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A Literature Survey: Methods for the Removal of Iodine Species from Off-Gases and Liquid Waste Streams of Nuclear Power and Nuclear Fuel Reprocessing Plants, with Emphasis on Solid Sorbents

D. W. Holladay

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A LITERATURE SURVEY: METHODS FOR THE REMOVAL OF IODINE SPECIES FROM OFF-GASES AND LIQUID WASTE STREAMS OF NUCLEAR POWER AND NUCLEAR FUEL REPROCESSING PLANTS, WITH EMPHASIS ON SOLID SORBENTS

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D. W. Holladay

ABSTRACT

A literature survey was conducted to provide information for the assessment of the various processes available for removing iodine species from the off-gases and from the low-level-radwaste aqueous streams that arise at nuclear power facilities and nuclear fuel reprocessing plants. Particular emphasis was focused on the operating parameters that most strongly affected the optimization of the processes used to treat actual process or feed streams which simulated actual compositions occurring at nuclear facilities. These parameters included gas superficial velocity, temperature, types of organic and inorganic contaminants, relative humidity, iodine feed-gas concentration, iodine species, column design (for both acid-scrub and solid sorbent-based processes), sorbent particle size, run time, intense radiation (solid sorbents only), and scrub-acid concentration. Based on the ability of a process to deliver high decontamination factors and high loading capacity for iodine species under practical operating conditions, the most promising acid-scrub process for removal of iodine species from off-gases appears to be Iodox. The most promising solid sorbent for removal of iodine species from off-gases is the West German Ag-KTB--$AgNO_3$-impregnated amorphous silicic acid. The tandem silver mordenite--lead mordenite sorbent system is also quite attractive. Only a limited number of processes have thus far been studied for removal of iodine species from low-level liquid waste streams. The most extensive successful operating experience has been obtained with anion exchange resins utilized at nuclear power reactors. Bench-scale engineering tests have indicated that the best process for removal of all types of iodine species from liquid waste streams may be treatment on a packed bed containing a mixture of sorbents with affinity for both elemental and anionic species of iodine. Further experimentation at the pilot plant scale, comparison of the ease of process operations under remote handling conditions, and in-depth cost analyses should be made before the final process is chosen for removal of iodine species from either off-gases or liquid wastes.

1. INTRODUCTION

One of the major fission products of nuclear power reactors is ^{129}I, which constitutes a radionuclide hazard both at power plants and when released as organic iodides and elemental iodine into the process off-gas of nuclear fuel reprocessing plants. A model Light-Water Reactor (LWR) fuel reprocessing plant, such as that of Allied-General Nuclear Services (AGNS) at Barnwell, South Carolina, would process annually fuel that contained 1500 metric tons of heavy metal (MTHM, uranium plus plutonium) as charged to reactors that produce about 42,000 MW(e)-year of energy while operating for one year. This 1500 MTHM would contain more than 50 Ci of ^{129}I (>300 kg) and, when processing is performed at 160 days after discharge of fuel from the reactors, greater than 1000 Ci of ^{131}I (>10 mg).[1] Much of this iodine would be discharged from the plant in the stack gas unless extensive iodine recovery systems were applied. The current EPA release limits[2] for iodine require that normal operations within the uranium fuel cycle be conducted to provide reasonable assurance that: (1) the annual dose equivalent does not exceed 25 millirems to the whole body, 75 millirems to the thyroid, and 25 millirems to any other organ of any member of the public; and (2) the quantity of ^{129}I released to the environment per gigawatt-year of power produced by the entire fuel cycle does not exceed 5 mCi.

Detailed analyses of different levels of sophistication in fuel reprocessing design to achieve ^{129}I control (along with other major reactor products) have been described.[3,4] Seven cases and their corresponding flowsheets for treating the gaseous and liquid streams for a model LWR fuel reprocessing plant are discussed in ref. 3. The lowest-cost and simplest-treatment technology were presented for the base Case 1. For each succeeding case, additional processes were considered which either initiated or enhanced the removal of the basic off-gas fission products. The most elaborate plant design was given in Case 7, in which "near zero release" concepts were applied to treatment and/or recycle of gaseous and liquid effluents. The studies described in refs. 3 and 4 served as valuable guidelines for providing the reference processes, stream flow rates, and stream compositions to be reviewed in this survey.

During nuclear fuel reprocessing, most of the radioiodine that has been produced in the reactor fuel (from tellurium decay) is released into the dissolver off-gas during dissolution and subsequent sparging procedures. This iodine appears mostly as elemental iodine and aliphatic iodides, although very low concentrations of more complex inorganic and organic iodides may be present. Those systems which are candidates for iodine species removal from the off-gas must be capable of trapping both inorganic and organic iodides and should maintain acceptable removal efficiencies for off-gas streams containing water vapor, tritiated water, carbon dioxide, noble gases, nitrogen oxides, and organics evolved during solvent extraction. Candidate processes for iodine species removal from off-gases are:

1. Iodox;
2. mercuric nitrate--nitric acid scrubbers; and
3. sorption on the solid sorbents, including
    (a) silver and base-metal zeolites,
    (b) silver and base-metal mordenites,
    (c) silver-nitrate impregnated, amorphous silicic acid, and
    (d) macroreticular resins.

Most of the iodine that is carried with the aqueous stream from the dissolver is volatilized in the feed adjustment-iodine evolution step; thus only a small fraction of the original iodine in the nuclear fuel manages to enter the solvent extraction system. Waste streams (primarily aqueous with ^{129}I and trace organics) from the solvent extraction system, the high-activity waste treatment loop, and the nitric oxide-nitric acid scrubber will be processed in the low-activity liquid waste process loop. These waste liquid streams may contain levels of iodine intolerable for release. Increased emphasis on "near-zero release" constraints placed on fuel reprocessing plants makes it imperative to treat these combined waste streams (either as a vapor or in both vapor and condensate states) for iodine removal before the streams are recycled or released to the atmosphere.

Candidate processes for iodine removal from neutral and mildly acidic streams are: (1) macroreticular resins, (2) charcoal, (3) ion exchange resins, and (4) metal oxide-impregnated sorbents.

A literature survey was conducted to provide information concerning the background, experimental development, and present status of each of the above processes for removing iodine species from gas and/or aqueous streams.

2. IODINE SPECIES REMOVAL FROM FUEL REPROCESSING OFF-GASES BY LIQUID-GAS SCRUBBING OPERATIONS

Although the primary goal of this review was to assess the capabilities of various solid sorbents for removing radioiodine species from liquid and gaseous wastes, two processes based on transfer of iodine between gaseous and acidic streams were reviewed. Iodox and the mercuric nitrate-nitric acid iodine removal processes were summarized because of their proven ability and wide acceptance for achieving high removal efficiencies for elemental iodine and aliphatic iodides. In addition, much of the effort that has been devoted to studying the iodine chemistry in these processes could contribute to a better understanding of the complex sorption chemistry involved in solid sorbent interaction with iodine in mildly acidic and neutral streams. Finally, any arguments that are to be made for utilization of solid sorbents as the primary or secondary procedure for iodine removal must also include a consideration of the two most efficient methods utilizing acidic solutions for scrubbing iodine from process gases.

2.1 Iodox Process

2.1.1 Background

The Iodox process is an advanced procedure for scrubbing elemental iodine and organic iodides from off-gases by utilizing hyperazeotropic (>20 M) HNO_3 in a gas-liquid contactor. The process appears to be adaptable not only for treating primary dissolver off-gas but also as a final polishing step for off-gas containing very low levels of iodine such as previously scrubbed dissolver off-gases or off-gas streams from particular process vessels. The primary unit operations for an integrated Iodox system are: (1) absorption of iodine species and oxidation to soluble, nonvolatile pentavalent iodate with hyperazeotropic HNO_3 in a gas-liquid column (preferably bubble-cap); (2) concentration of iodine-rich HNO_3 scrub solution in an evaporator; (3) recycle of iodine-free

HNO_3 concentrate from the evaporator to the plant HNO_3 system; and (4) transfer of iodine-nitric acid concentrate from the first evaporator to a second evaporator where it is collected as the pentavalent iodine in a dehydrated form of HI_3O_8.

2.1.2 Chemical mechanism

Mailen[5] has written an excellent review of four processes that have been developed on an engineering scale for removing iodine species from off-gases. The specific focus of that review was on evaluation of the chemical mechanisms involved with four iodine-trapping systems. The systems included iodine removal by both acidic scrubbing solutions and solid sorbent beds.

To better understand the Iodox process and to develop correlations that could be useful in future engineering scale-up considerations, the chemistry of the Iodox process has been studied in depth. The reaction between iodine and hyperazeotropic HNO_3 has been intensively studied.[6-8] The equilibrium and kinetic data were consistent with the two-step reaction:

$$I_2 + 4HNO_3 \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2I^+ + 2NO_3^- + N_2O_4 + 2H_2O \ , \tag{1}$$

$$I^+ + 3HNO_3 + NO_3^- \underset{k_4}{\overset{k_3}{\rightleftarrows}} IO_3^- + H^+ + 2N_2O_4 + H_2O \ . \tag{2}$$

Generally, the first reaction proceeds rapidly, but the second is relatively slow. Thus at short reaction times, when the N_2O_4 content of the liquid is small, another equilibrium is rate controlling. Although the kinetics and stoichiometry were not elucidated for this equilibrium reaction, it can be represented by:[9]

$$K_3 = \frac{C_{I^+}}{C_{I_2}} , \tag{3}$$

where C_{I^+} and C_{I_2} are molar concentrations of I^+ and I_2 respectively. For increased N_2O_4 concentrations, the equilibrium for Eq. (1) controls:

$$K_1 = \frac{C_{I^+}^{\ 2} C_{N_2O_4}}{C_{I_2}} , \tag{4}$$

and

$$\ln K_1 = 48.1 - 17.4 \ln C_{HNO_3} , \tag{5}$$

where $C_{N_2O_4}$ is the molar concentration of N_2O_4. For the assumption of a pseudo-first-order reaction, the consumption of I^+ to IO_3^-, based on reaction (2), can be described by:

$$\frac{dC_{I^+}}{dT} = -k_3 \ C_{I^+} . \tag{6}$$

Values of k_3 can be calculated from (ref. 7),

$$\ln k_3 = -45.25 + 13.69 \ln C_{HNO_3} , \tag{7}$$

where k_3 is the rate constant in sec^{-1} and C_{HNO_3} is the HNO_3 molarity. It was determined[10] that the data for the distribution of elemental iodine between air and HNO_3 at 25°C fit the equation:

$$K_G^{\ L} = 98.2 - 1.11 \ C_{HNO_3} , \tag{8}$$

where the distribution coefficient $K_G^{\ L}$ is (moles of I_2/liter of liquid)/(moles I_2/liter of gas). Because of the importance of NO_2 in the Iodox process [it is in equilibrium reaction (1) and is a major component of fuel reprocessing off-gases], study of the distribution of NO_2 between air and hyperazeotropic HNO_3 was begun.[11] Initial data indicated that at a high temperature the equilibrium

$$2NO_2(g) \rightleftarrows N_2O_4(\ell) \tag{9}$$

could have a strong effect on the Iodox process.

An actual fuel reprocessing off-gas stream will contain organic iodides such as methyl iodide (CH_3I) in addition to I_2; it was therefore necessary to consider the effect of other such iodides on the reactivity of I_2 in Iodox. The initial reaction of CH_3I in hyperazeotropic HNO_3 is a fast nitrolysis:[12]

$$CH_3I + 2HNO_3 \xrightarrow{k_5} CH_3NO_3 + 1/2\ I_2 + 1/2\ N_2O_4 + H_2O\ . \tag{10}$$

The I_2 formed from the initial I_2 conversion then reacts as if it were normal I_2 in the previously discussed reactions (1) and (2). The CH_3I decontamination factors (DFs) obtained in Iodox for equal feed concentrations are less than those for I_2 because of the considerably lower distribution of CH_3I from air to HNO_3.[10,13] The methyl nitrate distributes favorably from HNO_3 to air by a factor of about 15; thus the hazard of explosion caused by CH_3NO_3 buildup is reduced, because most of the CH_3NO_3 leaves the Iodox system in the treated off-gas stream.

2.1.3 Experimental results and engineering data useful for process design

The Iodox contactor as a packed column. The Iodox process was originally called Iodex and involved the removal of I_2 and CH_3I from air by countercurrent scrubbing with $\geq$70% HNO_3 in a packed column. Only the summary Iodex report[14] is reviewed here to provide background information on the original development of the iodine-HNO_3 scrubbing concept and to indicate the evolution of the integrated Iodox process. The countercurrent Iodox process was conducted in glass towers 0.04 m in diam and 0.56 or 1.17 m long. Packing was 6.4×10^{-3}-m (1/4-in.) ceramic Berl saddles. To remove elemental iodine from air, the DFs were as much as 3.5×10^4 in the 0.56-m column (1.3×10^8/m of packing).

Iodine and CH_3I feed concentrations were in the range 20 to 4000 ppm. Appendix A describes the general concentration ranges that are anticipated for nuclear power plant and fuel reprocessing off-gases.

The DFs for iodine species removal (I_2 and CH_3I) were determined to vary directly with temperature and HNO_3 concentration, and inversely with gas superficial velocity. These observations were consistent with a mass transfer process for which the controlling diffusional resistance was in the liquid film, and the chemical conversion of iodine to iodate was essentially first order. Acceptable scrubbing efficiencies for I_2 removal were obtained at >80°C with 70% HNO_3, or at >30°C with 80% HNO_3. Methyl iodide was less effectively removed than I_2 (maximum DF for CH_3I of 9.6×10^4/m for a 1.17-m long column vs maximum DF for I_2 of 1.3×10^8/m for a 0.56-m column). Boiling temperatures were necessary to achieve efficient removal of CH_3I for acid concentrations of 70% HNO_3. In very limited tests, the addition of a hexane contaminant to the feed gas had little effect on the DF for a once-through liquid flow of CH_3I. When hexane was added with CH_3I to a feed gas in the 0.04- by 1.17-m packed column, the DF for CH_3I was reduced by a factor of 5 when the scrub acid was recycled. However, the DFs for CH_3I removal from air-CH_3I-aromatic mixtures in the packed column were minimally affected by benzene and iodobenzene (at very low concentration).

The data obtained from the operation of the laboratory-scale Iodex process were utilized to make some preliminary estimates for scaling-up the operation. Based on the small column, it was estimated that to remove iodine species from a 2.8-m^3/min (100 scfm) air stream (air only, with no contaminants) so that a DF of 10^6 could be achieved for CH_3I by utilizing 18.0 M HNO_3 at 60°C, a packed column that was 0.86 m ID by 2.51 m long would be sufficient.

Based on the Iodex experience, the Iodox process was designed to operate with very large HNO_3 concentrations, and the primary contactor design was changed to a bubble-cap column to maximize liquid holdup while retaining lower liquid velocities than are used for a packed column.

The Iodox contactor as a bubble-cap column. To extend the development of the Iodox process to a more practical gas-liquid contactor, the removal of I_2 and CH_3I from air with hyperazeotropic HNO_3 was studied in a 0.076-m-ID bubble-cap column.[15] It was found that:

1. Bubble-cap columns were superior for the primary Iodox contactor because scrubbing acid is conserved, and long residence times are gained at the low operating liquid flow rates,
2. For scrubbing CH_3I from air, DFs for the individual plates were about 3. Larger DFs between 5 and 10 could be obtained by lowering the air flow rate or by increasing HNO_3 concentrations to 21 M,

3. In a test of simulated HTGR feed gases (those which would contain large amounts of carbon dioxide), CO_2 had no effect on DFs for CH_3I,
4. The DFs for I_2 removal were larger than those for CH_3I in a test gas containing I_2, CO_2, and CO in air; CO and CO_2 apparently had a minimal effect on the process,
5. No measurable reduction in scrubbing effectiveness occurred as the number of plates increased and the corresponding CH_3I concentration in the gas stream decreased. For example, as the feed-gas CH_3I concentration was reduced from 170 ppm to 0.04 ppm on seven plates, the DF per plate remained at ∿3.0. This observation indicated that Iodox could be utilized for secondary polishing treatment.

<u>Correlations useful for engineering scale-up</u>. Both Mailen[9] and Groenier[15] derived expressions that were useful in describing the experimental nature of the Iodox process. The development of Mailen's correlation was dependent on the basic assumption that equilibrium existed at each plate of the bubble-cap column, whereas Groenier's expressions were developed by assuming that film diffusion, not chemical equilibria, was the controlling factor for packed-bed and bubble-cap scrubbing of iodine with HNO_3.

Mailen utilized laboratory data for the gas-HNO_3 distribution of I_2 [Eq. (8)], chemical equilibria [Eqs. (3) and (4)], and kinetics [Eqs. (6) and (7)] to derive a correlation to predict the DF for the Iodox process in a bubble-cap column. With no NO_2 or other contaminants present, the values calculated from Mailen's model for removal of I_2 from air agreed well with experimental data obtained in a 0.0254-m-ID bubble-cap column. For the more realistic case of trapping I_2 from gas streams containing NO_2, the following assumptions were made: (1) the I_2 in the liquid phase was neglected; (2) I_2 was the only volatile species; (3) the equilibrium of Eq. (3) was obeyed; and (4) conversion of I^+ to IO_3^- was negligible. The model predicted unrealistically high DFs for stages past 3 (the maximum theoretical DF is 37 for one bubble plate in the absence of NO_2) for the cases of 1 and 2% NO_2 in the feed gas.

Mailen also developed a correlation to predict the DF for CH_3I removal from air in a bubble-cap column by utilizing Eq. (10) for the CH_3I-HNO_3 reaction and the model of a gas-liquid bubbler with no NO_2. There was a greater difference between the calculated and experimental DFs for CH_3I removal than between the calculated and experimental DFs for I_2 removal in bubble-cap columns in the absence of NO_2.

It should be stressed that Mailen's correlations were derived for simple gas compositions such as air containing either I_2 or CH_3I with or without NO_2 (1 to 2%). These correlations are not applicable to actual fuel reprocessing off-gases which would contain both I_2 and organic iodides, trace organics, water, noble gases, CO_2 and CO, and air as the balance. However, the chemical mechanism data and correlations for estimating the DF were very useful in predicting trends in the Iodox process. As will be discussed later, the correlations correctly estimated the effect of high NO_2 concentrations on the DFs obtained in the initial two or three plates of the bubble-cap column.

Groenier utilized the classical two-film theory in countercurrent contacting with these major assumptions: (1) $k_5 >> k_3$ so that CH_3I can be ignored [Eqs. (10) and (2)]; (2) the I_2-HIO equilibrium was obeyed; (3) diffusional resistance was in the liquid film only; (4) gas- and liquid-phase flow rates remained constant; and (5) absorption and reaction constants were not functions of iodine concentration. A correlation for the overall mass transfer coefficient was determined to fit the data for I_2 and CH_3I removal in both packed-bed and bubble-cap column Iodox operations:

$$K_La = 0.000387\ M^{-1/3}\ , \tag{11}$$

where

K_La = overall mass transfer coefficient, overall liquid phase, g-moles/(sec-cm^3),

M = absorption factor, $M = K_G^L \frac{L_v}{G_v}$, and

L_v = liquid volumetric flow rate, cm^3/sec, and

G_v = gas volumetric flow rate, cm^3/sec.

Overall mass transfer coefficients ranged from 1.7×10^{-4} to 3.3×10^{-4} g-moles/cm^3-sec in the packed column, and from 6.0×10^{-4} to 10.2×10^{-4} in the bubble-cap column. For operation scale-up, Eq. (11) must be utilized with the expressions derived from the two-film countercontacting model for mass transfer accompanied by a two-step chemical reaction. These expressions contain such key operating parameters as DF, M, liquid inventory in the contactor, number of transfer units, effective contacting volume, and liquid phase chemical properties. By utilizing these expressions, Groenier was able to design an Iodox unit that would theoretically produce a DF of 10^5 for treating 2.8 m^3/min (100 scfm) of off-gas containing 100 ppm of either I_2 or CH_3I. The method predicted that this DF could be obtained for a 0.508-m-ID column having about 50 bubble caps on each of ten plates (total contacting volume of 22 liters per plate), with a 90% HNO_3 flow rate of 1.5 liters/min at room temperature.

It must again be stressed, however, that Groenier's expressions were shown to be applicable for only simple feed gases such as air containing only I_2 or CH_3I. They were not applicable for predicting DFs for total iodine removal from feed gases containing both CH_3I and I_2, NO_2, water, CO_2, etc.

2.1.4 Process capacity

The ultimate capacity of the Iodox process is limited by the solubility of iodic acid in >20 $\underline{M}$ HNO_3:[6]

$$\ln S = 13.28 - 0.4515\, C_{HNO_3} - 1170/T \ , \tag{12}$$

where

S = the solubility of HI_3O_8 in g/liter,

T = absolute temperature, K.

