Sp.gr. 1.4) was added slowly with stirring. Stirring was immediately stopped when gel formation occurred. The gel was aged one week, dialyzed one week with distilled water, filtered, air-dried, and then dried in an oven at 50°C. The dried product was ground and sieved into 20 to 50 mesh and 50 to 100 mesh fractions. Sorbent conditioning was begun with 0.25M HNO_3, gradually increasing to 4M HNO_3. Rapidly changing the nitric acid concentration caused osmotic shock and produced fines.

CdI_2 on Chromosorb P

Cadmium metal was dissolved in excess HI solution to give 0.1M cadmium.[10] Enough of this solution was added to *Chromosorb P* to thoroughly wet the support. The mixture was air-dried and purged in a tube furnace with air at 200°C until iodine evolution ceased. The purged material was equilibrated in air at ambient temperature for 48 hours before use.

Lead Zeolite and Copper Zeolite (sulfide form)

These metal zeolites were prepared from a 1/8-in.-diameter molecular sieve extrudate.[10,19] The extrudate was ground and sieved into 20 to 40 mesh and 40 to 60 mesh fractions and water-washed by decantation to remove fines. Batches of 100 g were loaded into a water-jacketed glass column at 80°C, and 100 ml of saturated solution of metal (lead or copper) acetate was poured into the column. The saturated acetate solution was changed daily for 10 days. The metal zeolite was rinsed with distilled water and dried at 100°C. Analysis showed about 97% conversion to lead zeolite and about 95% conversion to copper zeolite. The copper zeolite was converted to the sulfide form by passing hydrogen sulfide through a bed of the material at 150°C; unreacted hydrogen sulfide was removed by air purging at 200°C. The product was equilibrated in air at ambient temperature for 48 hours before use.

Silver Zeolite

Two silver zeolites were prepared and tested. Both were prepared from *Linde** Molecular Sieve 13X extrudate.[19] The extrudate was ground and sieved into 20 to 40 mesh and 40 to 60 mesh fractions and water-washed by decantation to remove fines. Batches of 100 g were loaded into a water-jacketed glass column at 80°C, and 100 ml of a 200 g/ℓ silver nitrate solution was added. This solution was changed daily for 10 days. The silver zeolite was then washed with distilled water until a negative silver (chloride) test was obtained. The product was air-dried, and then oven-dried at 100°C before using.

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* Product of Linde Division, Union Carbide Corp., New York, New York.

Additional silver zeolite was purchased from Coast Engineering Laboratory, Gardena, California, as silver-exchanged 1/8-in.-diameter *Linde* Molecular Seive 13X extrudate. This material was also ground and sieved to obtain 20 to 40 mesh fractions. Fines were removed by water-washing and decantation, the desired fractions were air-dried and then oven-dried at 100°C.

Analysis of both silver zeolites showed >99% conversion to silver form.

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