2.1.5 Present process application

An integrated Iodox system has been tested extensively by personnel in the Experimental Engineering Section of the Chemical Technology Division at ORNL. A schematic diagram of the system is shown in Fig. 1. The Iodox column is made of 0.102-m-ID glass (Pyrex) and contains eight bubble-cap plates. The feed location is at the third plate from the top

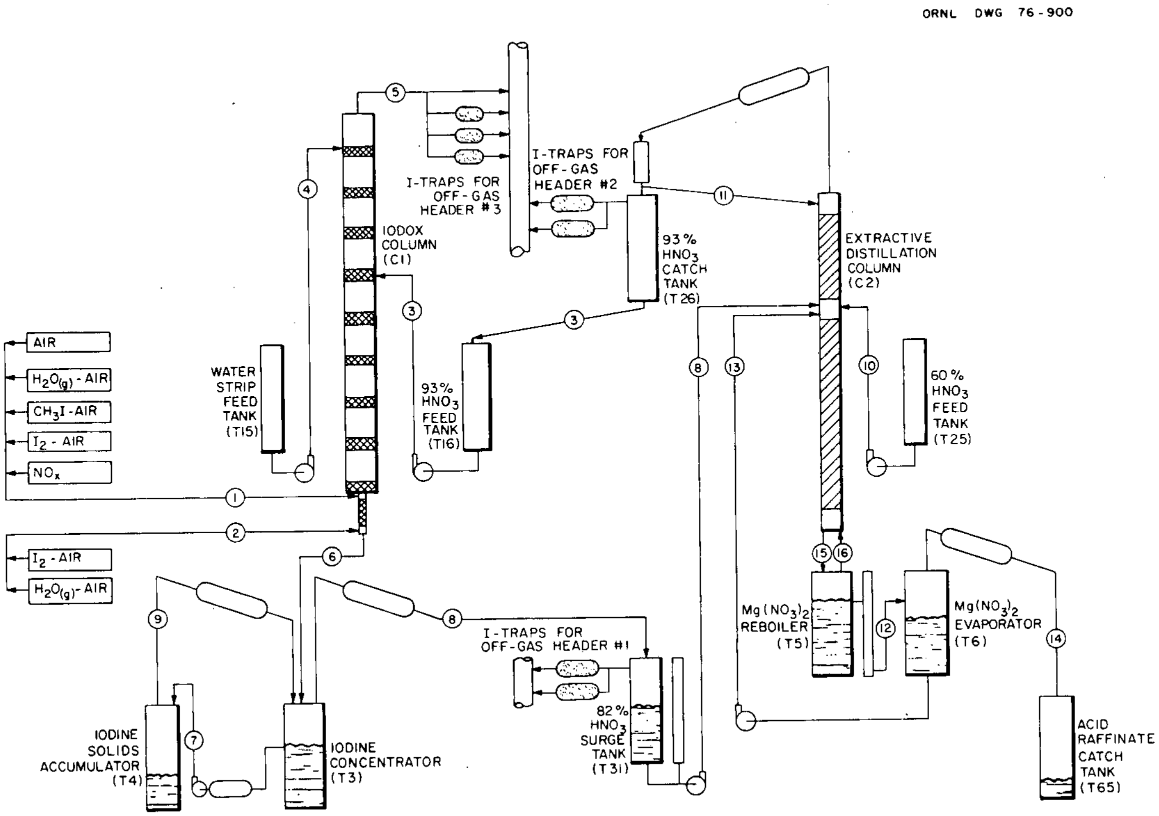

Fig. 1. Schematic diagram of process equipment in the Iodox Demonstration Facility.

(with >20 M HNO_3), and the top two plates are normally fed with H_2O to achieve acid-vapor removal from the discharged off-gas. The most realistic types of feed gases (similar to actual fuel reprocessing off-gases) are now being tested. These compositions include NO_2 at more than 2%, water vapor at >50% relative humidity, other halides such as bromides, and sudden increases in CH_3I concentration.

The I_2 and CH_3I concentration in feed gases to Iodox are adjusted to match those expected for actual head-end LWR and LMFBR fuel reprocessing off-gases. These are about 0.8×10^{-6} to 1.6×10^{-6} mole of I_2 per liter of air (∿18- to 36-ppm I_2), and 1.0×10^{-6} mole of CH_3I per liter of air (22 ppm CH_3I). Nitric acid flow rates are in the range 0.05 to 0.10 liter/min, whereas gas feed rates are about 100 liters/min.

When 2% NO_2 was initially introduced into the feed gas,[16] the DF for CH_3I of the first stage (as predicted by Mailen) was drastically reduced from the range of 4 to 5 to about 1.3. Thereafter, the DF was recovered on subsequent ascending plates. The DF for CH_3I with 2% NO_2 in the feed gas (air) was ∿2.7 per plate for a concentration of 20 to 20.9 M HNO_3. Additional runs with feed gases containing CH_3I in air with 2% NO_2 and 2% H_2O produced poor DFs[17] at relatively low acid concentrations of 19 to 20 M. However, HNO_3 concentration can be maintained in a more desirable range of 20.5 to 22.5 M by proper control of the feed acid concentration and flow rate and by careful limitation of the water feed rate to the upper portion of the column (above the acid feed plate) where nitric acid vapors are absorbed in water.[18] A superior method to recover acid-vapor recovery would employ a chilled plate or condenser above the acid feed plate, followed by an external water scrubber for the chilled gas stream. Because it is largely absorbed on the bottom plate, water vapor entering the bottom of the Iodox column has a much less diluent effect on the scrub acid than does the acid-vapor scrub water at the top of the column.

It was demonstrated in an extended run[19] that the variation of individual plate DFs for CH_3I removal with time was related to small variations in HNO_3 concentration. As shown in Table 1, the overall column DF was 4.6×10^6 for removing CH_3I from air containing 1.9% NO_2 and 2.1% H_2O; the increase in DF was attributed to an increased initial scrub-acid concentration of 23.4 M HNO_3. Also, for removal of I_2 from air containing 2% NO_2 and 2.4% H_2O, the DF was increased to 5×10^5 by utilizing a scrub acid with an initial concentration of 23.5 M.

Table 1. Iodox decontamination factors (DFs) for ^{131}I-traced CH_3I in air containing 1.9% NO_2–2.1% H_2O[a]

Conditions: Feed rate of 23.4 M HNO_3 = 0.045 ℓ/min; gas feed rate = 98 slm; CH_3I in feed gas = 264 μg I/liter (47-ppm CH_3I); T = 43°C plate 1, 50°C plate 8; run duration, 43 hr.

Plate No.	Acid concentration on plate (M)	DF
1	20.2-20.9	2.94 (±22%)
2	20.1-22.4	6.59 (±13%)
3	22.3-22.5	7.11 (±13%)
4	22.3-22.6	8.27 (±14%)
5	22.1-22.8	4.37 (±24%)
6	22.5-22.8	
Column, overall[b]		4.6×10^6

[a] The information in this table was taken from ref. 19.

[b] Based on ^{131}I averaged samples of feed and effluent gas streams.

An experiment in which the CH_3I feed concentration was increased threefold in a step change[20] demonstrated that the Iodox process can cope with the kind of concentration changes expected for a real system where the rate of evolution of iodine from dissolver solution is known to be influenced by temperature, sparge rates, etc.[21] The ability of the Iodox process to maintain satisfactory iodine trapping in the presence of a high concentration of NO_2 is illustrated by the results shown in Table 2. For acid concentrations of 22.7 to 23.1 M, the deleterious effect of high-NO_2 concentration was minimized beyond the second plate.

Table 2. Run IXD-13: Decontamination factors (DFs) for ^{131}I-traced CH_3I in air containing 7.6% NO_3--1.9% H_2O[a]

Plate	DF[b]
1	0.65 ± 0.12 (±18%)
2	2.62 ± 0.70 (±27%)
3	5.65 ± 0.68 (±12%)
4	5.48 ± 1.33 (±24%)
5	7.07 ± 2.63 (±37%)
6	48.0 ± 3.93 (±8%)
Average[c]	5.11
Column, overall	1.8×10^4
Column, overall[d]	3.2×10^5

[a] This table was taken from ref. 22.

[b] Average and standard deviation for three time periods: 300, 390, and 440 min.

[c] Average = $[(DF)_1 \times (DF)_2 \times \ldots (DF)_6]^{1/6}$.

[d] Based on the feed rate of ^{131}I-traced CH_3I from the gas cylinder (5.24×10^6 cpm) divided by the rate of ^{131}I at the two final off-gas traps (16.6 ± 1.9 cpm).

A pragmatic test of the Iodox bubble-cap column for treatment of actual off-gas from dissolution of nuclear fuel pins has recently been conducted at the Transuranium Processing Facility (TRU) at ORNL.[21] (The remaining three operations in the Iodox process were not utilized in these tests.) The Iodox column was employed as the primary equipment for removing iodine from off-gas produced during dissolution of irradiated TRU curium targets. There was close similarity between the concentrations of fission products in this dissolver solution and the concentrations calculated for spent Fast-Flux Test Facility (FFTF) fuel that was irradiated to 45,000 MWd/ton, cooled 30 days, and dissolved to 100 g per liter of heavy metal.

The conditions of the Iodox column tests were as follows:

1. Iodox column, 7.62 cm ID; six bubble-cap plates, spaced 20.3 cm apart; three bubble caps on each plate;
2. 21 to 23 M HNO_3;
3. gas flow rate about 7 slm (1.55 m/min);
4. liquid flow rate, 250 to 420 ml/hr (5.5 to 9.3 cm/hr);
5. column operated in a cell at 40°C.

The composition of the off-gas from the dissolver was dependent on the various modes of sparging utilized during four separate tests. However, the off-gas generally contained iodine, N_2, O_2 (N_2 and O_2 from air sparge), and such fission products as the noble gases xenon and krypton, and other gases such as trace carbon dioxide from the air sparge, and NO_x's arising from HNO_3 dissolution. The concentration of the other off-gas components was not established, but their presence served to authenticate the off-gas as a reasonable facsimile of a gas that would arise in processing spent fuels from the Fast-Flux Test Facility.

Although the evolution of the iodine from the dissolver varied according to the various sparging schedules, the Iodox column, for the operating conditions, column design, and off-gas composition as discussed, produced DFs for iodine from 1.2×10^4 to 8.0×10^4 (or 5 to 7 per stage). Virtually all of the iodine may be assumed to be in an inorganic state, because there were no probable sources for the formation of organic iodide. Feed concentrations were of high ^{131}I activity but relatively low overall iodine concentrations, or about 0.1 Ci ^{131}I/liter for 30 hr of averaged column operation time.

2.1.6 Process advantages

1. The Iodox process can be operated to tolerate feed gases at their dew point by proper location of the feed plate and utilization of very high scrub acid molarities (>22 M).
2. Nitrogen oxide (2% NO_2 level) can be tolerated in the process, although there is some reduction in the DF on the first one or two plates. DFs are satisfactory even at high (∿8%) NO_2 concentrations.
3. In the Iodox process, high DFs ($>10^4$) for feed gases containing either I_2 or CH_3I can thus be obtained in the presence of NO_2 and H_2O.
4. No new chemicals are introduced into the fuel reprocessing plant.
5. Reaction rates and DFs appear to be enhanced by higher off-gas temperatures.

6. The product from Iodox is essentially 100% HI_3O_8. Iodine as iodic acid is not in an acceptable form for long-term storage. The leaching characteristics of radioiodine, which is included as insoluble $Ba(IO_3)_2$ in Portland cement, have been described.[23] Iodic acid, HIO_3 (the behavior of HI_3O_8 was equivalent to that of HIO_3), was reacted with aqueous barium hydroxide [$Ba(OH)_2$] supplied so that the slurry was always alkaline, to produce $Ba(IO_3)_2$. Specimens containing from 5.4 to 11.9 wt % iodine as $Ba(IO_3)_2$ showed incremental leaching rates of ∿3 μm/day after 100 days of leaching according to standard leaching procedures. It was estimated that the fission product iodine after one year of decay would consist of 75% ^{129}I--25% ^{127}I. A $Ba(IO_3)_2$-Type 1-cement product containing 9.05% of this fission product iodine generated about 3.0 μW per kg of product. Both the leach rates and quantities of heat generated by fission product decay are acceptable for storage of the $Ba(IO_3)_2$-cement preparation in presently specified repositories. The calculation of storage space for the $Ba(IO_3)_2$-cement product was based[23] on an LMFBR fuel reprocessing plant handling 5 MTHM/day, which would produce ∿1.6 kg of iodine per day. This amount of iodine could be incorporated into $9.5 \times 10^{-3}\ m^3$ ($2.85\ m^3$/year) of concrete containing 9.05 wt % iodine.
7. The integrated Iodox system has been tested for a scale of equipment design which was of sufficient magnitude to

minimize difficulties in scale-up of the process to pilot plant or full-size plant magnitude. Runs have been completed with the Iodox integrated system in which it has been shown that all of the unit operations function as expected. The product, as a dehydrated form of HI_3O_8, has been shown to be amenable to reaction with $Ba(OH)_2$ to produce a solid that appears very promising as a candidate for long-term storage after incorporation in concrete.

2.1.7 Process disadvantages

The Iodox process has been compared[24] to the Allied Chemical INEL process for iodine sorption on tandem beds of silver-exchanged and lead-exchanged mordenites, with subsequent regeneration of the first bed (see Sect. 3.4 for a description of this process, which is still under development). Following are some of the operational limitations that have been interpreted as disadvantages for the Iodox system, with comments in brackets:

1. If NO_x scrubbing is conducted prior to Iodox, corrosion effects are associated with iodine in the scrubber acid. Hazards are also associated with holding large amounts of iodine in DOG scrubber bottoms in an easily volatilized form. [An Iodox experiment with ∿8% NO_2 in the feed gas has indicated that NO_x scrubbing prior to Iodox may possibly be eliminated.[22]]
2. If fluorides are introduced into the fuel reprocessing flowsheet (e.g., in processing denatured thorium-uranium fuel in the Zirflex process), serious corrosion could be

introduced by fluoride-zirconium — boiling nitric acid.

3. The Iodox system involves a fairly complex set of processes requiring extensive instrumentation and flow control. [Recent experience with the removal of iodine from dissolver off-gas from curium targets[21] showed that control of Iodox was straightforward, and that acceptable iodine DFs could be retained for excursions of iodine feed concentration and off-gas flow rate.[25]]
4. With its three major operations (tower, iodine accumulator-reboiler, and salt extraction distillation), Iodox could well-entail high capital costs.
5. Operation of Iodox would require internal plant production of hyperazeotropic HNO_3.
6. There is a possibility of accumulating explosive nitrates in Iodox scrubber bottoms and condensates. Hyperazeotropic HNO_3 is an excellent nitrating solution, so that care must be exercised to prevent CH_3NO_3 (and other organic nitrates, especially aromatic nitrates) from accumulating in the condenser. [The formation of CH_3NO_3 has not been yet identified as detrimental to the Iodox process.[25]]

2.2 Mercuric Nitrate--Nitric Acid Scrubbers

2.2.1 Background

One of the early processes developed for iodine species removal from fuel reprocessing off-gases was the mercuric nitrate--nitric acid

[$Hg(NO_3)_2$-HNO_3] scrubbing process in packed or bubble-cap columns featuring complete mercury recycle. This process was shown to be applicable for removal of both organic and inorganic iodides from recirculated LWR-LMFBR fuel reprocessing off-gases. When adequate residence time is provided to decompose the organic iodides in the feed gas, the overall efficiency of the process is controlled by the extent of bleed-off of accumulated iodine from the recycle solution.

2.2.2 Chemical mechanisms

The reaction between I_2 in air and a solution of $Hg(NO_3)_2$ in subazeotropic HNO_3 was:[26]

$$6I_2 + 6Hg(NO_3)_2 + 6H_2O \rightarrow 5HgI_2 + Hg(IO_3)_2 + 12HNO_3 \ ; \qquad (13)$$

however, the rate for reaction (13) was not established experimentally because the rate-controlling step for $Hg(NO_3)_2$ scrubbing of feed gases containing both I_2 and CH_3I occurred in the CH_3I-$Hg(NO_3)_2$ reaction. Due to the low solubility of mercuric iodate [$Hg(IO_3)_2$] in HNO_3, it would be preferable to operate the process to minimize the formation of iodate that was shown in reaction (13). This formation can be prevented by inclusion of nitrite in the $Hg(NO_3)_2$-HNO_3 scrub solution. It was speculated[5] that the stoichiometry of the reaction between CH_3I and $Hg(NO_3)_2$-HNO_3 solution could be either:

$$CH_3I + \frac{1}{2}Hg(NO_3)_2 \rightarrow \frac{1}{2}HgI_2 + CH_3NO_3 \qquad (14)$$

or

$$CH_3I + \frac{1}{2}Hg(NO_3)_2 + H_2O \rightarrow \frac{1}{2}HgI_2 + CH_3OH + HNO_3 \ . \qquad (15)$$

The kinetics of the CH_3I-$Hg(NO_3)_2$ reaction could be represented by a pseudo-first-order reaction.[27,28] The pseudo-first-order reaction-rate constant was 0.44 min^{-1}, and the CH_3I half-life was 1.6 min at 30°C for a CH_3I concentration of 1.6×10^{-6} M and 7.9×10^{-6} M. The reaction rates between CH_3I and very low $Hg(NO_3)_2$-HNO_3 concentrations were measured[29] and found to be proportional to both $Hg(NO_3)_2$ and HNO_3 concentrations. There were indications that the rate could be increased by a factor of 100 by increasing the HNO_3 concentration from 0.2 to 12 to 13 M.

An expression was developed[30] to describe the scrubbing efficiency of $Hg(NO_3)_2$-HNO_3 solutions for removal of CH_3I from air in a single stage. The main assumptions were: (1) the reaction to form HgI^+ (following gas to liquid distribution) was irreversible, slow, and the rate-controlling step; (2) there was perfect mixing on the stage; (3) there were no diffusion limitations. The resultant expression was

$$DF = \frac{L_v}{G_v} D_G^L + \frac{V_{LH}}{G_v} D_G^L \frac{(0.693)}{t_{1/2}} + 1 \ , \qquad (16)$$

where

D_G^L = liquid-vapor distribution coefficient for CH_3I, with a value of 4 to 8 as HNO_3 molarity increases from 0 to 12 M;

V_{LH} = liquid holdup, cm^3;

L_v, G_v = same as Eq. (11);

$t_{1/2}$ = half-life for fixation reaction, sec.

This equation can be used to estimate DFs for the CH_3I-[$Hg(NO_3)_2$-HNO_3] reaction in bubble-cap columns when appropriate stage efficiencies are available.

2.2.3 Experimental results and engineering data useful for process design

Initial studies of $Hg(NO_3)_2$-HNO_3 scrubbing of iodine. Initial studies for simple bubble-column operation indicated that large DFs could be obtained for CH_3I removal from air with $Hg(NO_3)_2$-HNO_3 solutions. So that large DFs ($>10^3$) could be maintained for CH_3I scrubbing in packed columns, it was necessary to: (1) utilize porous packing to maximize liquid holdup,[31] (2) greatly increase the HNO_3 concentration (from 0.1 M to 8 to 15 M),[29] and (3) reduce iodine bleed-off from the recirculating scrub. This reduction was achieved to some extent by the addition of an iodine recovery loop to the process.[29] The recovery loop was based on a reflux condenser, which allowed iodide to be recovered as mercuric iodate[32] while the supernatant and the distillate were being recycled.

$Hg(NO_3)_2$-HNO_3 scrubbing in packed columns. When CH_3I and I_2 were scrubbed from air in 2.54-cm-ID packed columns with 0.2 M $Hg(NO_3)_2$--14 to 15 M HNO_3 solutions with continuous iodate recovery and recycle for part of the scrub solution, DFs $\geq 10^4$ were obtained for 5 to 10 slm.[33,*] The utilization of a second column in series with the first column increased the DF no more than an order of magnitude. The DF decreased when the operating temperature was increased from 40 to 80°C. The DFs obtained for CH_3I removal in a 0.4 M $Hg(NO_3)_2$--8 M HNO_3 solution in a packed column decreased from 10^5 to 10^2 as the gas flow was increased from 2.5 to 9.5 slm.[34] Best DFs for CH_3I were obtained with a mercury concentration of 0.4 M.[35] Removal of organic contaminants from the mercury scrub solutions prior to application to the column resulted in

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[*] For the studies with $Hg(NO_3)_2$-HNO_3 scrubbing solutions, slm was for 1 atm and 25°C.

only marginal improvement in the column performance.[36,37] The DF for I_2 was much less affected by gas flow rate than was the DF for CH_3I. In tests with I_2-containing feed gases, the DF decreased by a factor of only 8 (the DF for CH_3I was reduced by 10^3) when the air flow was increased from 2.5 to 9.5 slm.[37] A schematic of the $Hg(NO_3)_2$-HNO_3 scrubbing process as conducted with the packed column is shown in Fig. 2.

<u>$Hg(NO_3)_2$-HNO_3 scrubbing in bubble-cap columns</u>. In studies of simulated bubble-cap columns (2.54 cm ID with up to eight stages, 15.2 cm/stage), DFs for CH_3I removal in 0.4 <u>M</u> $Hg(NO_3)_2$--10 <u>M</u> HNO_3 were very similar to those obtained in packed beds. When the diameter of the bubble-cap column was increased from 2.54 to 4.06 cm,[37] there was an improvement in the DF. The DF for CH_3I again varied inversely with gas velocity, decreasing from 4.4 per stage at 3.3 liters/min to 3.25 per stage at 5.3 liters/min.[38] In addition, the simultaneous removal of I_2 and CH_3I from air was studied in bubble-cap columns for feed concentrations of about 50-ppm I_2 (500 to 600 mg I_2/m^3) and 6-ppm CH_3I (40 mg CH_3I/m^3). Overall DFs were about 5×10^4 for both CH_3I and I_2 in a 2.54-cm-ID eight-stage bubble-cap column. The addition of N_2O_3, octane, and dodecane contaminants to the gas feed had little effect on the DF. However, when aromatics (xylene, diethylbenzene) were added to the feed gas, the DF was <u>decreased</u> by 2 to 3 orders of magnitude. The DF for trapping phenyl iodide was at least 2 orders of magnitude less than the DF for CH_3I. Other alkyl iodides were absorbed with efficiencies similar to that for CH_3I.[38]

A study[39] was conducted to ascertain the capability of the bubble-cap operation (1) to treat feed gases similar to fuel reprocessing

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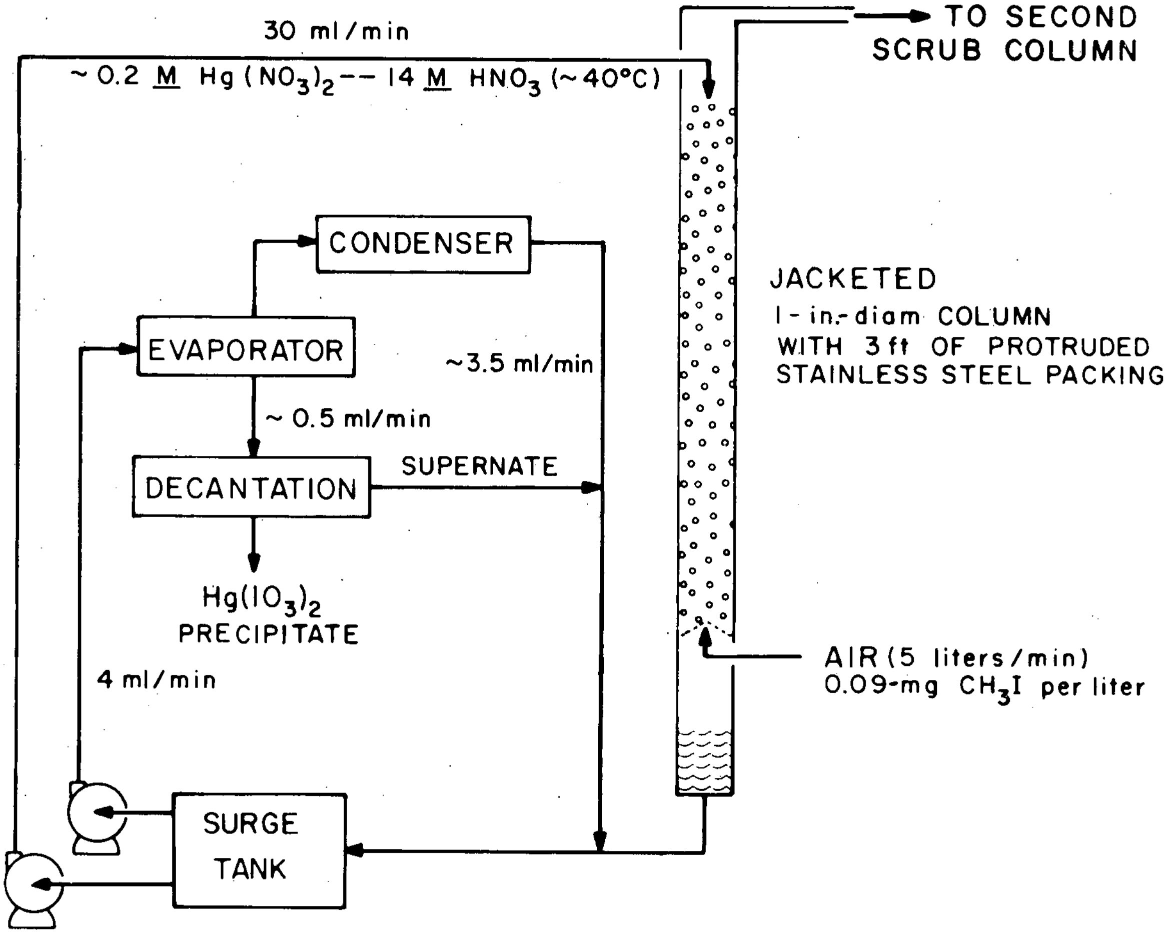

Fig. 2. Schematic of equipment for scrubbing methyl iodide from air with 0.2 M $Hg(NO_3)_2$--14 M HNO_3 in a packed column.

head-end off-gases (I_2 at 50 ppm), and (2) to treat feeds that would simulate effluent streams which were products from primary iodine treatment or were off-gases from vessel and process off-gas bleeds (0.05-ppm I_2). The DFs for I_2 removal showed a slight dependence on I_2 feed gas concentration, with a reduction in DF of one order when the I_2 concentration was decreased by 3 orders of magnitude. Decontamination factors of about 10^3 to 10^4 were obtained for I_2 removal from air (at 0.05-ppm I_2) with $Hg(NO_3)_2$-HNO_3 scrubbing for a wide range of iodine concentrations in the scrub liquor, which varied from 0.01- to 8-g I^-/liter. In summary, a fairly constant DF for I_2 scrubbing was maintained in both bubble-cap[38,39] and packed columns[31,33,34,37] for variations of gas residence time, column geometry and packing material, concentrations of $Hg(NO_3)_2$ and HNO_3, and I_2 feed concentration. This behavior seemed to indicate that the DF for I_2 during $Hg(NO_3)_2$-HNO_3 scrubbing was controlled primarily by bleed-off of iodine from the circulating solution in the form of relatively stable organic iodides (produced by the reaction of iodine with organic impurities in the solution).

<u>Correlations useful for engineering scale-up</u>. The DFs for CH_3I and I_2 at low flow rates were similar for bubble-cap scrubbing.[38] However, the DF for I_2 showed very little change when the operating parameters were varied. Conversely, the DF for CH_3I in both bubble-cap[37,38] and packed-bed operations[31-36,39] could be correlated with such parameters as $Hg(NO_3)_2$ concentration, HNO_3 concentration, gas residence time, and type of packing. A useful correlation for the parameter ranges outlined above was developed:[5]

$$\ln DF = \left(\frac{\tau}{A}\right) \exp^{\left(-0.282 + 0.288\ C_{HNO_3} + 4.54\ C_{Hg}\right)} ; \tag{17}$$

for a DF $\leq 10^3$. However, for a DF $\geq 10^3$, the expression was:

$$\ln \mathrm{DF} = 1.893 + \left(\frac{\tau}{A}\right) \exp\left(-0.62 + 0.288\ C_{HNO_3} + 4.54\ C_{Hg}\right) ; \qquad (18)$$

where τ is the gas residence time (min), C_{HNO_3} is HNO_3 molarity, C_{Hg} is $Hg(NO_3)_2$ molarity, and A is a column packing parameter. The ranges of variables for which the two empirical correlations produced useful predictions for acid recycle operation are:

DF	1 to 10^5
τ	0.02 to 0.34
C_{HNO_3}	0.005 to 14
C_{Hg}	0.005 to 0.4

2.2.4 Process capacity

The capacity of the $Hg(NO_3)_2$-HNO_3 scrubbing process is determined by the need to maintain a mercury to iodine ratio of about 4 to prevent HgI_2 precipitation.[5] Thus for a 0.4 M $Hg(NO_3)_2$ solution, the iodine concentration can be no higher than 12.75-g I_2/liter. The presence of nitrite in the scrub solution prevents formation of iodate precipitates at conditions of low operating temperatures and high HNO_3 concentrations. In actual plant operation, the presence of NO_x in the off-gas will result in production of HNO_2 (nitrous acid) and, thus, prevention of iodate formation.

2.2.5 Current process application

The $Hg(NO_3)_2$-HNO_3 scrubber process has been used in series with other processes such as caustic scrubbing and charcoal sorption to remove iodine species from dissolver off-gases (e.g., the TRU Facility at ORNL[40,41]). Practical operating DFs of 10^2 were obtained with the mercury scrubber. The $Hg(NO_3)_2$-HNO_3 scrubbing system was installed in the full-scale LWR fuel reprocessing plant constructed by AGNS at Barnwell, South Carolina. A plant DF of 10 for ^{129}I and ^{131}I is claimed when mercury recycle and iodine isolation by evaporation and condensation are not used; if iodine volatilization and recovery as a solid condensate are used, a DF of 75 would be claimed.[3] In general, bleed-off in the recirculating scrub of previously sorbed iodine will probably limit the effective overall iodine DF to about 10^2 for acid recycle operation; the iodine loading of the waste scrub mercury solution is about 1 mole of I^- per 4 moles of Hg. The effluent stream from a $Hg(NO_3)_2$ scrubber in a 5 MTHM/day fuel reprocessing plant might typically consist of 100 liters/day of 8 M HNO_3 and 0.4 M $Hg(NO_3)_2$ containing 1300 g of I_2. If not recycled, this would amount to 30 m^3 of liquid wastes per year. Thus an obvious alteration that could improve the process would be the development of complete recycle of the mercury.[42] It has recently been shown in bench-scale studies[43] that the mercury in the $Hg(NO_3)_2$-HNO_3 scrubbing process can be recycled. The mercuric iodate product [$Hg(IO_3)_2$] was contacted with NaOH to yield HgO and $NaIO_3$. The HgO could then be recycled with HNO_3, while the $NaIO_3$ was reacted with $Ba(OH)_2$ to recover iodine as $Ba(IO_3)_2$. The $Ba(IO_3)_2$ was cast into a Type-I concrete which was 15 wt % iodine as barium iodate.

2.2.6 Process advantages

1. Both I_2 and CH_3I can be removed simultaneously from off-gases, with appreciable DFs, by utilizing $Hg(NO_3)_2$-HNO_3 scrubbing.

2. The removal of I_2 and CH_3I is relatively unaffected by other alkyl iodides and such trace organic contaminants as octane and dodecane in the feed gas.
3. The removal of iodide species would probably be affected very little by water vapor up to 100% humidity.
4. The $Hg(NO_3)_2$-HNO_3 scrubbing process actually benefits from the presence of NO_2 in the feed gas, since it acts to prevent formation of insoluble $Hg(IO_3)_2$.
5. The contactor can be constructed from stainless steel.

2.2.7 Process disadvantages

1. Further studies are required to optimize conversion of the mercury-iodide species to a suitable disposal form, which would simultaneously provide recycle of the bulk of the $Hg(NO_3)_2$-HNO_3 solution back to the process.
2. Considerable reduction in DF occurs as a result of high iodine bleed-off at high iodine-to-mercury ratios in the scrub solution.
3. No test results have been obtained for full-scale process columns. Additional tests of the process in engineering equipment would be desirable to further substantiate the process efficiency and to provide better scale-up information.
4. Perhaps the most serious diminution of process DF occurs if aromatics are present in the feed gas.

3. THE REMOVAL OF IODINE SPECIES FROM OFF-GASES BY UTILIZING SOLID SORBENTS

The nitric acid scrubbing methods previously discussed have been proposed primarily for removing iodine species from off-gases produced in large-scale fuel reprocessing plants. These acid scrub methods could also be utilized in smaller-scale nuclear operations [e.g., the cleaning of ventilation air and off-gases from such experimental facilities as the ORNL High-Flux Isotope Reactor (HFIR) operation or the TRU Facility]. However, solid sorbent beds have been proposed as alternatives to the acid scrub operations, because solid sorbents may be inherently less complicated, less expensive, and less affected by process equipment failures than are the wet scrub operations. Among the solid sorbents that have been used or show promise in the processing of nuclear power-associated off-gases are: (1) charcoal for controlling iodine removal from air and gas cleaning systems in experimental nuclear facilities and commercial nuclear power plants; (2) silver-exchanged zeolites for polishing effluents from primary iodine removal processes in fuel reprocessing plants; (3) silver- and lead-exchanged mordenites for direct treatment of fuel reprocessing head-end dissolver off-gas; and (4) macroreticular resins for polishing dilute-in-iodine off-gases that could be produced during volatilization of low-level liquid radwastes from fuel reprocessing.

Four measures of performance are normally used to determine the capability of a solid sorbent to remove iodine species from off-gases. These include sorbent loading capacity and three definitions for the fraction of iodine removed from the feed gas: penetration, efficiency, and decontamination factor (DF). The latter three factors are related as follows:

Penetration = 1-efficiency

$$\text{Decontamination factor} = \frac{1}{\text{1-efficiency}} = \frac{1}{\text{penetration}} .$$

The most-often utilized measure of removal performance is the DF. It is defined as the moles of an iodine compound in the feed gas divided by the moles of the same iodine compound in the effluent gas. The DF is normally measured by utilizing a highly radioactive iodine isotope, because removal efficiencies are usually so large that nonradiotracer methods do not provide the required sensitivity to detect low levels of iodine. The most-often used radioiodine isotopes are ^{131}I with a half-life of 8.06 days, and ^{130}I with a half-life of 12.4 hr. Along with a measure of the fraction of the iodine that is removed from the feed gas, it is necessary to specify the quantity of iodine that can be loaded on the sorbent of interest while maintaining the fractional removal. The loading capacity is generally expressed as either milligrams of iodine sorbed per gram or per cubic centimeter of sorbent.

3.1 Removal of Iodine Species from Nuclear Reactor Operation Off-Gases by Utilizing Activated Charcoal

3.1.1 Background

For large gas-flow rates such as in air ventilation and air cleanup systems at nuclear installations, adsorption on activated charcoal is the method most frequently used to trap radioiodine species. The capacity of activated charcoal to sorb organic iodides can be enhanced by impregnation with chemicals. The most widely used impregnants are I_2, KI, KI-I_2, KOH-I_2, triethylenediamine (TEDA), and hexamethylenetetramine (HMTA). However, charcoal has not generally been considered as a sorbent for off-gases from nuclear fuel reprocessing plants because: (1) it is deleteriously affected by nitrogen oxides (with the possible generation of explosive compounds[44]); (2) it desorbs iodine readily at high temperatures; (3) it has a low ignition temperature; (4) these cumulative effects render activated charcoal hazardous in treatment of off-gases and untrustworthy as a solid for long-term burial. Although activated charcoal is not normally considered a candidate for treatment of fuel reprocessing off-gases for the reasons listed, it is possible that banks of charcoal traps could be installed as a final emergency air-cleaning system for the ventilation air in reprocessing plants.

Because activated charcoal cannot seriously be considered as a sorbent for nuclear fuel reprocessing plants, only a brief survey will be presented here of the voluminous literature associated with its utilization in cleanup of reactor operation off-gases. Emphasis is placed on references detailing early studies with activated charcoal for iodine removal, particularly those studies which examined the basic chemical mechanisms and attempted elucidation of the effects of the many parameters that are present in the iodine-charcoal binding process.

Perhaps no process involving the treatment of radionuclide contaminated off-gases is as complicated as the use of activated charcoal to remove iodine species from very dilute concentrations in off-gases. Activated charcoal-bed filters have been used worldwide to treat nuclear power plant exhaust gases, and extensive experimental studies have been directed toward ascertaining the mechanistic intricacies of the charcoal-iodine species interaction. However, the complexity of the chemical reaction and the effects of many operating parameters have defied tractable correlations; therefore, the utility companies and research installations generally rely on strict filtering schedules that have been established empirically after years of operating experience. These operating procedures must be adhered to and monitored very closely to ensure that one of the many process variables that can disrupt charcoal filter bed operation does not introduce a serious excursion into the iodine removal operation.

The complexity of attempting to define the function of activated charcoal filter beds for any prolonged period can be attributed to the multiparameter dependency of the iodine-charcoal sorption mechanism. In many studies, it has been shown that the sorption of CH_3I (and to a much smaller degree, molecular iodine) onto activated charcoal is dependent on the following parameters: inlet concentration, superficial velocity, relative humidity, intense radiation field, temperature, charcoal mesh size, manufacturer, impregnant, bed depth, and run duration, and aging, weathering, and poisoning (these three may be intimately related). This list of parameters may not be totally inclusive of all possible operating condition effects. Few attempts have been made to collect and analyze the voluminous data obtained from experimental studies and actual plant operation for the removal of airborne iodine with activated charcoal. However, an in-depth and contemporary summary of the state of the art involved in use of charcoal to remove airborne iodine species from the gaseous effluents of nuclear facilities has recently been published.[45]

3.1.2 Chemical mechanism

Regardless of the impregnant in the charcoal, most investigators have agreed that molecular iodine is apparently adsorbed physically on active carbon sites. However, in a study of the capabilities of various impregnated charcoals to retain iodine at elevated temperatures (4 hr at 180°C),[46] it was found that the iodine capacity was strongly dependent on the pH and alkali-metal content of the charcoals. The following expression was proposed to represent the interaction between K^+, I^-, and pH where conversion of elemental iodine to ionic iodine was the reaction that enhanced sorption:

$$I_a \text{ (atomic iodine)} + 2K^+ + 2OH^- \rightarrow 2K^+ + 2I^- + H_2O + \frac{1}{2}O_2 \ . \qquad (19)$$

In a strongly basic environment, there could also be formation of other ionic forms of iodine such as iodate, hypoiodite, or periodate. It was concluded that because of its natural high content of K^+ and high pH, coconut carbon was preferred as the natural base material for nuclear air cleaning applications; nevertheless, it was shown that a product equal to or better than I_2-impregnated coconut carbons could be prepared from low-potassium carbon by treating it with $KOH-I_2$ mixtures.

The theory for the CH_3I-charcoal interaction is still being debated, but the mechanism that has been most widely accepted is that organic iodides are chemisorbed on activated carbon that has been impregnated with iodides by an isotopic exchange reaction. For example, for a $K^{127}I$ impregnate,[47]

$$CH_3{}^{131}I\text{(air)} + K^{127}I\text{(charcoal)} \rightarrow CH_3{}^{127}I\text{(air)} + K^{131}I\text{(charcoal)} \ , \qquad (20)$$

where $CH_3{}^{131}I$ is assumed to be a representative aliphatic iodide. Although only the iodine of the CH_3I compound is involved in the isotopic exchange mechanism, the removal efficiency of $CH_3{}^{131}I$ is assumed to be the same as that of ${}^{131}I^-$.

Heterocyclic amines appear to be excellent ligand molecules for sorption of organic iodides because the amine is more reactive with organic iodide than with water, and the double amine groups provide a strong attachment to both the charcoal and the organic iodide. The reaction is generally shown as:

$$R_3N + CH_3{}^{131}I \rightarrow R_3N^+CH_3{}^{131}I^- \;, \qquad (21)$$

so that the quaternary amine is then adsorbed strongly to the charcoal.

Recently, a somewhat different mechanism than that shown in Eq. (20) was proposed, although the end product is the same. It was hypothesized that iodine is trapped by charcoal sorbents as a catalytic process where the carbon acts as a catalyst support, but it would not be completely inert in the reaction. The proposed mechanism was:

$$CH_3{}^{131}I(g) + K^+OI^-(c) \rightarrow CH_3OI(g) + K^{131}I(c) \;, \qquad (22)$$

$$CH_3OI(g) + K^+(OH)(c) \rightarrow CH_3OH(g) + K^+OI^-(c) \;, \qquad (23)$$

where g is gas and c is charcoal. The mechanism provides an explanation for the experimental observation that removal efficiency increases with pH. The chain reaction, involving regeneration of the active OI^- species, could be terminated by acidification arising from organic poisons collected from the air stream, by reaction products (CH_3OH), or by poisons inherent in the charcoal itself.

3.1.3 Standard operating conditions for activated charcoal beds utilized in iodine species removal from nuclear power plant off-gases

In the event of a major accident at a nuclear reactor, the concentration of iodine in the ventilation air could be as much as 5000 mg/m^3 (∿500 ppm I_2), depending on reactor size, degree of fuel burnup at the time of the accident, and the nature of the accident. One of the main design considerations in iodine containment at a nuclear reactor is to ensure the capability of charcoal bed filters to remove iodine from the off-gas at routine concentrations of $\leq 10^{-3}$ μg I_2/m^3; in addition, the filters must retain an acceptable removal efficiency for the treatment of concentrations as large as 10^3 mg I_2/m^3 for short bursts at times of accidental release. Thus in the many experiments that have involved charcoal filtration of iodine-bearing gas streams, feed concentrations have been used that vary from 10^{-6} μg/m^3 to 3000 μg/m^3 of $CH_3{}^{131}I$. The variation in DF with inlet concentration has been one of the major functional dependencies of the iodine-charcoal sorption process, along with the variation of DF with superficial velocity, relative humidity, aging, and weathering. However, it has been stressed[49] that much of the concern about the ability of charcoal to interact with iodine concentrations below 10^{-3} μg/m^3 may have been unnecessary, because the typical average total (normal and radioactive) iodine content in the atmosphere is in the 10^{-2} to 10^{-3} μg/m^3 range. Thus the lower concentrations can be expected only for such dilute radioactive species as ${}^{131}I_2$, $CH_3{}^{131}I$, or $HO{}^{131}I$.

In the United States,[50] representative samples matching the history of those in the filter trays are tested periodically in a laboratory with

$CH_3{}^{131}I$ and ${}^{131}I_2$, whereas leak tests of the actual functioning tray configuration are conducted with freon.[51,52] Minimum efficiencies for I_2 and CH_3I at low (21°C) and high (80°C) temperatures and low (70%) and high (>95%) relative humidity are specified in ANSI N509 and RDT/M/16-1.[52,53] Any good grade of activated carbon, with or without impregnant, will deliver a DF of 100 for I_2 with any combination of temperature and humidity that would be encountered in a nuclear air-cleaning system. However, impregnated charcoals are required to trap highly penetrating organic iodides (or HOI). The efficiency of these charcoals is dependent on flow conditions, so that performance of the activated charcoals for organic iodides in the United States must be qualified under a range of operating conditions specified in RDT/M/16-1. In Europe, the testing of charcoal filters at nuclear facilities is achieved in situ for the installed system by periodic injection of CH_3I and/or I_2.[54]

3.1.4 Experimental results and present applications of activated charcoal to filter iodine species from nuclear facility off-gases

No effort was made to review every study in which charcoal, either activated only or also with impregnants, has been used to remove I_2 and CH_3I from gas streams. However, certain key studies, inclusive of the time from process introduction to present status of the art, are shown in Table 3, along with the parameters of iodine-charcoal sorption operation specifically investigated.[44,46-48,55-80]

Among the major developments was the introduction[59] of impregnated charcoals for iodine species removal. At about the same time, Collins et al.[60] found that KI-impregnated carbons demonstrated better removal efficiency for $CH_3{}^{131}I$ than did untreated carbons. After the publication of these

Table 3. Summary of literature survey of the main operating parameters and their effect on the decontamination factor (DF) for CH_3I and I_2 removal from gases with activated charcoal

Parameter	General variation in DF for CH_3I	Relevant studies (ref.)	General variation in DF for I_2	Relevant studies (ref.)
Inlet concentration	Inversely	55,56	None	56-58
Superficial velocity	Inversely	56,59-62	None	56-58,61
Charcoal mesh size	Inversely	56,60,63	None	56,63
Manufacturer	Strong effect	56,60,61,64,65	None	46,56,64,66-68
Impregnant	Directly; generally improved performance	47,48,56,59-65,69	Better with high alkali	46,56,64,66-68
Bed depth	Directly	56,59,62,64,65	Directly	64
Aging, weathering, poisoning	Inversely	56,60,61,63-74	Inversely	57,58,61,64,66-69
Run time	Inversely	[a]	Inversely for extended times	46,57,58,66-68
Temperature	Inversely	60,61,63,64,75	Inversely at high temperatures	46,57,58,61,66-68
Ignition	Destructive	44,48,75-80	Destructive	Same as for CH_3I
Relative humidity	Inversely	55,56,59-61,63,64,69	None under 100%	55-58,61,69
Highly intense radiation field	Inversely	61,63,66-69	Inversely	61,63,69

[a] Run time is a parameter whose effects are very closely related to those of aging, weathering and poisoning, so that generally DFs deteriorate with extended run time, aging, etc.

two articles describing the initial discovery of the advantages of I_2- and K^+-impregnated charcoals, there was a proliferation in the number of studies of impregnated charcoals.[81-83] The Collins paper[60] was essentially a classic study of the efficiency of KI- and TEDA-impregnated charcoals to remove CH_3I. The effect on the DF and loading capacity of CH_3I was studied as a function of CO_2, temperature to superheated steam, H_2O condensation effect, relative humidity, charcoal mesh size, manufacturer, aging, organic weathering, and run time. An extensive parametric study concerning the DFs for I_2 and CH_3I obtained on various charcoals for very low feed concentrations was published later.[56]

Only a few attempts have been made to develop empirical correlations to predict the DF for CH_3I removal from off-gases as a function of some or all of the parameters listed in Table 3,[56,84] but no attempt has been inclusively successful.

A few studies have indicated that flooding of charcoal beds with water effectively destroys their capability to trap iodine in any form and would also result in the release of any radioiodine that has been trapped.[60,85]

Some iodine loss will occur at desorption temperatures in excess of the adsorption temperature, particularly from impregnated charcoals. The higher temperatures may also desorb some of the impregnant and further reduce the capacity for organic iodides.

Two major concerns in the application of activated charcoal to treat off-gases containing radioiodine are: (1) the possibility of a slow release of large concentrations of iodine which have been sorbed onto charcoal during accidental conditions or after long periods of routine treatment of off-gases from reactor facilities,[66-69,75] and (2) the possibility of ignition of the charcoal due to the decay heat generated by collected fission products (particularly ^{131}I).[75-79]

Numerous studies have been conducted to define the major parameters that affect the slow release of iodine from preloaded activated charcoal. It has been determined[69] that the release was dependent on at least four environmental parameters: (1) the service history, (2) organic contaminants in the air, (3) the relative humidity, and (4) ionizing radiation. For coconut-based charcoals in 28 cm^3 beds, with iodine loads ranging from 50 to 570 Ci (relative humidity was 47% at the bed-inlet temperature of 70°C), it was found[61] that radioactive iodine was released from test beds for all charcoals tested. The chemical form of the released iodine, which was very highly penetrating with respect to several different kinds of commercial impregnated charcoal, was not determined (it could possibly have been HOI or some similar unusual iodine species). The formation of this highly penetrating iodine species was apparently promoted by moisture and radiation.

For removing airborne iodine with impregnated activated charcoal, the ignition temperature of charcoal is a function of adsorbed fission product concentration, internal surface area, ash content, impurities, mesh size, ignition temperatures of impregnants, bed depth, and gas flow through the bed.[47,61,76-80,85] The ignition point may be further affected by adsorbed compounds (such as solvents and hydrocarbons). The lowest ignition point for KI-impregnated coconut-based charcoals has been about 300°C.[78] Ignition of TEDA-impregnated charcoals may occur at temperatures as low as 180°C depending on the degree of impregnation, the gas flow rate, and bed depth. The only method of bed cooling normally utilized for charcoal filters is forced-air circulation. It is generally suggested that ignition caused by radioiodine decay heat can be avoided by maintaining air flow in excess of 5 fpm. According to Lorenz et al.,[61] when the velocity of moist air was decreased from 28.5 fpm (25°C) to 0.71 fpm, the temperature of the charcoal bed preloaded with radioiodine reached the ignition point in three cases. Charcoal exposed for 4 years ignited at 283°C, as compared with ignition at 368°C for unused charcoal from the same batch. For 28 cm^3 of charcoal, the ignition temperatures and radioiodine loading were: (1) 283°C at 260 Ci of ^{130}I; (2) 307°C at >291 Ci of ^{130}I; and (3) 310°C at 240 Ci of ^{130}I.

3.1.5 Process capacity

The loading capacity of activated charcoal for iodine species is intimately related to many operating parameters, but apparently the most important variables are type of iodine species, relative humidity, temperature, run time (and effects of weathering and poisoning), bed depth, and superficial velocity. In general, to maintain efficient iodine removal $\geq 99\%$ (DF $>10^2$) for feed gases containing highly penetrating iodine species (HOI or organic iodides), it is necessary to restrict the run time and thus reduce loading capacity to maintain DF, or to elongate the bed to both maintain the DF and retain loading capacity.

In early studies utilizing activated charcoal for iodine species removal from off-gases, loadings of 0.005 to 0.08-mg CH_3I/g impregnated charcoal were obtained[59] for a wide range of run conditions, which included as much as 70% relative humidity, while retaining a DF $>10^2$ for up to 28 hr. To maintain DFs of 10^3 for CH_3I removal for run times up to 27 hr, Collins[60] limited his loading to 0.1-mg CH_3I/g of KI-impregnated charcoal and to 1-mg CH_3I/g of TEDA-impregnated charcoal. For feed concentrations of 10-mg CH_3I/m^3, Ludwick[64] achieved loadings of 1 to 2-mg CH_3I/g of charcoal for flow conditions as stringent as 100°C and 100% relative humidity; however, the DFs were reduced to about 10 for 2.54-cm-long beds and to ∿100 for 5.08-cm-long beds. The DFs for elemental iodine were always higher than those for CH_3I at similar operating conditions. In studies of the utilization of silver-exchanged zeolites for iodine species removal, Pence et al.[86] investigated comparative CH_3I loading capacities of AgX and activated charcoal. They were able to obtain CH_3I loading on activated charcoal of as much as 11-mg CH_3I/g of charcoal for a 200-mg CH_3I/m^3 feed, but the penalty was a reduction in DF to only 100 for CH_3I in dry air at 25°C. Note that the DFs achieved for both AgX and charcoal are drastically reduced at ambient conditions with increasing relative humidities.

Recently, Wilhelm[45] stated that to maintain removal efficiencies consistent with existing environmental standards for the iodine content of nuclear power plant off-gases, loadings should not exceed 0.1 mg of CH_3I and 1 mg of molecular I_2 per gram of charcoal for KI-impregnated charcoals; however, for TEDA-impregnated charcoals, loading should not exceed 1 mg of CH_3I/g of charcoal.

3.2 Removal of Iodine Species from Off-Gases by Utilizing Metal-Exchanged Zeolites

3.2.1 Background

Silver and other metal-exchanged zeolites were among the first alternative sorbents proposed to replace charcoal for removal of iodine species from nuclear facility off-gases. These sorbents are prepared by a replacement of sodium ions in the zeolite structure by the other cations. The most extensive studies have been conducted and the best iodine removal efficiencies have been obtained with silver-exchanged zeolites (AgX). Among the other cations that have been studied are Cd, Cu, Pb, K, Hg, Zn, Mn, Co, and Ni. Promising cation zeolites were those derived from Pb, K, and Cd, but none of these were as efficient as Ag. The silver zeolites offered advantages such as stability, nonflammability, low-explosion hazard, and a stable disposal form.

3.2.2 Chemical mechanism

The chemical mechanism involved in the sorption of iodine species on metal-exchanged zeolites has not been rigorously determined. However, the kinetics of the silver zeolite--iodine interaction may be similar to those proposed by Wilhelm et al.[45] for silver-substituted amorphous alumina-silicates where silver iodides are postulated as the end product.

3.2.3 Experimental results and engineering data useful for process design

Maeck et al.[87] screened a variety of organic and inorganic sorbents used to remove molecular iodine and methyl iodide from water-saturated air (at 25°C) and steam-air mixtures. The most efficient adsorbent was silver-exchanged 13X-molecular sieve (zeolite). The AgX (∿99% exchanged) could efficiently adsorb iodine up to 500°C and could retain it to 1000°C. Based on iodine retention at high temperatures, flammability, and performance in steam, silver-exchanged zeolites were superior to KI-impregnated charcoal.

Subsequently, more extensive experiments[86] were conducted to determine the CH_3I removal efficiency of AgX as affected by the parameters of relative humidity, temperature, superficial velocity, bed depth, loading capacity, feed concentration, and inorganic and organic feed contaminants. The DF for CH_3I varied inversely with relative humidity for a given temperature, but the variation was less at higher temperatures. When the relative humidity was increased from 80 to 100%, the trapping efficiency decreased from 99.8 to 92.5% in one series of tests with the following parameters: feed concentration, 10 μg of CH_3I/m^3; superficial velocity, $\sim$35.0 m/min; and temperature, 60°C. The DF for CH_3I also varied inversely with superficial velocity. When CH_3I was removed from dry air at 25°C, the loading capacity of AgX increased as the CH_3I concentration decreased. The loading capacity increased from 37 to 84-mg CH_3I/g of AgX when the CH_3I concentration was decreased from 5000 to 230 mg/m^3 (850 to 39 ppm), but the DF was maintained at 10^4. The loading capacity of Barnebey-Cheney-727 impregnated charcoal was comparable to that of AgX at high CH_3I-feed concentrations, but it was significantly lower for CH_3I concentrations <0.5 g/m^3 (85 ppm). Methyl iodide was much more susceptible to leaching with water when sorbed to charcoal than when sorbed to AgX. When molecular iodine was removed from air at 25°C and 92 ft/min, AgX was found to be reasonably resistant to poisoning by the contaminant gases NO_2, CO_2, O_2, SO_2, H_2S, propane, and hexane. Details of the operating conditions and their effects on the AgX-iodine interaction for some of the most significant studies of AgX are summarized in Table 4.[86,88-90]

Maeck and Pence[91] also determined that the CH_3I loading capacity and the CH_3I achievable on AgX could be increased significantly, expecially in the presence of H_2O, by heating the AgX beds (see data for ref. 86 in Table 4). This effect was attributed to a reduction in relative humidity and an increase in the reaction rate between AgX and CH_3I. The adsorption capacity for molecular I_2 of lead-exchanged zeolite was strongly dependent on the relative humidity. The alternate use of tandem beds of AgX and PbX for iodine removal was suggested to minimize the cost of once-through use of AgX beds. Increased I_2 sorption on PbX could also be obtained by heating the PbX bed. Silver zeolite had a high affinity for hydrogen at temperatures >100°C. The capacity of AgX for CH_3I was at least 20 times that of charcoal (100 vs 5-mg CH_3I/g sorbent). However, AgX was at least 20 times as expensive as an equal weight of charcoal. Because it was less flammable and less affected by high temperatures than charcoal (both, however, are deleteriously affected by high concentrations of NO_x gases at 100% relative humidity), AgX was proposed for use in treating off-gases from nuclear fuel reprocessing plants.

In further tests, Pence et al.[89] studied the effect on CH_3I removal with AgX beds of such variables as high bed temperature, high relative humidity, steam atmosphere, particle size, contaminant gases, and feed CH_3I concentration. The adsorption efficiency of CH_3I from air at 90°C, 90% relative humidity (feed level of 0.1 μg CH_3I/m^3 or 1.7×10^{-5} ppm), and 14 m/min was not affected by O_2, CO_2, NO_2, H_2,

Table 4. Effects of variations in feed concentration, temperature, and relative humidity on the capability of silver zeolites to remove iodine species from off-gases

Ref. No.	Sorbent	CH_3I feed concentration[a] (per m^3)	I_2 feed concentration (per m^3)	Gas superficial velocity (m/min)	Ambient[b] H_2O concentration (%)	Relative humidity (%)	Feed gas temp (°C)	Loading capacity	DF	Run time (hr)	Bed depth (cm)
88	90% AgX[c]	$\sim$222 mg		12	2.3	90	27	12 mg CH_3I/cm^3[d]	27	4	5.08
	90% AgX[c]	$\sim$200 mg		12	0	0	26	11.2 mg CH_3I/cm^3	1×10^4	4	5.08
	98% AgX[c]	4.4 mg		19	2.3	0.14	200	9.1 mg CH_3I/cm^3	2×10^4	100	5.08
	98% AgX[c]	129 mg		19	2.3	0.14	200	10.6 mg CH_3I/cm^3	3×10^4	4	5.08
	90% AgX[c]	816 mg		19	2.3	0.14	200	74 mg CH_3I/cm^3	1×10^4	4	5.08
	90% AgX[c]		$\sim$12 mg	15	2.3	2.3	100	6.6 mg I_2/cm^3	1×10^5	31	5.08
	90% AgX[c]		$\sim$8.0 mg	19	2.3	0.14	200	5.7 mg I_2/cm^3	3×10^5	31	5.08
86	99% AgX[e]	0.1 to $\sim$10 μg		28	2.8	90	25	ND[f]	16.6	1.0	5.08
	99% AgX[e]	0.1 to $\sim$10 μg		28	3.0	95	25	ND	12.5	1.0	5.08
	99% AgX[e]	0.1 to $\sim$10 μg		28	3.2	100	25	ND	10	1.0	5.08
	99% AgX[e]	0.1 to $\sim$10 μg		17	17.7	90	60	ND	142	1.0	5.08
	99% AgX[e]	0.1 to $\sim$10 μg		19	62	89	90	ND	330	1.0	5.08
	99% AgX[e]		5 to 100×10^3 μg	28	$\sim$2.0	100	22	ND	$>10^4$	ND	5.08
	99% AgX[e]	230 mg		14	0	0	25	84 mg CH_3I/g	$>10^4$	26	5.08
89	99% AgX[e]	0.1 to 10 μg		15		90	90	ND	1.2×10^5	1-6	10
	99% AgX[e]	10^{-5} to 10^{-4} μg		15		90	90	ND	4×10^3	1-6	10
	99% AgX[e]	10^{-5} to 10^{-4} μg		30		90	90	ND	4×10^3	1-6	10
	99% AgX[g]	0.1 to 10 μg		15		90	90	ND	2×10^3	1-6	10
90	AgX		500 mg	60	5[h]	5	100	42 mg I_2/g[d]	2×10^2[i]	5-16	10
	AgX		500 mg	60	5[h]	0.32	200	55 mg I_2/g	2×10^2	5-16	10
	AgX		500 mg	60	0	0	100	139 mg I_2/g	2×10^2	5-16	10

[a] For 21°C and 1 atm, 1 μg $CH_3I/m^3 = 1.7 \times 10^{-4}$ ppm, 1 μg $I_2/m^3 = 9.5 \times 10^{-5}$ ppm.

[b] Assuming water vapor as ideal gas.

[c] 1/16-in. pellets.

[d] Dry density of AgX is about 0.8 g/cm^3.

[e] 12-14 mesh beads.

[f] Not determined.

[g] 10-20 mesh beads.

[h] For these cases, feed gas contained 2% NO_2.

[i] Loading until breakthrough.

propane, hexone, or kerosene (remaining at 99.9%), but it was seriously decreased by H_2S and SO_2 (reduced to 30 to 40%). Deleterious effects were indicated for high concentrations of NO_2 and C_3H_8. Exposure of AgX to high-temperature saturated steam (139°C) for 5 hr resulted in a severe loss in CH_3I removal efficiency; however, no known solid sorbent would be able to withstand this treatment. The granular AgX sorbents produced much better CH_3I removal than did the beaded AgX sorbents. The DFs for CH_3I obtained with 12- to 14-mesh granulated AgX were as much as 20 times greater than the DFs obtained with 14- to 18-mesh beaded AgX sorbent.

Although the normal atmospheric concentration of iodine is 10^{-2} to 10^{-3} $\mu g/m^3$ (9.5×10^{-6} to 9.5×10^{-7} ppm),[49] some of the hazardous organic radionuclides (and HOI) may be included in off-gases at concentrations in the 10^{-10} to 10^{-2} $\mu g/m^3$ range; it is therefore important to know how these low concentrations affect the function of the AgX beds. For a feed gas at 90°C and 90% relative humidity, Pence et al.[89] studied the effects of bed depth (2.5 to 10 cm), CH_3I concentration (10^{-5} to 10 $\mu g/m^3$), and face velocity (25 and 50 cm/sec) on the DFs obtained with beads of AgX, KI-I_2- and TEDA-impregnated charcoals, and granular AgX. The relationship between CH_3I removal and run conditions was extremely complicated, with the CH_3I-AgX interaction being affected by variables such as adsorbate concentration, relative humidity, presence of contaminant gases, adsorbent efficiency, superficial velocity, particle size, temperature, and chemical species of iodine. For sufficiently long beds (10 cm), there appeared to be no sizeable dependency of DF for CH_3I on the airborne

CH_3I concentration in the range 10^{-5} to 10 μg/m^3. This observation has been thoroughly discussed in other works.[45,55]

In a review of methods used to remove airborne radioiodine by primary and secondary processes (primary for raw off-gas, secondary as a polishing step), and based on the limited operational experience at that time, it was concluded[92] that:

1. Due primarily to consideration of chemical cost, an acid-scrubbing process such as the use of $Hg(NO_3)_2$-HNO_3 might be more widely used than solid sorbents for iodine species collection. However, insufficient costing and pilot plant operation data were available to allow a final selection of a process to remove iodine from fuel reprocessing off-gases.
2. In a secondary iodine removal system, the solid sorbents appeared to be more desirable because of ability to handle relatively larger flow rates in a simpler operation than that provided by acid-scrubbing methods.

Staples et al.[90] conducted tests to determine: (1) iodine loading capacities of AgX, CdX, NaX, PbX, ZnX, and CuX; and (2) a method of regenerating AgX, after loading it with I_2, with hydrogen at elevated temperatures. For air containing 90 mg I_2/m^3 and 1.5% water vapor at 100°C and 200°C, the only two metal-exchanged zeolites for which I_2-removal efficiencies remained greater than 99% were cadmium and sodium. The amounts of I_2 chemisorbed at 150°C were 30-mg I_2/g NaX, 214-mg I_2/g AgX, 26-mg I_2/g PbX, and 45-mg I_2/g CdX. The molecular iodine loading capacity of AgX at breakthrough (DF ∿200) varied inversely with temperature and superficial velocity and directly with bed depth. The three critical parameters (temperature, pressure of NO_2, and water vapor) affected the I_2-capacity of AgX in an interdependent manner. The I_2-capacity decreased significantly at both 100°C and 200°C in the presence of 2% NO_2. The I_2-loading capacity decreased for increased temperature in the presence of 5% water vapor. The combined effects of 2% NO_2 and 5% water vapor resulted in increasing I_2 loading at 200°C compared to 100°C, but the water vapor--NO_2 effect generally decreased the bed capacity. An increase in any one of the parameters resulted in a decrease in I_2 capacity. The smallest capacity reduction occurred when the temperature increased from 100 to 200°C. The largest capacity reduction occurred for 100°C and 2% NO_2.

It has been noted in several studies[86,88,91] that higher CH_3I DFs and loading capacities can be obtained for feed gases containing H_2O vapor when the AgX beds are heated to 150 to 200°C. Based on the work of Staples et al.,[90] an increase in temperature resulted in a small but significant decrease in I_2 loading capacity. In actual plant operation, sufficient bed depth will have to be provided to balance the enhancing effect of temperature on CH_3I collection vs the reducing effect on I_2 capacity. Part of the loss in I_2 capacity when temperature was raised may well have been due to the much higher than normal loading capacity obtained when beds were loaded to breakthrough.[90]

Recycle tests[90] were made for three 5-cm-deep AgX beds. The beds were repetitively loaded with I_2 and then stripped with H_2 at temperatures of 400 to 600°C. Best regeneration results were obtained at temperatures of 400 and 500°C for which I_2-loading capacity declined about twofold after five cycles. For regenerating at 600°C, loading capacity decreased about a factor of 3 after only three cycles. Because of low cost and high-I_2 capacity, PbX was determined to be the most acceptable zeolite to trap HI at elevated temperatures during regeneration of AgIX beds. The desorbed I_2 in the H_2-stream was sorbed onto PbX at 150°C and 500-cm/min face velocity to an average loading capacity of 317-mg I_2/g PbX. Although the stability of PbIX to temperature and leaching effects was not established, the PbIX solid is relatively inexpensive and offers some promise as a solid that can be converted to a form suitable for long-term burial (e.g., by encapsulation of the cannister containing the PbIX solid in concrete).

Ackley and Combs[88] studied the utilization of silver- and metal-exchanged zeolites to remove iodine species from simulated LMFBR fuel reprocessing off-gas (Fig. 3). A schematic of the general experimental layout for testing silver zeolite beds is shown in Fig. 3. Standard experimental conditions included temperatures of 100 and 200°C (CH_3I trapping is enhanced at higher temperatures), CH_3I and I_2 feed concentrations of 100 to 140 mg/m^3, 3% H_2O (90% relative humidity at 25°C), face velocity of 12.0 m/min, and sorbent depth of 5.08 cm. Efficient performance was defined by DFs for both CH_3I and I_2 greater than 10^3, with loading not less than 5-mg I/cm^3. Based on these conditions and criteria, the following sorbent-temperature combinations were considered satisfactory: 27% AgX (1/16-in. pellets) at 200°C, and 90% AgX (1/16-in. pellets) at 100 and 200°C. For higher loadings, 90% AgX was effective at 100°C for loading 13-mg I/cm^3 and at 200°C for loading 20 mg I/cm^3. For a feed gas at 200°C and 0.14% relative humidity treated on 90% AgX at 19.2 m/min,

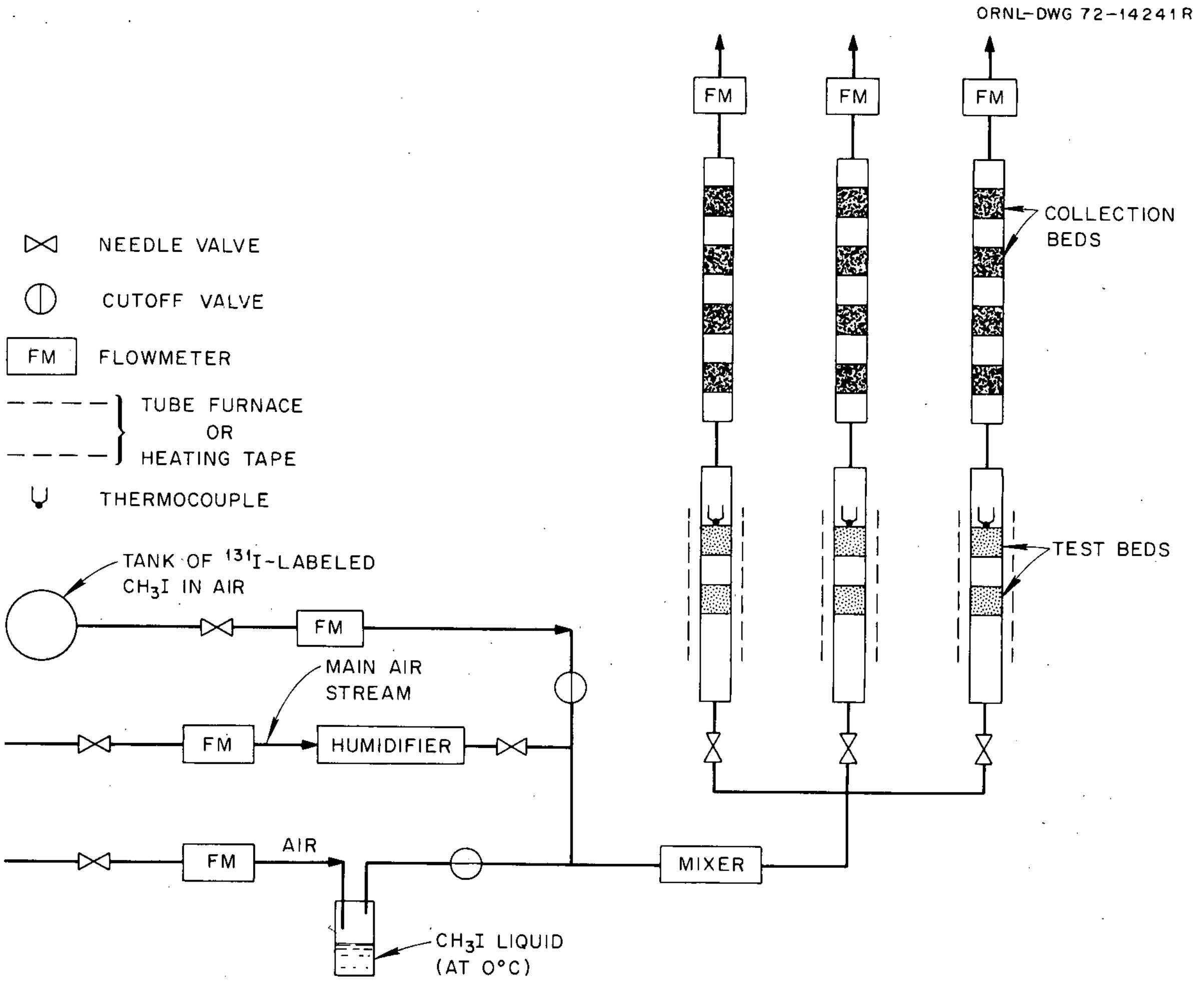

Fig. 3. Schematic of apparatus used to investigate the efficiency of various sorbents for trapping iodine in the form of methyl iodide at elevated temperatures.

a DF of 10^2 could be obtained for loading 178-mg CH_3I/cm^3, and a DF of 10^4 could be obtained for loading 74 mg/cm^3. Other cations studied were Li, Na, K, Cu, Mg, Sr, Ba, Zn, Cd, Hg, La, Ce, Pb, Cr, Mn, Fe, Co, and Ni. The most promising were potassium and cadmium preparations, but neither preparation was sufficient at a loading of 10-mg I/cm^3. When the operating temperature was reduced to 26°C, DFs of 10^4 and loadings of 11-mg CH_3I/cm^3 could be obtained on 90% AgX in a dry atmosphere. However, for the same flow conditions, but with the inclusion of 3 vol % H_2O, the DF of CH_3I was very seriously reduced (≥ 30), although the loading capacity remained about the same; the I_2 DF was not seriously affected by water vapor. The first part of Table 4 shows the Ackley and Combs data for the effects of relative humidity and increased temperature on DFs and the loading capacities that are obtained for CH_3I. The characteristics of 90% AgX for trapping CH_3I were not significantly affected by 10 vol % CO_2 in air, but exposure of the AgX to chlorine at 100°C reduced iodine trapping capacity. Also, exposure of the 90% AgX to dodecane resulted in a temperature dependence in sorbing characteristics over the 100 to 450°C range.

Solid sorbent beds utilized for either cleanup of nuclear facility ventilation and building air or for iodine removal from fuel reprocessing off-gases would, according to present design criteria, undergo extended exposure to the off-gas flows. The most extensive, prolonged exposure tests for silver zeolites were conducted by Ackley and Davis[93] in studying iodine species removal from simulated LMFBR fuel reprocessing off-gas. The conditions were: bed dimension, 2.67 cm ID by 5.08 cm long; superficial velocities of 14 to 19 m/min; 85% relative humidity at

26°C (∿3 vol %); dodecane concentrations, 1.5 x 10^{-6} g/liter; nitric oxide, 1.2 x 10^{-5} g/liter; I_2 concentration, about 10 μg/m^3; CH_3I, about 2 x 10^5 μg/m^3. Efficient sorbent trapping performance was defined as DFs for CH_3I >9 x 10^3 and DFs for I_2 >5 x 10^2. Based on the conditions and criteria described above, the following sorbent-temperature-exposure time combinations were considered satisfactory: (1) 26% AgX, 1/16-in. pellets, at 200°C, exposure times of 286 and 350 days; (2) 90% AgX, 1/16-in. pellets, 100°C, exposure times of 195 and 259 days; (3) 88% AgX, 10- to 20-mesh beads, 200°C, exposure times of 90 and 154 days. The exposure times are for CH_3I and I_2 respectively. At these experimental conditions, an I_2-feed concentration of 40 μg/m^3 was equivalent to a loading capacity of 5 mg of iodine per cm^3 of sorbent per year in a 2.67 by 5.08-cm bed. The useful life of an iodized activated charcoal, 8 to 16 mesh, (from WITCO) would be limited to 60 days or less at similar operating conditions.

3.2.4 Process capacity

One of the major limitations to the use of AgX sorbents for the removal of iodine species is the deleterious effect that results from interaction of temperature and humidity. Pence et al.[86] showed that for I_2 removal from air containing 5 x 10^3 to 100 x 10^3 μg/m^3, a DF of 10^4 could be obtained at 22°C for a superficial velocity of 28 m/min, and a 100% relative humidity on a 5.08-cm-long bed. Ackley and Combs[88] showed that when I_2 is removed from air containing 9.1-mg I_2/m^3, a DF of 10^5 could be obtained (for a loading of 6.4-mg I_2/g AgX) at 200°C for a superficial velocity of 19 m/min and 3% H_2O (0.14% relative humidity) on a 5.08-cm-long bed. Ambient temperatures were not included in this study. In general, for I_2 trapping, the DF obtained with AgX is not significantly different for gas feeds containing up to 3% H_2O at temperatures from 22 to 200°C. There was a slight reduction in I_2-loading capacity when the temperature was increased from 100 to 200°C.[90]

However, when CH_3I is removed from off-gases, the DF is drastically decreased for high relative humidities at ambient temperature. For example, a DF of only 27 was obtained for CH_3I at 27°C for 90% AgX in a 5.08-cm bed, a superficial velocity of 12 m/min and 3% H_2O (90% relative humidity).[88] When the air was bone dry at 27°C, the CH_3I DF at the same operating conditions increased to 10^4. The loading capacity was about 10 mg/cm^3 for both bone dry and 90% relative humidity feeds. Table 5 shows the range of conditions at elevated temperatures at which AgX is an excellent sorbent of I_2 and CH_3I. The highest loading of 209-mg CH_3I/g AgX was achieved by Ackley and Combs.[88] This high loading represented about 58% of the theoretical CH_3I capacity.

More than 20 other cations[88-91] have been investigated as replacements for the expensive Ag in the preparation of metal-exchanged zeolites. Only potassium and cadmium zeolites showed promise for removing iodine as I_2 or CH_3I from air streams. Ackley and Combs[88] obtained DFs of about 50 at a loading of 10 mg CH_3I/cm^3 for using CdX to remove CH_3I from an air feed at 200°C and 3 vol % H_2O. However, DFs were very poor for CH_3I removal with CdX from air streams at 27°C and 3 vol % H_2O (that is, condition of high relative humidity). Lead zeolite has been shown to be ineffective for CH_3I removal but effective for I_2 removal (however, its capacity for I_2 is considerably less than that of AgX).[91]

Table 5. General comparison of iodine sorption characteristics of AgX and the Ag-KTB sorbent[a,b]

Material	Ref.	Iodine species	H_2O concentration (%)	NO_2 concentration (%)	Temp (°C)	$\frac{\text{mg species}}{\text{g support}}$ Loading capacity	DF
AgX	86	CH_3I	0	0	25	84	$>10^4$
AgX	88	CH_3I	3	0	200	209	$>10^2$
AgX	88	CH_3I	3	0	200	87	$>10^4$
Ag-KTB	94	CH_3I	3	2.5	150	40	$>10^2$
AgX	90	I_2	5	2	200	55	2×10^2

[a] Silver content of Ag-KTB is about 78-mg Ag/g Ag-KTB as compared to 360-mg Ag/g AgX. Ag-KTB is available from Bayer, Federal Republic of Germany.

[b] The information in this table was taken from ref. 90.

A serious deficiency of these three base metal zeolites is their inability to remove iodine from air streams which contain NO_2 and water vapor.[5]

3.2.5 Present application

Staples et al.[90] suggested the following proposed design for scaled-up utilization of AgX for iodine species removal from fuel reprocessing off-gas:

Typical plant: Handling 1500 MTHM/year;
600 kg iodine/year;
140 m^3/min.

Assumption: Superficial velocity of 60 m/min, DF of 10^3,
and loading capacity of 50-mg I_2/g AgX.

Bed dimensions: 1.71 m ID by 0.86 m long;

Loading time for one bed: 40 days;

Regeneration time for one bed: 4 days;

Number of recycles per year: 4 (20 to 30 recycles in 5 years).

For 600 kg of I_2, about 2.5 metric tons of waste generated per year. However, this design requires the AgX to maintain an acceptable I_2 loading capacity for 20 to 30 recycles. This capability was not demonstrated in the study (it was previously stated that regeneration at 400 and 500°C resulted in a twofold loss in capacity after five recycles). In plant slipstream tests, DFs greater than 10^3 have been obtained for CH_3I and I_2 removal from fuel reprocessing off-gases. In the Barnwell Plant of AGNS, silver zeolite was installed to act as a backup for the primary iodine-removal system, which is a $Hg(NO_3)_2$-HNO_3 scrubber.

3.2.6 Advantages

1. Silver zeolites exhibit low flammability and maintain iodine sorption efficiencies to 500°C and iodine retention capabilities to 1000°C.
2. The CH_3I removal efficiency and capacity of silver zeolites increase with temperature, with efficient sorption to 500°C.
3. Silver zeolites present a low explosion hazard when used to treat air streams containing nitrogen oxides.
4. The final silver zeolite--iodine complex is a solid which has good handling properties.
5. The final silver zeolite--iodine complex is a solid which has the stability needed for long-term burial.
6. Silver zeolites have a high capacity for CH_3I to $\underline{20}0$-mg CH_3I/g sorbent.
7. The removal efficiency of silver zeolites for elemental iodine has been affected by very few contaminants.
8. Silver zeolites have been effective in reducing the iodine in waste streams to $\leq 10^{-10}$ mg/m^3.

3.2.7 Disadvantages

1. Silver-exchanged zeolites are the most expensive of the solid sorbents which are candidates for adsorption of iodine species. They are 10 times as costly as the same volume of charcoal, about 20 times as costly as the same weight of charcoal, and 5 to 10 times as costly as the German Ag-KTB sorbent.

2. The efficiency of silver zeolites for CH_3I removal varies directly with temperature.
3. The removal efficiency of silver zeolites for CH_3I is affected by SO_2, H_2S, propane, and NO_2.
4. Standard silver zeolites are not acid resistant. Thus for off-gases containing high concentrations of water vapor and NO_x gases, it is necessary to use Norton-type acid-resistant zeolites.
5. There is some loss in capacity for elemental iodine at higher operating temperatures.
6. Much of the experimental work with AgX has been conducted in 2.54-cm-ID beds. Additional runs should be conducted with AgX beds of intermediate engineering scale to provide results useful for process scaleup (for example, 7.5 to 12.5-cm-ID column of appropriate length).

3.3 Removal of Iodine Species from Gases by Utilizing Silver Nitrate-Impregnated, Amorphous Silicic Acid (Ag-KTB and AC 6120)

3.3.1 Background

The removal of iodine species from nuclear fuel reprocessing off-gases in the Federal Republic of Germany has been based on the development of nonregenerable solid sorbents having a high affinity and capacity for iodine. This sorbent is a $AgNO_3$-impregnated, amorphous silicic acid, commonly called Ag-KTB, Ag-KTC, or AC-6120 (commercially available in Germany).[95] The different grades are indications of varying silver content. The normal range of silver content is 7 to 12 g of silver per

100 g of material. This material has been successfully utilized to process actual dissolver off-gas from the Karlsruhe Reprocessing Pilot Plant with efficiencies that satisfy the German environmental standards for iodine emissions.

3.3.2 Chemical mechanisms

The removal of iodine species on AC-6120 beds occurs by conversion of the $AgNO_3$ impregnant into the very insoluble silver iodide and silver iodate,[94,96] which results in:

$$AgNO_{3(s)} + I_{2(g)} \rightarrow AgI(s) + INO_{3(s)} \tag{24}$$

$$2INO_{3(s)} + AgNO_{3(s)} \rightarrow AgIO_{3(s)} + 3NO_{2(g)} + 1/2\ I_{2(g)} \tag{25}$$

$$INO_{3(s)} \rightleftarrows NO_{2(g)} + 1/2\ O_{2(g)} + 1/2\ I_{2(g)} \ . \tag{26}$$

Silver iodide is also the product of the reactions between alkyl halides (e.g., methyl iodide) and the silver nitrate impregnant:

$$AgNO_{3(s)} + R\text{-}I(g) \rightarrow (NO_3 \cdot RI \cdot Ag)(s) \rightarrow RNO_{3(g)} + AgI(s) \ . \tag{27}$$

3.3.3 Experimental results and engineering data useful for process design

In 1970, Wilhelm and Schuettelkopf[95] used $AgNO_3$-impregnated amorphous silicic acid (Ag-KTC) to remove fission product iodine from gases at elevated temperatures and in oxidizing gases. This development was largely precipitated by the recognition that impregnated charcoal could not be used to remove fission product iodine from fuel reprocessing off-gases, because charcoal had a relatively low desorption temperature, a low-ignition temperature, and was relatively susceptible to poisoning. Normal operating parameters for these studies with the Ag-KTC were: feed gas at 30°C, 70% relative humidity (3% H_2O), and 15 m/min; maximum loading, 1 to 2-mg CH_3I/g Ag-KTC for a feed concentration of 70- to 130-mg CH_3I/m^3 (10 to 22 ppm); 2- to 10-mg I_2/g Ag-KTC for a feed concentration of 20- to 250-mg I_2 per m^3 of air (1.9 to 24 ppm).

At standard operating conditions, the DFs for CH_3I and I_2 generally varied directly with bed depth but inversely with relative humidity. When the silver content of the Ag-KTC sorbent was varied from 20 to 180-mg Ag/g Ag-KTC, the DF varied directly with the degree of Ag-impregnation. For a 10-cm-deep bed of 1 to 2 mm Ag-KTC beads with a silver content $\geq$78-mg Ag/g Ag-KTC, the DFs for CH_3I were $>10^4$. The DF for CH_3I was 3×10^3 for a bed depth of 7.5 cm, but 2×10^4 for a bed depth of 10 cm. When superheated steam was the carrier gas for otherwise standard operating conditions, DFs for CH_3I were $>10^4$ for a 10-cm bed depth of Ag-KTC with 7.8% silver. However, when the Ag-KTC material was soaked in water, practically no removal efficiency was measured for CH_3I under otherwise standard conditions. For 10-cm-deep beds with residence times of 0.4 sec, DFs were reduced to 10^2 to 10^3 in the removal of I_2 and CH_3I from air-NO_2 mixtures containing up to 10% NO_2 at 30°C and 70% relative humidity (3% H_2O). Decontamination factors for I_2 removal from air at 30°C and 70% relative humidity were $>10^4$ for Ag-KTC at 7.8% Ag content. However, an unknown iodine compound (possibly HOI) was detected for I_2 in wet air that was more penetrating than CH_3I. It was suggested that the negative effect of high humidity could be counteracted by heating the feed gas. The Ag-KTC material was assessed to be about three times more expensive than iodine-impregnated charcoal but about one-tenth the cost of standard AgX.

Wilhelm[97] reported that the respective surface area and porosity of the Ag-KTB and Ag-KTC materials were 110 m^2/g and 700 mm^3/g, and 185 m^2/g and 980 mm^3/g. Silver content was normally 6 to 8% (60- to 80-mg Ag/g KT material).* It was more desirable to use the Ag-KTB material than Ag-KTC in reprocessing plants because of its higher mechanical strength and abrasion resistance. The removal efficiency of Ag-KTB sorbent was detrimentally affected by high relative humidity in the sweep gas. For air at atmospheric pressure, a temperature of 30°C, superficial velocity of 15 m/min, and CH_3I feed concentration of about 100 mg/m^3, the DF of CH_3I decreased from 10^6 to 10^2 when the humidity was increased from 20 to 80%. To efficiently and economically remove CH_3I with the Ag-KTB material, the relative humidity of the feed gas should be limited to about 70% at 20 to 40°C. When heating feed gas to avoid condensation of water and acid on the surface of the sorbents during processing of off-gases, a temperature of 150°C appeared to be the optimum operating point for a reprocessing plant iodine filter. For a feed gas at atmospheric pressure, a temperature of 150°C (relative humidity 0.9%, 4.2 vol % H_2O), and superficial velocity of 15 m/min, DFs were reduced slightly, from 10^5 to 10^4, when the NO_2 concentration in the feed gas was increased from 1 to 10%. The optimum granular size of the Ag-KTB sorbent was 1 to 2 mm. The DF for CH_3I showed a strong inverse variation with loading capacity, so that the DF decreased from 10^4 for loading of 1- to 10-mg CH_3I/g Ag-KTB to 25 for a loading of 41-mg CH_3I/g Ag-KTB. The DF for I_2 also decreased as I_2 loading capacity exceeded

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*The $AgNO_3$-impregnated KTB material is available from Bayer in Leverkusen, Germany, under the product number AC-6120.

20-mg I_2/g-Ag-KTB. Iodine could not be eluted from the Ag-KTB sorbent by continuous air sparge at 300°C for 33 days. Irradiation to 8.6×10^8 rads caused no significant changes in iodine DFs on Ag-KTB. Finally, when Ag-KTB samples were exposed to actual off-gas in a fuel reprocessing plant, DFs were $>10^3$ for dissolver off-gas but lower for solvent and waste tank off-gas.

Wilhelm et al.[94] recently reported on the status of application of $AgNO_3$-impregnated amorphous silicic acid for iodine species removal from off-gases at the Karlsruhe Reprocessing Pilot Plant. Included in the study were discussions of the flowsheet for dissolver off-gas (DOG) cleaning, the reaction of different organic iodine compounds with the sorbent bed and the effect of such reactions on CH_3I and I_2 removal, the effects of various sorbent-bed poisons, and the loading capacity and removal efficiency of the solid sorbent for dissolver off-gas before and after NO_2 removal. If the iodine can be removed directly from the dissolver off-gas stream before NO_2 removal, the volatilization of iodine from the NO_2 scrubber is avoided, and the concentration of NO_2 scrubber acid is simplified.

A serious reduction in the I_2 and CH_3I removal efficiencies resulted when AC-6120 (or Ag-KTB) was used to treat the vessel off-gas from the reprocessing pilot plant. This was attributed to the conversion of $AgNO_3$ to Ag_2O caused by the reducing effect of organic impurities in the vessel off-gas (VOG). It was later determined that the impairment of operation and the discoloration due to the VOG could be eliminated by using a NO_2-air sweep. Thus the NO_2 had a beneficial effect on the function of the AC-6120 bed. To avoid the contamination effect in actual feul reprocessing operations, it was recommended that NO_2-bearing dissolver off-gas should be cleaned in a first-step iodine sorption filter and then mixed with the VOG upstream of the iodine sorption filter installed for the VOG. Experimental results obtained for high-loading tests with I_2, including 1 to 5% NO_2 in humid air, are shown in Table 6. Shown in Fig. 4 is a schematic of the facility for testing beds of AC-6120/H_1 to determine their capacity to sorb iodine from the dissolver off-gas of the Karlsruhe Reprocessing Plant.

Correlations for engineering scale-up. No correlations have been developed to specify design criteria for scaling up applications of the AC-6120 material.

3.3.4 Present applications

A filter bed of 26 kg of low-impregnated AC-6120 (7% Ag) was utilized in the Karlsruhe Reprocessing Plant (WAK) in 1975. Operating conditions included an average dissolver off-gas flow rate of 148 m^3/hr, giving a residence time of 1.0 ± 0.4 sec, at a temperature of 130°C. The average NO_x concentration in the off-gas was ≤ 2 vol %, with peaks of 20 vol %. Based on ^{129}I analysis in influent and effluent streams, the DF of the iodine sorption (primarily for I_2, because there would be very little organic iodide) ranged from $1.0 \pm 0.4 \times 10^4$ to $2.0 \pm 0.5 \times 10^4$ over 120 days of service life of the filter. At the cessation of the operation, total sorbed iodine was $\sim$1.3 kg I_2, which comprised about 60% of the capacity of the solid-sorbent filter AC-6120.

The design of a large reprocessing plant will be very similar to that of the WAK. A two-stage solid-sorbent filter will be used in which

Table 6. Use of silver nitrate-impregnated silicic acid (AC-6120/H_1)[a] to remove elemental iodine from simulated fuel reprocessing off-gases. Laboratory tests at bed depths comparable to those proposed for a large reprocessing plant[b]

Conditions (dew point, 30°C)[c]	Bed depth (cm)	Superficial velocity (cm/sec)	Removal efficiency (%)	DF	Loading (g I_2)
Humid air + 1% NO_2, 150°C	10	∿25	99.9998	5×10^4	18.1
Humid air + 2.5% NO_2, 150°C	10	25	99.9987	7.6×10^4	18.1
Humid air + 5.0% NO_2, 150°C	10	25	99.9997	3×10^5	18.1
Humid air + 5.0% NO_2, 120°C	10	25	99.9998	5×10^5	18.1

[a] AC-6120/H_1 is a highly impregnated form of AC-6120, containing up to 12 wt % Ag, whereas AC-6120 normally contained 7 to 8 wt % Ag; grain size, 1 to 2 mm.

[b] The information in this table was taken from ref. 94.

[c] Relative humidity of ∿1.0%, 4.0 vol % H_2O at 30°C.

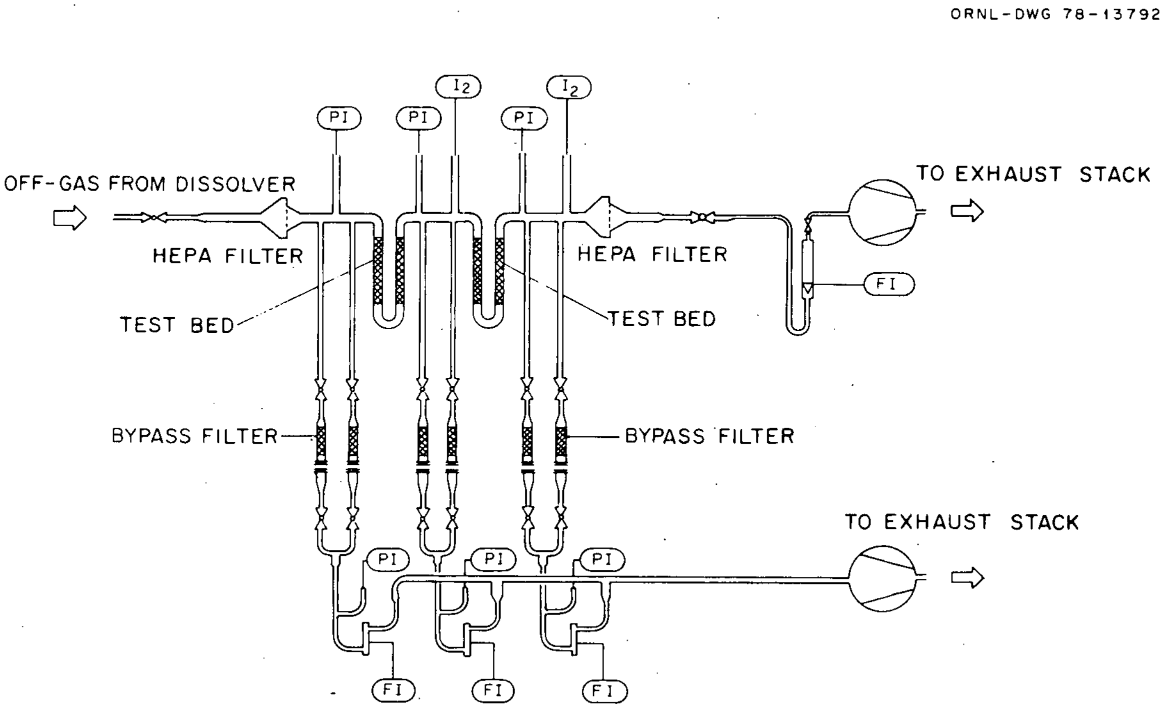

Fig. 4. Schematic of test equipment for sorption of iodine from the dissolver off-gas of the Karlsruhe Reprocessing Plant (WAK).

the first stage will be loaded until breakthrough; the backup filter will then be loaded to breakthrough while a fresh filter drum is being readied in the first stage for a second loading. A filter must be replaced every 6 days to maintain nominal operation in a large reprocessing plant. It is planned that the filter elements will be included for disposal in 200-liter iron-hooped drums that will probably be further cemented in 400-liter drums for long-term burial in a high-activity waste burial ground. The long-term stability of iodine-loaded AC-6120/H_1 in salt deposits still must be determined.

3.3.5 Process capacity

As much as 60% of the Ag in the AC-6120 sorbent beds was reacted in actual pilot plant tests. In AC-6120/H_1 with a 12% Ag content, 143 g of ^{129}I can theoretically be removed with 1 kg of sorbent, based on 100% reaction of the $AgNO_3$ with iodine (I_2); however, the capacity should be limited to 1 to 10 mg CH_3I/g of AC-6120/H_1.

3.3.6 Process advantages

1. Iodine is bound to a sorbent with a high affinity, producing a complex suitable for long-term waste disposal.
2. Iodine sorption with Ag-KTB provides a high-percentage utilization of the silver impregnant.
3. The cost of Ag-KTB is attractive, being about one-tenth that of silver zeolite for equivalent removal efficiencies and operational characteristics.
4. The Ag-KTB material has been used with actual dissolver LWR-fuel-reprocessing off-gas, where it was determined

that for DOG only, the filter was not affected by NO_x; it could therefore be located either before or after the NO_x scrubbing step.

5. The presence of NO_2 actually has a beneficial effect in protecting the Ag-KTB sorbent from organic poisoning produced by organics in the vessel off-gases.
6. The capability of locating the Ag-KTB filter prior to acid scrubbing simplifies acid recovery and iodine volatilization of the NO_2 scrubber bottoms.
7. In air of 70% relative humidity (about 4% H_2O), and with superheated steam at 150°C, the Ag-KTB sorbent showed good removal of CH_3I.
8. Solid filters can be handled in canisters in remote operation at an actual reprocessing plant.

3.3.7 Process disadvantages

1. The Ag-KTB sorbent appears to be adversely affected by organics in the absence of NO_x.
2. The Ag-KTB is very seriously affected by a dew-point temperature excursion.

3.4 Removal of Iodine Species from Gases by Utilizing Silver and Lead Mordenites

3.4.1 Background

The necessity of developing an alternative to AgX as a sorbent for removal of iodine species from off-gases arose because of several observations. Preliminary cost analyses have indicated that silver-exchanged zeolite type-13X (AgX) sorbents would be very expensive to use in the removal of iodine from gases if they could not be regenerated. Additionally, no efficient alternate metal-exchanged zeolite material has been developed. Finally, the standard AgX material was affected deleteriously by acidic gases. Lewis[98] has shown that the Norton-Zeolon molecular-sieve material was superior in acid resistance to the standard Linde 13X, 5A, and 4A molecular-sieve material. Pence and Thomas[99] have shown that the Zeolon mordenites (synthetic hydrogen and sodium mordenites) maintain sufficient integrity in the presence of NO_x so that they may be used to catalyze the ammonia reduction of NO_x-bearing off-gases. Catalytic operation was at 350 to 400°C for feed streams of air containing 5000-ppm NO_x and humidified with a dew point to 46°C (9 to 10 vol % H_2O). Leist et al.[100] later extended the use of the mordenites as a catalyst for NO_x reduction to the pilot plant scale. The Zeolon mordenites are specifically acid-resistant sieves containing calcium and potassium in addition to the usual sodium found in ordinary zeolites. A major constituent of Zeolon is a proprietary acid-resistant binder.[101]

3.4.2 Chemical mechanisms

The chemical reactions between mordenites, molecular iodine, and organic iodides have not yet been fully explained. However, it has been reported that preexposure of the silver-exchanged mordenite Zeolon 900 (AgZ) to air at a temperature of 100°C decreased the capacity of that material for I_2. An attempt was made to explain this capacity reduction based on an equilibrium such as

$$Ag_2O(S) \rightleftarrows 2Ag(S) + 1/2\ O_2(S) \ . \qquad (28)$$

Thus hydrogen pretreatment would reduce the oxygen effect by protonating the oxygen anion, thereby reducing the Ag to the metallic state. The reaction between I_2 and the silver zeolites is probably very similar to the reaction between I_2 and the standard 13X-based AgX sorbents. The reaction between I_2 and PbX in the presence of H_2 has not been elaborated, but it is generally assumed that lead iodide is formed.

3.4.3 Experimental results and engineering data useful for process design

Experimental results. Initial studies were conducted by Slansky et al.[102,103] to develop a regenerable sorbent system based on synthetic zeolites, which would offset the economic disadvantages of once-through use of silver-based zeolites. It was determined that I_2 sorbed as AgI with a silver-exchanged zeolite (AgX) could be desorbed as HI (at 500°C) and chemisorbed with a following lead-exchanged zeolite (PbX) in a pure hydrogen stream. The successful operation of the tandem process would provide for the economic sorption of iodine, because the iodine would first be collected on the regenerable AgX bed. It would then be eluted from that bed into a second PbX bed that had the desirable characteristics of being inexpensive and able to complex the iodine into a product with the stability needed for long-term storage.

However, the silver-exchanged mordenite Zeolon 900 (AgZ)[*] is apparently superior to AgX, both because of a greater stability when exposed to acidic

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[*] The silver-exchanged mordenite in an untreated state is normally designated by AgZ. However, pretreatment of the AgZ with H_2 at 500°C for 24 hr prior to utilization reduces the silver to the metallic state, which is designated by Ag°Z. The mordenite as Ag°Z always showed a higher iodine capacity than did the unreduced AgZ.

vapors, and in maintaining its loading capacity and removal efficiency in cycling operation. The loading capacity of the silver-exchanged-mordenite 900 (not reduced with hydrogen prior to use) for molecular iodine was determined to be about 60 mg I_2/g AgZ for an average DF of 250 (low because of loading until breakthrough). It had the following operating conditions:[103] bed depth, 5 cm; superficial face velocity, 15 m/min; mesh size, 10 to 20; bed temperature, 100°C; carrier gas, dry air. The loading rate for the AgZ bed was about 0.44 mg I_2 min^{-1} cm^{-2}, whereas the regenerating desorption rate was about ten times the loading rate. The loading capacity of the AgZ for binding I_2 was reduced by at least 50% for dry air at 100°C,[104] but this effect was eliminated by a following equilibration with hydrogen. Much of the loading capacity can also be retained without H_2 pretreatment by raising the test temperature to 150°C.

The effects of water vapor, bed temperature, NO, and NO_2 on the iodine capacity of silver-exchanged mordenite, Ag°Z, with silver in the metallic state, were studied for the following conditions: bed diameter, 5 cm; bed depth, 15 cm; bed weight, 270 g; superficial face velocity, 15 m/min; bed temperature, 150°C; I_2 concentration in air, 1500 mg I_2/m^3; DF at breakthrough, 10^3 to 10^4.[105] The maximum loading capacity for I_2 was obtained when the silver-exchanged mordenite AgZ was pretreated with H_2 at 500°C and 5 liters/min for 24 hr (resulting in Ag°Z). Maximum I_2-loading capacity for simulated DOG streams containing 6% H_2O, 2% NO_2, and 2% NO was an average loading of 119 ± 12 mg I_2/g Ag°Z for the total 15-cm bed depth. Loading capacity for <u>no</u> H_2O, NO, or NO_2 was 113 ± 12 mg I_2/g Ag°Z. The addition of only NO to the feed gas resulted in an increase in I_2 loading of the Ag°Z from 113 ± 12 to 129 ± 10 mg I_2/g Ag°Z. The addition of only NO_2 to the feed gas resulted in a decrease in I_2 loading of Ag°Z to 68 ± 12 mg I_2/g Ag°Z. It was speculated that the effect of NO and NO_2 on Ag°Z might be due to an equilibrium such as

$$2Ag^\circ(s) + NO_2(g) \rightleftarrows Ag_2O(s) + NO(g) \ , \qquad (29)$$

where NO acts as a reductant even in the presence of O_2 to maintain the silver in a metallic state. The presence of NO_2 alone might slowly oxidize silver to Ag_2O with a resulting reduction in iodine loading. The presence of NO_2 with NO and H_2O resulted in very little change in the I_2 capacity of the Ag°Z. The large interaction noted between NO and NO_2 apparently negated the effects of NO_2 alone. The I_2 loading capacity of AgZ (silver not in reduced form) was about half of the I_2 capacity of Ag°Z (69 mg I_2/g AgZ vs 124 ± 17 mg I_2/g Ag°Z). No significant reduction was observed in iodine loading on Ag°Z for simulated off-gases containing up to 6% water vapor and varying in temperature from 100 to 250°C.

After loading and regeneration of a Ag°Z bed for 13 cycles, the average loading of the first eight cycles was in the range 117 to 140 mg I_2/g Ag°Z, but the I_2 loading was reduced in the last five cycles to 90 to 100 mg I_2/g Ag°Z (about a 20% loss in initial I_2 capacity). After the seventh cycle, it was necessary to double the regeneration time to 32 hr to achieve greater than 90% iodine removal. Extrapolation of the data indicated that no less than 20% loss and no greater than 50% loss in the loading capacity would occur after 18 cycles.

Apparently, using either PbIZ or PbIX for final collection and storage of ^{129}I would be economically superior to storage of ^{129}I on Ag°Z.

Based on instantaneous DF loading capacity for I_2, the optimum bed temperature for HI chemisorption on lead-exchanged zeolites seemed to be in the range 100 to 150°C. Further studies are probably necessary to delineate the optimum loading temperature for PbZ. About 70% of iodine eluted from AgIZ beds and loaded onto NaIX beds was bound by undesirable and unstable physisorption to the NaX. The I_2 loading on Pb°X was about one-half that of PbX and PbZ. However, the unexpected poor loading capacity of Pb°X was attributed to pore collapse during preparation at 500°C in hydrogen. Iodine loading of 408-mg I_2/g PbX was obtained with iodine vapor pressures less than 4×10^{-8} atm. The lead-exchanged mordenite with lead in the metallic state (Pb°Z) may provide the best combination of high-I_2 loading and low-iodine vapor pressure for all of the zeolite-mordenite sorbents that were studied for final iodine sorption and storage.

It has been reported[90,106] that the chemisorption of I_2 in PbX doesn't appear to be thermodynamically favored. However, the reaction between PbO and HI is favored, so that for H_2 carrier gas, and the absence of O_2, the chemisorbed PbI_2 (PbI_2X) is stable at 150°C. The PbI_2X apparently remains kinetically stable in air after cooling to room temperature.

3.4.4 Present applications

An integrated small-scale system[105] containing two regenerable Ag°Z beds and a follow-up PbX bed for final sorption of the I_2 eluted from the Ag°Z beds, has been utilized to treat simulated LWR fuel reprocessing dissolver off-gas. The operating conditions for this integrated system are shown in Table 7. Although scale-up criteria must be obtained to ensure that the same results can be obtained for a full-scale reprocessing plant, the performance of the small-scale system has been very promising. The DFs produced were 10^4 to 10^5 for I_2 removal from simulated DOG gases containing up to 2% NO_2 and 2% NO. Operation was continued until the first 5 cm of the 15-cm-deep Ag°Z beds were essentially saturated with I_2. Utilization of the Ag°Z in the saturation zone was ∿80% of the 237 mg I_2/g Ag°Z capacity. After 5 recycles of the Ag°Z bed, virtually no reduction in elemental iodine loading was observed. The iodine eluted from the Ag°Z bed was successfully sorbed onto the PbX disposable bed during regeneration of the Ag°Z bed, and about 90% of the PbX was utilized (400 mg I_2/g PbX). Figure 5 is a schematic which shows the arrangement of operating equipment and beds of Ag°Z and PbX for removing iodine from off-gas.

3.4.5 Process capacity

The maximum loading for full saturation of the bed was about 190 mg I_2/g Ag°Z, which is about 80% utilization of the available Ag (∿25% of the sorbent substrate). The maximum loading on the lead zeolite was 400 mg I_2/g PbX.

3.4.6 Process advantages

Many of the advantages cited for zeolites are also valid for mordenites. However, mordenites have additional advantages relative to zeolites when utilized to remove elemental iodine from off-gases:

Table 7. Operational conditions used to test the effect of hydrogen recycle on the capacity of reduced silver zeolon (Ag°Z) beds for reaction with elemental iodine[a]

Bed parameters: diam, 5 cm; depth, 15 cm; particle size, 10 to 20 mesh; superficial face velocity, 15 m/min

Experimental parameter	Iodine loading	Iodine stripping
Inlet pressure, mm Hg	700	760
Carrier gas	Air	Hydrogen
Bed temperature, °C	150	500
Iodine concentration at 21°C and 1 atm, mg/m^3	1500[b]	7400
NO_2 concentration, %	2	0
NO concentration, %	2	0
Dew point, °C	35	Nil
Iodine flux to and from bed, $mg\ min^{-1}\ cm^{-2}$	1.5[c]	4.5
Decontamination factor	10^4-10^5	

[a] The information in this table was taken from ref. 105.

[b] Actual DOG concentration is anticipated to be ∿400 mg I_2/m^3 (38 ppm); 1500 mg I_2/m^3 is 142 ppm.

[c] Actual DOG iodine flux would be about 0.4 mg $min^{-1}\ cm^{-2}$.

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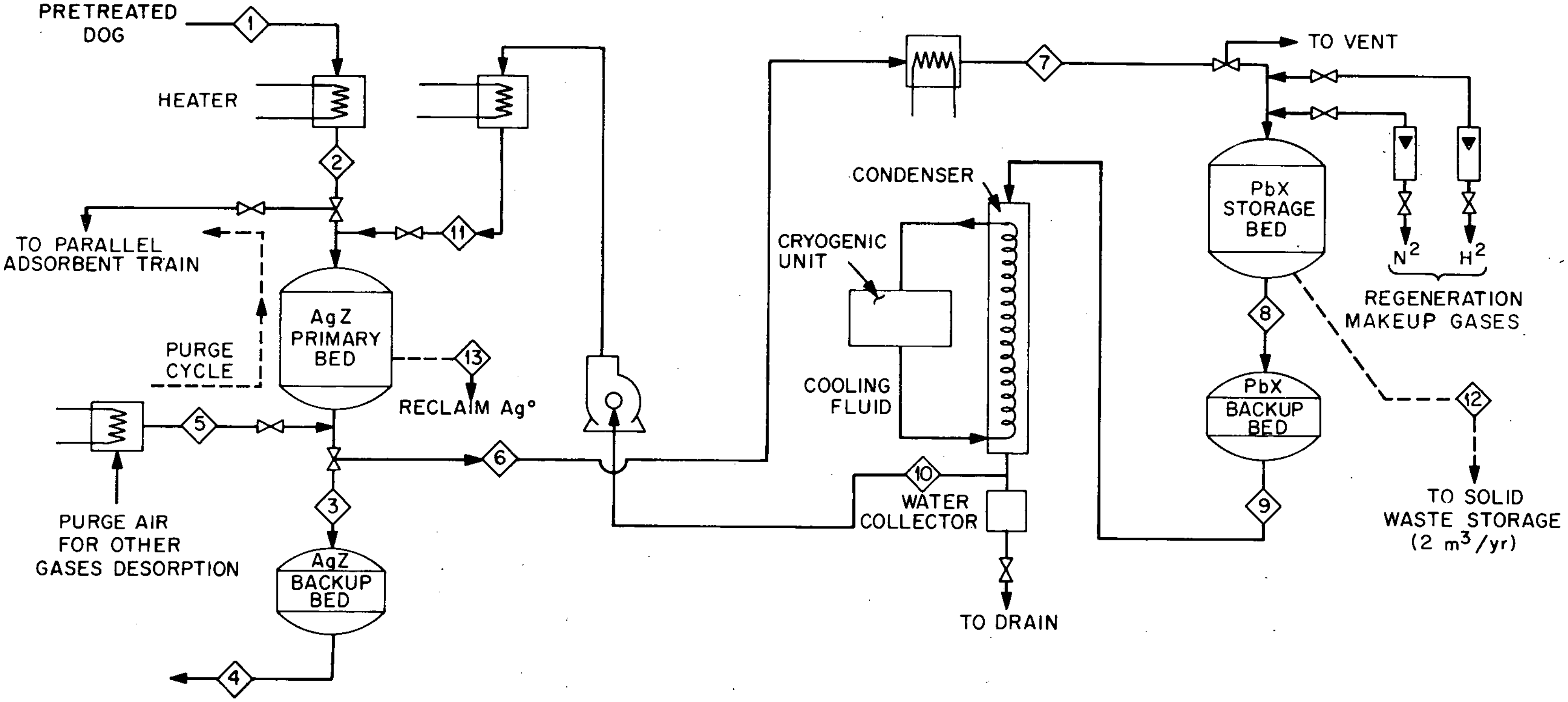

Fig. 5. Schematic of test equipment for sorption of iodine from dissolver off-gas using mordenite beds.

1. The capability of multiple regeneration reduces the process cost. Silver-exchanged mordenites maintain loading capacity for many more cycles than do silver-exchanged zeolites, AgX.
2. In general, Ag°Z materials are much more resistant than silver zeolites to the corrosive effects of NO_x's in humid gas streams.
3. The presence of up to 2% NO in gas streams containing up to 6% H_2O has been shown to actually increase the loading capacity of Ag°Z.
4. The location of Ag°Z prior to NO_x scrubbing would allow direct treatment of DOG. The problem with iodine inventory in recovered head-end acid would be avoided.
5. Mordenites should be able to tolerate fluorides in the off-gas for thorium-based fuel cycles. However, this interaction is untested and it is possible that problems could be introduced by irreversible reaction between the sorbents and fluorides.

3.4.7 <u>Process disadvantages</u>

To optimize the application of the silver mordenite--lead mordenite system for iodine species removal from off-gases, consideration should be given to the following suggestions.

1. All of the studies with the silver mordenite--lead zeolite (or mordenite) tandem system have been conducted with only elemental iodine. To ensure

the future applicability of this process, it is imperative that studies be conducted to determine the loading capacity (and removal efficiency or DF) of the process for organic iodides. Also, the possible poisoning effect of organic contaminants in dissolver off-gas should be studied.

2. The effect of a dew-point excursion on the continuous operation as related to uninterrupted loading and removal efficiency should be studied.
3. Further studies should be directed towards establishment of the total recycle life of the Ag°Z material.
4. Additional studies should be conducted to determine which lead-exchanged zeolite or mordenite is the proper choice for long-term storage of ^{129}I.
5. Because the process would be much safer and simpler if the unreduced AgZ form could be used instead of Ag°Z, the effects of H_2O, NO, and NO_2 on the DF and loading capacity for I_2 should be determined.
6. Because of obvious safety concerns, it is highly improbable that a pure hydrogen stream would be allowed in a fuel reprocessing plant. Further studies should be conducted to discover an alternative method for regeneration of the AgZ beds.
7. The DF, loading capacity, and iodine vapor pressure should be determined for Pb°Z.
8. Most of the studies have been conducted in small-scale equipment. Additional tests should be conducted in engineering equipment.

3.5 Removal of Iodide Species from Gases by Utilizing Macroreticular Resins

3.5.1 Background

Moore and Howerton[107] studied the application of macroreticular resins for removing molecular iodine and organic iodides from dry or moist air. These experiments were designed to assess the feasibility of using the resins to replace zeolites in off-gas iodine removal processes.

3.5.2 Chemical mechanisms

In general, the macroreticular resins attract molecules based on their relative hydrophobicity or hydrophilicity. Thus they are basically nonionic in their function and can be expected to show relatively strong attraction for uncharged molecules such as elemental iodine and organic iodide compounds, and relatively weak attractions for ionic iodide species. We could find no mechanistic studies conducted with these resins that would delineate the kinetics of their interaction with molecular iodine or organic iodides. In all cases, the macroreticular resins showed greater loading capacities for iodine species in air than in liquid streams. For more detail, see Sect. 4.3.2.

3.5.3 Experimental results and engineering data useful for process design

Initial studies[107] indicated that the resins of the Amberlite series XAD-2 through XAD-12 were capable of producing DFs of 10^4 for removing I_2 from dry air at a flow rate of 7.65 m/min through a 0.5-cm-ID column, with an I_2 feed concentration of 3×10^3 mg/m^3. The operating conditions and experimental results obtained with representative members of the

Amberlite series, limited to the three different types of matrix chemistry, are shown in Table 8.[108-110] In additional studies[108] with XAD-12 for removing I_2 from dry air, it was determined that the capacity and DF generally decreased as the temperature was increased to 100°C. Also, the DF and loading capacity decreased as the relative humidity increased. Studies with other plastics such as polystyrene, polymethane, and polyethylene were not pursued because they showed too little capacity for the simplest case of removing I_2 from dry air.

In this same group of experiments,[108] CH_3I was sorbed from dry air at 21°C on all of the following macroreticular resins: Bio Bead SM-1 and Bio Bead SM-2; Amberlite XAD-2, XAD-4, XAD-7, XAD-8, XAD-9, XAD-11, XAD-12, and XE-284. Methyl iodide loading was studied for flow rates of 7.65 m/min of dry air containing 1 to 4 x 10^3 mg CH_3I per m^3. All of the polymers except XE-284 and XAD-12 sorbed less CH_3I at elevated temperatures. Loading capacity of XAD-12 increased to a temperature of 50°C and then decreased as the temperature was increased. The only two sorbents that sorbed more than 10 mg CH_3I/g sorbent while delivering a DF >100 were XAD-4 and XAD-12, but neither one could predictably maintain its CH_3I sorption capacities above 100°C.

A comparison has also been made of loading capacities and DFs that could be achieved for I_2 and CH_3I removal from dry air on XAD-12, silver zeolite (AgX), iodized charcoal, and the anion exchanger Dowex 1-X4[110,111] (see ref. 110 in Table 8). Compared to charcoal and Amberlite XAD-12, the Dowex 1-X4 and AgX beds had relatively low capacities for iodine. The DF for molecular iodine on AgX was as good as that obtained on any of the exchangers, with the iodized charcoal providing the largest loading

Table 8. Sorption of iodine species from dry and humid air with macroreticular resins

Ref.	Resin	Bed size (cm)	Feed (per m^3)	Flow rate (m/min)	Loading capacity[a]	Temp (°C)	Relative humidity	DF
107	Amberlite XAD-2[b] (Styrene-DVB) 20-50 mesh	0.5 x 10 (S = 0.916 cm^2)[c]	3 x 10^3 mg I_2 ($\sim$285 ppm)	7.65	172 mg I_2/g	$\sim$21	Dry air	>10^4
	Amberlite XAD-4[b] (Styrene-DVB)	0.5 x 10	3 x 10^3 mg I_2	7.65	218 mg I_2/g	$\sim$21	Dry air	>10^4
	Amberlite XAD-8[b] (Acrylic ester)	0.5 x 10	3 x 10^3 mg I_2	7.65	171 mg I_2/g	$\sim$21	Dry air	>10^4
	Amberlite XAD-12[b] (Acrylic ester with nitrogen-oxygen group)	0.5 x 10	3 x 10^3 mg I_2	7.65	209 mg I_2/g	$\sim$21	Dry air	>10^4
108	Amberlite XAD-12	0.5 x 10	2.8 x 10^3 mg I_2 ($\sim$266 ppm)	NS[d]	1390 mg I_2/g	21	Dry air	10^2-10^3
		0.5 x 10	2.8 x 10^3 mg I_2	NS[d]	990 mg I_2/g	50	Dry air	10^3-10^4
		0.5 x 10	2.8 x 10^3 mg I_2	NS[d]	627 mg I_2/g	100	Dry air	10^2
	Amberlite XAD-4	0.5 x 10	1-4 x 10^3 mg CH_3I (170-680 ppm)	7.65	12 mg CH_3I/g	25	Dry air	$\sim10^2$
		0.5 x 10	1-4 x 10^3 mg CH_3I	7.65	1.1 mg CH_3I/g	140	Dry air	1-2
	Amberlite XAD-12	0.5 x 10	1-4 x 10^3 mg CH_3I	7.65	15 mg CH_3I/g	25	Dry air	1.6 x 10^3
		0.5 x 10	1-4 x 10^3 mg CH_3I	7.65	84 mg CH_3I/g	50	Dry air	>10^4
		0.5 x 10	1-4 x 10^3 mg CH_3I	7.65	10 mg CH_3I/g	160	Dry air	16

Table 8. (Continued)

Ref.	Resin	Bed size (cm)	Feed (per m^3)	Flow rate (m/min)	Loading capacity[a]	Temp (°C)	Relative humidity	DF
109	Amberlite XAD-4	1 x 5.08 (S = 0.785 cm^2)	300-400 mg I_2 (28.5-38 ppm)	12.2	50 mg I_2/cm^3 sorbent	25	60%	3 x 10^3
	Amberlite XAD-12	1 x 5.08	300-400 mg I_2	12.2	50 mg I_2/cm^3 sorbent	25	60%	7 x 10^3
	Silver zeolite	1 x 5.08	300-400 mg I_2	12.2	50 mg I_2/cm^3 sorbent	25	60%	7 x 10^3
110	Iodized charcoal[e]	0.5 x 5	2 to 4 x 10^3 mg I_2	7.65	2.13 g I_2/g	25	Dry air	2 x 10^3
	Amberlite XAD-12[e]	0.5 x 5	2 to 4 x 10^3 mg I_2	7.65	1.39 g I_2/g	25	Dry air	166
	Dowex 1-X4 (OH form)	0.5 x 5	2 to 4 x 10^3 mg I_2	7.65	0.362 g I_2/g	25	Dry air	20
	Silver zeolite	0.5 x 5	2 to 4 x 10^3 mg I_2	7.65	0.126 g I_2/g	25	Dry air	1.2 x 10^3
	Iodized charcoal	0.5 x 5	1 to 3 x 10^3 mg CH_3I	7.65	0.125 g CH_3I/g	25	Dry air	∿50
	Silver zeolite	0.5 x 5	1 to 3 x 10^3 mg CH_3I	7.65	0.150 g CH_3I/g	25	Dry air	3 x 10^3

[a] Loading capacity is milligrams of iodine species per gram of sorbent of interest.

[b] Amberlite macroreticular resins are manufactured by Rohm & Haas.

[c] S = column cross-sectional area.

[d] NS, not specified.

[e] Adding 24 wt % n-dodecane to iodized charcoal caused a decrease in I_2 DF by a factor of 6 and a small decrease of 15% in loading capacity. Addition of 25 wt % dodecane to XAD-12 resulted in an increase in I_2 DF from 100 to 500, but loading capacity was decreased by 42%.

capacity (2.13-g I_2/g charcoal, and an I_2 DF of 2 x 10^3) of the four studied sorbents. Preloading the charcoal and XAD-12 with about 25% of their weights as dodecane reduced the DF on the charcoal and the loading capacity of the XAD-12. The iodized charcoal sorbed 20 times more I_2 than CH_3I, and the DF for I_2 was 40 times that of CH_3I. Decontamination factors achieved with AgX for both I_2 and CH_3I removal from feed gases at 25°C and very low humidity agreed well with the results obtained by Ackley.[88]

In a final limited study to determine the effect of humidity on the operation of the Amberlite resins, Moore[109] investigated the sorption capacity of XAD-4 and XAD-12 for removal of I_2 from air at 25°C and 60% relative humidity. The results were promising, with DFs greater than 10^3 being obtained on 5.08-cm-deep beds for loadings to 50 mg I_2/cm^3 sorbent. The other Amberlite macroreticular resins (XAD-2, XAD-7, XAD-8, XAD-9, XAD-11) did not show promising DFs for I_2 in air-feed concentrations of 300 to 400 mg I_2/m^3 (28 to 38 ppm).

3.5.4 Present application

Utilization of macroreticular resins to remove iodine species from gas streams were of an experimental nature, as discussed above.

3.5.5 Process capacity

Maximum capacity of XAD-12 for molecular iodine removal from dry air at room temperature was 1.4-g I_2/g resin (DF, 10^2 to 10^3), and for CH_3I removal from dry air at 50°C, the capacity was 84-mg CH_3I/g (DF, 10^4). When dry air was the carrier, maximum capacities for XAD-4 were 218-mg

I_2/g (DF >10^4) and 12.0-mg CH_3I/g resin (DF, 10^2). Feed concentrations of I_2 and CH_3I were in the range 200 to 700 ppm.

3.5.6 Process advantages

The studies to delineate the ability of macroreticular resins to remove I_2 and CH_3I were too limited to allow establishment of many process advantages. One obvious advantage is that macroreticular resins are acid resistant and thus they may function well in off-gases containing NO_x.

3.5.7 Process disadvantages

1. The process DF and loading capacity appear to be seriously affected by high temperature and high humidity.
2. Organics are strongly attracted to macroreticular resins; thus the presence of organics in fuel reprocessing off-gas could result in serious deterioration in loading capacity.
3. All of the studies thus far have been conducted in small-scale equipment (0.5 to 1.0-cm-ID columns). Any additional studies should be made in engineering-sized equipment.

4. METHODS OF REMOVING IODINE SPECIES FROM FUEL REPROCESSING WASTE LIQUID STREAMS

4.1 Background and Introduction

A paramount consideration in minimizing the environmental impact of both nuclear fuel reprocessing plants and nuclear power generating facilities is the removal of radioactive iodine species from off-gases and waste liquid streams. The report by Finney et al.,[3] which includes a comprehensive discussion of the optimization of LWR fuel reprocessing, provides information needed to establish as-low-as-practicable emission limits for the various radionuclides encountered in reprocessing (see Fig. 6). A single case for a specific plant design will be used as the basis for providing working estimates of the amount of iodine that could be released into the environment for those processes following the iodine removal partial evaporator (IRPE). It is assumed that the off-gas will be treated to minimize effluent iodine and iodides.

Based on efficient iodine volatilization from the dissolver solution (possibly in combination with some form of voloxidation for the chopped fuel prior to dissolution), it is also assumed that 99.5% of the iodine (mostly ^{129}I and ^{131}I) would enter the primary off-gas treatment system. Thus the maximum quantity of iodine that could enter the liquid rad-waste treatment system would be 0.5% of F_I (moles of iodine into the plant per unit time). The three primary streams comprising the feed to the liquid treatment system, as input to the low-activity liquid-waste fractionator, would be the acid bottoms from the NO_2 absorber, the condensate from the high-activity waste concentrator, and the raffinate from the solvent cleanup. If 0.5% of the iodine fed to the reprocessing plant became concentrated in the IRPE, about 0.025% of the total plant iodine could be discharged to the excess-water vaporizer. Since the yearly input of ^{129}I to the standard plant discussed by Finney[3] (1500 MTHM/year, fuel irradiated to 33,000 MWd/ton at 30 kW/kg, and cooled 160 days before reprocessing) would be approximately 286.5 kg (49.95 Ci) ^{129}I/year, the discharge to the environment from the liquid waste treatment loop

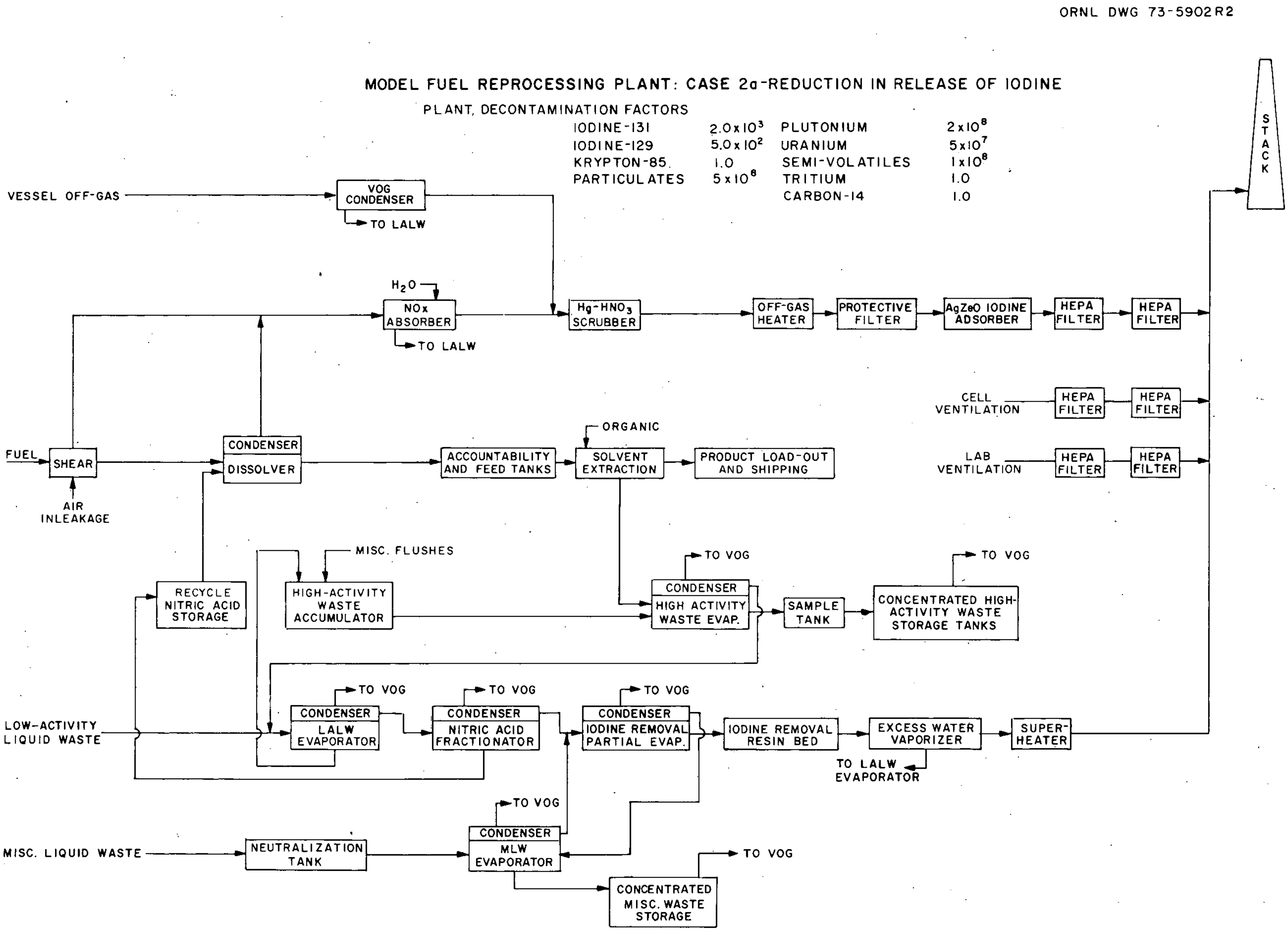

Fig. 6. Model fuel reprocessing plant: Case 2a - reduction in release of iodine.

could be as much as 1.3×10^{-2} Ci/year. For Finney's case 2a, in which 99.5% of the iodine is volatilized, the iodine concentration in a reference 20-gpm liquid discharge would be 0.85×10^{-8} $\underline{M}$ in $^{129}I_2$. The waste stream is expected to contain 0.05 to 0.10 $\underline{M}$ HNO_3. If all the I_2 were discharged to the stock in 3000 scfm, the I_2 level would be 0.18-ppb $^{129}I_2$, or 1.95-μg $^{129}I_2/m^3$. This analysis delineates the concentrations of iodine that should be included in simulated gas and liquid streams used in experiments to develop methods of obtaining zero release in the liquid radwaste treatment loop.

4.2 Removal of Iodine Species from Liquid Streams Utilizing Activated Charcoal

4.2.1 Background

Few reports are available concerning the application of charcoal for removal of iodine species from waste liquors. One of the rapidly growing industrial applications of activated charcoal is for the secondary and tertiary treatment of industrial and municipal sewages. This utilization is primarily focused on removal of hazardous organics, whereas only limited industrial effort has been directed towards the metal-removing capacity of charcoal.

4.2.2 Chemical species of dissolved iodine

A major consideration in the choice of a sorbent to treat liquid streams containing iodine is the chemical form of the iodine in the liquid of interest. For example, Eggleton[112] listed eight equilibria for the partitioning of iodine between water and air [where all species are in the aqueous phase except those specifically designated as gas phase species, that is, $I_2(g)$ and $HOI(g)$]:

$$I_2(g) = I_2 \qquad K_1 = 83 \qquad (30)$$

$$I_2 + I^- = I_3^- \qquad K_2 = 768 \qquad (31)$$

$$I_2 + H_2O = H^+ + I^- + HIO \qquad K_3 = 5.4 \times 10^{-13} \qquad (32)$$

$$I_2 + H_2O = H_2OI^+ + I^- \qquad K_4 = 1.2 \times 10^{-11} \qquad (33)$$

$$3I_2 + 3H_2O = IO_3^- + 5I^- + 6H^+ \qquad K_5 = 4 \times 10^{-48} \qquad (34)$$

$$HIO = H^+ + IO^- \qquad K_6 = 2.3 \times 10^{-4} \qquad (35)$$

$$IO^- + I^- + H_2O = I_2OH^- + OH^- \qquad K_7 = 0.13 \qquad (36)$$

$$HIO(g) = HIO \qquad K_8 = 10^2 \text{ to } 10^5 \qquad (37)$$

The concentration of the anionic species of iodine such as I^- and I_3^- would thus appear to be quite low for neutral solutions in normal circumstances. However, it is known[113] that the stability of elemental iodine (I_2) is greatly decreased at low concentrations because elemental iodine is both a better oxidizing and a better reducing agent when the concentration of elemental iodine is low. That is, in an aqueous solution at pH 7, for a total iodine concentration of 10^{-3} $\underline{M}$, elemental iodine is 8% hydrolyzed; however, at a concentration of 10^{-8} $\underline{M}$, elemental iodine is almost totally hydrolyzed (98%). At low concentrations of iodine, HIO is only slightly unstable in respect to decomposition into elemental iodine and IO_3^-, and any production of ionic iodine from HIO decomposition should be minimal.

Eggleton[112] also suggested that the equilibrium of iodine species in iodine-containing acidic solutions at values of pH down to 1 could be described by Eqs. (31)-(34).

Davis and Kibbey[114] investigated the various species of iodine in acidic, neutral, and basic solutions (ranging from 3 $\underline{M}$ HNO_3 to 1 $\underline{M}$ NaOH) for wavelengths from 190 to 700 nm. Utilizing a model for spectra analyses based on approximation by a series of overlapping bands of Gaussian shape, they reported iodine species for the various solutions listed in Table 9. The results shown in Table 9 are discussed here to provide background information concerning the kinds of iodine species that can be expected as a function of the pH of nitric acid solutions during dissolution of spent fuel or for other solvents used to extract or dissolve iodine.

Table 9. Most probable forms of iodine present in the acidic, neutral, and basic solutions of the indicated composition and concentration[a]

Solution	Iodine species assignment
10^{-4} M KI in water	I^-
1×10^{-3} to 5×10^{-4} M I_2 in water	I_2,[b] I^-,[b] I_3^-, $I_2 \cdot aq$
10^{-5} M I_2 and 10^{-2} M KI in water	I^-, I_3^-, $I_2 \cdot aq$[b]
10^{-3} M I_2 in 0.025 M HNO_3	I_3^-, I_2, $I_2 \cdot aq$
1.8×10^{-3} M I_2 in 3 M HNO_3 (from oxidation of 5×10^{-3} M KI)	I_2, I_3^-
1×10^{-3} M I_2 in 0.01 M NaOH	I^-, I_2,[b] IO^-[b]
1.8×10^{-3} M I_2 + 3.6×10^{-3} M NaI in 1.0 M NaOH	I^-, I^- and I_2, IO^-

[a] This information was taken from ref. 114.

[b] The absorption band could not be positively assigned to a molecular species.

Although further references will be made to Table 9 in the following discussions of the use of various solid sorbents for removing iodine species from liquid streams, a few introductory comments are appropriate. It should be noted that: (1) virtually all of the iodine was considered to exist as I^- in a 10^{-4} $\underline{M}$ iodide solution in H_2O; (2) small quantities of ionic iodine species, probably as I^- and I_3^-, were in a 10^{-4} $\underline{M}$ elemental iodine (I_2) solution in water; (3) for 10^{-3} $\underline{M}$ I_2 in mildly acidic solutions of 0.025 $\underline{M}$ HNO_3, there was again an ionic form of iodine (probably I_3^-), in addition to elemental iodine and $I_2 \cdot aq$; (4) when 10^{-3} $\underline{M}$ I^- was dissolved in 3.0 $\underline{M}$ HNO_3, essentially all of the I^- was oxidized to elemental iodine in about 4 to 5 hr (for intermediate times, most of the I^- was converted to I_3^- prior to oxidation to I_2); and (5) elemental iodine dissolved in NaOH was slowly reduced to I^- and IO^-.

4.2.3 Experimental results and engineering data useful for process design

Activated charcoal has been used to treat gas and liquid waste streams for many years in process industries, so that much of the present applicable charcoal technology has developed from the industrial sector. The utilization of granular activated charcoal for wastewater treatment has been given impetus by the development of economical carbon regeneration methods with ancillary transporting and processing equipment. Basically, granular activated charcoal is used either for tertiary treatment of liquid wastes following primary settling and secondary biological treatment, or for physical-chemical treatment in which raw wastewater is treated in a primary clarifier with chemicals prior to carbon adsorption.[115]

Lehmann[116] has compiled a list of 190 selected references which describe the use of activated charcoal to treat wastewaters (both at laboratory and plant scale), and for uses such as air pollution control, gas and water analysis, and adsorption of radioisotopes (no iodine studies).

Although activated charcoal is widely utilized to sorb organic compounds from aqueous solutions, it is only recently that an effort has been made to develop industrial processes to use charcoal for sorption of inorganic compounds from waste liquors. Sigworth[117] reviewed the literature of the metallurgical industries and discussed the applicability of activated charcoal for sorption of Sb, Ag, Bi, Cr, Sn, Ag, Hg, Co, Zr, Pb, Ni, Ti, V, Fe (all having fair to high adsorption potentials) and Cu, Cd, Zn, Be, Ba, Se, Mo, Mn, and W (all having low or unknown adsorption potentials). It was noted that of the halogens, chlorine and bromine were adsorbed well from water and reduced on the charcoal. When chlorine molecules accumulate on the carbon surface, a concentration can be reached at which a reaction between chlorine, water, and carbon produces HCl and CO_2. Bromine is more strongly adsorbed than is chlorine, with similar conversion to hydrobromic acid. When activated carbon is used as the sorbent, fluoride ion can be removed from H_2O at a pH of 3.0. Activated charcoal was reported to adsorb iodine very strongly when it was in the free-elemental I_2 or triiodide (I_3^-) state. Thus the sorption of free iodine would seem to be favored for high-elemental iodine concentrations (in the aqueous phase), and sorption of iodine as I_3^- would seem to be favored for very low concentrations of I_2 in aqueous solution (see Sect. 4.2.2 and ref. 113). When the elemental iodine was sorbed to the charcoal, it was not reduced to HI (although Cl_2 and Br_2 are normally converted to HCl and HBr). As a confirmation of the observed affinity of charcoal for iodine primarily as elemental iodine (I_2) or I_3^-, it was noted that iodides were sorbed to a lesser degree to charcoal. The iodine could be recovered fairly easily as elemental I_2 from its complex with charcoal.

The interaction between charcoal and elemental iodine was once exploited on a commercial scale for the recovery of iodine from oil brines in California.[118] The General Salt Company utilized charcoal to remove iodine from brines that had first been acidified and oxidized to ensure that iodine was in the elemental I_2 form. The iodine was then extracted from the charcoal with caustic soda or caustic potash. Concentration of iodine in the brines was usually in the 10 to 100-ppm range.

One of the earliest studies concerning the removal of radioactive iodine from water was conducted by Graham et al.[119] In an investigation to develop methods for purifying surface water for human consumption in the event of radioactive contamination from nuclear weapons testing or from nuclear waste disposal, a solution containing only ^{131}I as elemental iodine was sorbed with a commercial dechlorinator that contained activated charcoal. The feed solution contained 25 μCi of ^{131}I/liter, which, for a specific activity of 1.24×10^5 Ci/g ^{131}I, resulted in an ^{131}I concentration of only 7.7×10^{-13} <u>M</u>. Even at this very low feed concentration, DFs of 10^3 were obtained. The loading capacity was not determined.

Westvaco[120] uses the capacity of their charcoal for iodine as an analytical technique to specify relative activities of charcoals prepared by different processes.

In agreement with Sigworth's[117] observations, Kreusch[121] has recently reported that iodine is reversibly sorbed to activated carbon in the presence of organics. That is, elemental iodine was sorbed to charcoal to act as a bacteriostatic agent during treatment of water contaminated with bacterial growth. Iodine was applied to the charcoal bed in a 0.1 to 0.2 N solution at a rate of 0.03 to 0.167 cm^3/min (per m^3 of charcoal). When the elemental iodine interacted with the organics in the feed stream, free active I^- was apparently produced and eluted from the bed. The nature of the interaction between elemental iodine and the organic compounds was not elucidated.

Bansal et al.[122] studied the adsorption characteristics of carbon obtained from polyvinyl chloride (PVC). The PVC-derived charcoal had a greater affinity for removing iodine from chloroform in equilibrium shakeouts at 25°C than from water or benzene. The elemental iodine was bound to the charcoal from all three of the solutions by an almost equivalent combination of physical adsorption and chemisorption (slightly more I_2 was chemisorbed than physisorbed for all three solvents). For iodine removal from aqueous solution onto charcoal, the maximum amount physically adsorbed was 50-mg I_2/g, and the amount chemisorbed was 77-mg I_2/g. When iodine was sorbed from chloroform on the PVC carbon, the amounts increased to 228-mg I_2/g for physical adsorption and 203-mg I_2/g for chemisorption. It was concluded that sorption of iodine by PVC-derived carbon was maximum with chloroform as the solvent because of a much lower solute-solvent interaction than either in water (due to the presence of iodide ion) or in benzene (in which iodine is much more soluble). The increase in iodine sorption by the PVC carbon from organic solvents appears to be contradictory to Kreusch's observation, and the generally held conclusion that charcoal would have a greater affinity for organics than for iodine; in other words, less iodine would be sorbed in the presence of organics. However, the activated chemical structure of the PVC carbon may be different than that of ordinary wood-derived or coconut-based charcoals. Also, the sorptive capacity of iodine in the organic solvents must be considered.

Further evidence concerning the relative attraction of elemental iodine and iodide to activated carbon was given by Belogovskii.[123] To maximize regeneration of the carbon, samples of KAD-iodine-activated carbon, which had been loaded to a capacity of 37.5 g of iodine per liter of solid material, were treated with sodium hydroxide in an ultrasonic field. Based on a density of 0.3 g of charcoal per ml, this is a loading capacity of ∿100 mg per g of charcoal. The effect of the ultrasound probably was to promote contact between the NaOH and the iodine-laden charcoal so that adsorbed I_2 was converted from the elemental to the ionic form which had much less attraction to the activated charcoal and could be more easily eluted by caustic alkali.

Activated carbon has been utilized industrially in the Soviet Union for the production of iodine from oil well byproduct brines. A supportive study[124] investigated the partial pressure of iodine over aqueous salt solutions. Usually the brines are alkaline because of the presence of bicarbonates and salts of naphthenic acids. However, to prevent hydrolysis of iodine during the recovery process and to oxidize all iodine to the I_2 form, the brines are acidified with sulfuric acid to a pH of about 3.0 (0.0005 $\underline{M}$ H_2SO_4). The following conclusions were made concerning the distribution of iodine between air and the sulfate salts of sodium, potassium, and magnesium, and air and the chloride salts of sodium, potassium, magnesium, and calcium: (1) for a range of iodine concentrations of 10 to 272 mg/liter, the iodine partial pressure and distribution coefficient for the brines obeyed Henry's law (for acidification to pH 3.0); (2) for the temperature range 0 to 50°C, chlorides reduced the iodine partial pressure and distribution coefficient, but sulfates had the opposite effect.

In their program to investigate the capability of various solid sorbents to remove elemental iodine from liquid streams, Moore and Howerton[125] conducted limited experiments with activated charcoal. Elemental iodine at a concentration of 1 x 10^{-6} $\underline{M}$ I_2 (traces of ^{131}I) in water was sorbed with 20 to 50 mesh, Fisher-activated coconut charcoal in a 0.4 x 10-cm column. DFs of 10^4 were obtained for flow rates as high as 15 cm/min, but loading capacities were not determined. A summary of the various experiments using charcoal to treat liquid streams for iodine removal is given in Table 10.

The quantity of iodine removed from gas streams by activated charcoal is apparently dependent on the metal content (primarily as K^+) of the charcoal (Sect. 3.1.2).[46] It thus follows that to remove iodine from liquids in which the iodine is in both elemental and ionic forms, the capacity of activated charcoal for total iodine would be enhanced by the binding capacity that the metal in the structure has for ionic iodine species. The increase in capacity for ionic iodine that results from the presence of metals may account for the high DFs that were obtained[125]

Table 10. Removal of iodine species from liquid wastes by treatment with activated charcoal

Ref.	Charcoal form	Feed composition	DF[a]	Distribution ratio[a]	Bed size[a]	Retention time[a]	Loading capacity[a]
117	Activated	Aqueous	Good	NA	NS	ND	ND
119	Activated	25-μCi ^{131}I/liter or 7.7×10^{-13} $\underline{M}$ $^{131}I_2$, aqueous	10^3	NA	NS	ND	ND
122	From polyvinyl chloride	Iodine in H_2O	ND	ND	NA	Batch equilibrium	77-mg I_2/g of charcoal[b]
	From polyvinyl chloride	Iodine in chloroform	ND	ND	NA	Batch equilibrium	205-mg I_2/g of charcoal
123	Activated	ND[c]	ND	NA	NS	NA	∿100-mg I_2/g of charcoal
125	Fisher activated coconut base charcoal	1×10^{-6} $\underline{M}$ I_2^- in aqueous	10^4	NA	0.4 x 10 cm	1.0 min	ND

[a] NA - not applicable; ND - not determined; NS - not specified.

[b] Represents quantity chemisorbed. Approximately the same quantity was also physically adsorbed.

[c] Desorption by ultrasound and NaOH of charcoal preloaded with iodine.

when iodine was removed from a 10^{-6} $\underline{M}$ I_2 aqueous solution in which iodine was present primarily as elemental iodine (I_2), but also existed as traces of I^- and I_3^-.

4.2.4 Present applications

No references were encountered which described a functioning industrial operation in the United States in which activated charcoal was used for the specific recovery of iodine. However, from 1929 to 1934, the General Salt Company at Long Beach, California used activated charcoal to extract iodine from oil field brines on a commercial scale. This process was abandoned due to the inability to recover an iodine product that was economically competitive with the iodine produced from Chilean saltpeter. Dow Chemical Co. at Soul Beach, California has recovered iodine from oil field brines by a process involving flocculation with $FeCl_3$, acidification with H_2SO_4, blowing-out of iodine from the oxidized brine using air, absorption of blown-out iodine with an aqueous solution of HI and H_2SO_4 in a packed tower, reduction of elemental iodine to HI with SO_2 and H_2O, and recovery of I_2 from the HI and H_2SO_4 solution by sparging with Cl_2.

4.2.5 Process capacity

Based on other studies,[122,123] activated carbon would appear to have an iodine loading capacity in aqueous solutions of about 100-mg I_2/g carbon. However, there is such a paucity of established data concerning the iodine capacity of charcoal in acidic, neutral, and basic aqueous liquors that obviously much additional parametric work is needed on that subject.

4.2.6 Process advantages

Activated charcoal appears to be comparable to any medium used to remove iodine from very low concentrations in aqueous streams. We have cited examples of DFs of $>10^3$ being achieved for charcoal in treating iodine concentrations as low as 10^{-13} M.

4.2.7 Process disadvantages

Although some of the following statements may not be disadvantages for using charcoal as a sorbent of iodine from aqueous streams, the lack of experimental studies of that removal process have left many parametric relationships still to be determined.

1. When activated charcoal is used, most organics will generally displace elemental iodine, so that poisoning or competitive loading of charcoal beds by contaminant organics during removal of iodine from waste liquors must be considered probable. However, sorption of iodine that is dissolved in an organic solvent may be enhanced by low solute-solvent interaction.
2. The effect of a high concentration of iodine on removal efficiency and loading capacity of charcoal is not known.
3. The capacity of charcoal for iodine in elemental and ionic form should be determined. As part of that determination, the capacity for the different chemical species of iodine should be determined as a function of the K^+ (or other metal content) of impregnated charcoals.

4. The effect of elevated temperature on the removal efficiency and loading capacity of charcoal is unknown. However, the highest temperatures that would be reached in aqueous streams during fuel reprocessing would not likely pose the danger of charcoal ignition that has been observed for charcoal bed filtration of iodine from radioactive and thermally elevated off-gases.
5. However, studies would still be required to determine the suitability for disposal and methods of disposal of charcoal beds at the end of their effective filtering life.
6. The loading capacity and removal efficiency (i.e., DF) of charcoal to separate CH_3I and other organic iodides from aqueous streams has not been established.
7. Most of the studies in which charcoal was used to remove iodine from liquids have been either batch distribution or small-column experiments. Additional studies should be conducted in larger-scale engineering equipment.

4.3 Removal of Iodine Species from Liquid Streams by Utilizing Macroreticular Resins

4.3.1 Background

Most of the studies involving removal of iodine species from aqueous streams with macroreticular sorbents that were used in this literature survey were conducted at Oak Ridge National Laboratory (ORNL) or Battelle Northwest Laboratory (BNWL). These resins were initially attractive because of good flow properties, stability in highly acidic solutions, and good sorption capacity for iodine. Exploratory studies showed that both bromine and iodine could be sorbed from a gas stream with dry or wet anion exchangers.[126] Subsequent studies[127,128] had indicated that anion exchange resins could be used to sorb elemental iodine from air and aqueous solutions. Initial bench-scale studies[129] showed that elemental iodine could be sorbed from nitric acid solutions not only with macroreticular resins but also with polyethylene, PVC, polystyrene, and polyurethane foam. However, the plastic-based materials were not readily available commercially in a physical form that was amenable to process operations such as in a packed bed. Because of the commercial availability and favorable physical properties of macroreticular resins, they were chosen as the material with which to pursue parametric studies of elemental iodine (I_2) and CH_3I sorption from neutral and acidic aqueous solutions.

4.3.2 Physical properties

The Amberlite resins XAD-2 and XAD-4 consist of beads that are agglomerations of many very small microspheres. The individual beads have an open-cell structure around the microspheres, which results in both a continuous gel phase and a continuous pore phase. The backbone of the microspheres is a polystyrene structure that exerts a strong attraction for removing hydrophobic organics from polar solvents. Following are examples of the physical properties of the macroreticular resin XAD-4: stable at temperatures to 250°C; average bead diam, 0.35 to 0.45 mm; wet density, 1.02 g/cm^3; surface area of the dried resin, 750 m^2/g; average pore diameter of dried resin, 50 Å.

Considerable care must be exercised to prevent introduction of air into the hydrated resins, and extensive backwash and regeneration procedures are necessary when the macroreticular resins are recycled in situ in packed beds. It is generally desirable to load and elute the beds in ascending flow to maintain homogeneous sorbate loading zones.

4.3.3 Experimental results and engineering data useful for process design

Initial studies[129] showed that when the macroreticular resin Bio-Bead SM-2 was used in a small packed bed, a DF of 100 was produced for removing iodine from a 1.0 M HNO_3 solution containing 1.1×10^{-3} N I_2 (Table 11). Because of the low iodine loading capacity of the Bio-Bead SM-2 material (about 24-mg I_2/g), further studies were conducted with the Amberlite-XAD series.

In equilibrium batch tests,[130] the distribution coefficients were determined for elemental iodine distributing between neutral and nitric acid solutions and a series of macroreticular resins. The resins tested and their primary plastic composition are listed in Table 12. Testing conditions included variation in acid concentration of 0 to 7 M with an initial elemental iodine concentration of 5×10^{-5} M. The XAD-12 resin had by far the greatest removal efficiency for separating iodine from water; however, it showed an unpromising affinity for iodine in nitric acid solutions. The XAD-2 and XAD-4 resins showed the highest affinity for iodine in acidic solutions, with a surprisingly small variation in removal efficiency when the acid concentration was increased from 0.1 to 7.0 M. Experimental conditions and distribution ratios of iodine between the representative resins, H_2O, and 0.1 M HNO_3 are

Table 11. Sorption of iodine species from aqueous and acidic solutions with macroreticular resins at 21°C

Ref.	Resin	Bed size	Retention time[a]	Loading capacity	Feed	DF or DR[b]	Flow rate (m/min)
129	Bio-Bead SM-2, nonionic cross-linked polystyrene bead, -20+50 mesh	0.4 cm x 10 cm ($S = 0.125\ cm^2$)[c]	$\sim$4 min	24-mg I_2 per gram	1.1×10^{-3} M I_2[d]	$\sim$100	0.02
130	Amberlite XAD-2	Batch equil	Contact, 16 hr	ND[e]	5×10^{-5} M I_2 in H_2O	DR = 31	Batch
	Amberlite XAD-4	Batch equil	Contact, 16 hr	ND	5×10^{-5} M I_2 in H_2O	DR = 25	Batch
	Amberlite XAD-8	Batch equil	Contact, 16 hr	ND	5×10^{-5} M I_2 in H_2O	DR = 18	Batch
	Amberlite XAD-12	Batch equil	Contact, 16 hr	ND	5×10^{-5} M I_2 in H_2O	DR = 24000	Batch
	Amberlite XAD-2	Batch equil	Contact, 16 hr	ND	5×10^{-5} M I_2 in 0.1 M HNO_3	DR = 1100	Batch
	Amberlite XAD-4	Batch equil	Contact, 16 hr	ND	5×10^{-5} M I_2 in 0.1 M HNO_3	DR = 390	Batch
	Amberlite XAD-8	Batch equil	Contact, 16 hr	ND	5×10^{-5} M I_2 in 0.1 M HNO_3	DR = 1200	Batch
	Amberlite XAD-12	Batch equil	Contact, 16 hr	ND	5×10^{-5} M I_2 in 0.1 M HNO_3	DR = 720	Batch
131	Amberlite XAD-12	0.4 x 15 cm	15 min; run duration, 120 hr	77 mg/cm^3	5×10^{-4} M I_2 in H_2O	10^2-10^3	0.01
		0.4 x 15 cm	3.75 min; run time, 48 hr	130 mg/cm^3	5×10^{-4} M I_2 in H_2O	10^2-10^3	0.04
		0.4 x 10 cm	6.9 min; run time, 17 days	ND	1×10^{-6} M I_2 in H_2O	50-100	0.017
132	Amberlite XAD-4	0.4 x 25 cm	6.28 min; run time, 50 hr	$\sim$60 mg/cm^3	5×10^{-4} M I_2 in 0.5 M HNO_3	14-25	0.04
		0.4 x 25 cm	6.28 min; run time, 50 hr	$\sim$50 mg/cm^3	5×10^{-4} M I_2 in 3.0 M HNO_3	10^2 decreasing to 3	0.04
133	Amberlite XAD-12	0.4 x 15 cm	1.5 min; run time, 47 hr	ND	1×10^{-6} M I_2 in H_2O	50	0.1

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[a] Retention time based on total bed volume.

[b] DR = distribution ratio for batch equilibration, counts/min ^{131}I per g resin/counts/min ^{131}I per ml liquid.

[c] S = column cross-sectional area.

[d] All experiments were at 21°C.

[e] ND = not determined.

Table 12. Macroreticular resins tested to determine the optimum sorbent for removing iodine from neutral and nitric acid solutions

Sorbent	Type of plastic
Bio-Bead SM-1[a]	Polystyrene
Bio-Bead SM-2[a]	Polystyrene
Amberlite series[b]	
XAD-2	Styrene-DVB
XAD-4	Styrene-DVB
XAD-7	Acrylic ester
XAD-8	Acrylic ester
XAD-9	Acrylic ester-sulfoxide
XAD-11	Acrylamide polymer
XAD-12	Acrylic ester with nitrogen-oxygen group
XE-284	Styrene-DVB-sulfonic acid

Approximately 0.1 g of resin was contacted for 16 hr with 10 ml of solution containing 5 x 10^{-5} $\underline{M}$ I_2 traced with ^{131}I. The distribution ratio was counts min^{-1} g^{-1} resin/(counts min^{-1} ml^{-1} aqueous).[130]

[a] Bio-Bead macroreticular resins are available from Bio-Rad, Inc.

[b] Amberlite macroreticular resins are manufactured by Rohm & Haas, Inc., Philadelphia, Penn.

shown in Table 11. In later tests with the XAD-2, XAD-4, and XAD-12 resins in packed beds, it was never possible to obtain iodine DFs in dynamic bed operation that could compare to the distribution found for batch equilibration. After preparation of the 5×10^{-5} $\underline{M}$ I_2--HNO_3 solutions, undefined species of iodine resulted in significantly reduced distribution ratios unless the solution was aged 24 hr. It was reported[114] that after several hours in 3.0 $\underline{M}$ HNO_3, virtually all dissolved iodine would be present as elemental iodine (with I_3^- as an intermediate from I^-). Thus after initial preparation of the iodine-nitric acid solutions, aging was recommended[130] to be sure that all ionic-iodine had been oxidized to elemental iodine. However, for a dilute acidic solution, there is a strong possibility that some of the iodine will be in ionic form (I_3^-) at equilibrium. The presence of this species could reduce the DFs for sorbents with an affinity for molecular iodine only. Based on the chemical mechanism operating in the macroreticular resins, it is possible that a serious reduction in DF for iodine could be due to the growth of ionic species (I^-, IO^-, IO_3^-, I_3^-) into elemental iodine solutions.

Moore and Howerton[131] also determined the loading capacity and DF produced with XAD-12 for removing iodine from water, and the effective techniques for regenerating XAD-12 in situ in packed beds. For a 0.4 by 15-cm column of XAD-12 fed at flow rates of 0.01 m/min and 0.04 m/min, DFs of 10^2 to 10^3 were obtained when iodine was removed from 5×10^{-4} $\underline{M}$ I_2 in aqueous solution. Long run times were 120 hr and 48 hr for 0.01 m/min and 0.04 m/min respectively. For three sorption cycles of the XAD-12 columns, 85 to 94% of the sorbed iodine could be eluted with a 0.1 $\underline{M}$ $Na_2S_2O_3$--0.1 $\underline{M}$ NaOH solution. However, the DF for removing iodine from 10^{-6} $\underline{M}$ I_2 in aqueous solution was reduced to about 50, which was a possible indication that the iodine DF decreased as the feed concentration decreased. (This would be consistent with the observation that at low molarity of elemental iodine in aqueous solution, the elemental iodine becomes more unstable and dissociates to I^- and I_3^-, which have less affinity for macroreticular resins than does elemental iodine.) In agreement with later work at BNWL, it was also noted that preloading of the XAD-12 with nonradioactive elemental iodine appeared to enhance the iodine removal efficiency that could be obtained for the 10^{-6} $\underline{M}$ I_2 aqueous feed.

In summary, it appeared that the sorbent XAD-12 was the most efficient macroreticular resin for sorption of iodine from very dilute aqueous solutions. This effect might occur because of a slightly greater affinity of XAD-12 for I_3^- and I^- than is found for the other resin forms. The active group for XAD-12 was acrylic ester with a nitrogen-oxygen group.

Because earlier batch equilibration experiments had suggested that XAD-4 was the most efficient sorbent for iodine removal from nitric acid solutions, the XAD-4 resin was utilized in a 0.4- by 25-cm-long column to sorb iodine from a feed of 5×10^{-4} $\underline{M}$ I_2 in 0.5 $\underline{M}$ HNO_3.[132] The column DF for iodine varied from 14 to 25, increasing with increasing run time, and was maintained for 500-bed volumes of the feed. Only about 75% of the iodine could be removed from the column with 0.2 $\underline{M}$ NaOH. Some loss in capacity and DF occurred after regeneration. When the concentration of the feed was increased to 3.0 $\underline{M}$ HNO_3, DFs of as much as 100 were obtained; however, after 250-column volumes were fed to the column, this DF was reduced to only 3.0. Thus the effect of increasing the nitric acid concentration in the feed for long run times was to decrease the capacity of the XAD-4 resin for which a DF of 25 could be maintained. The 3.0 M HNO_3 feed affected the regeneration of the XAD-4 more than did the 0.5 M HNO_3 feed. Comparative studies of the sorption characteristics of charcoal, XAD-12, and silver zeolite were performed with 1×10^{-6} M I_2 aqueous solutions; Table 13 shows that the best results were obtained with the activated coconut charcoal.

Table 13. Comparison of DFs obtained for removal of I_2 from aqueous solution using activated charcoal, silver zeolite, and Amberlite XAD-12

Conditions: bed size, 0.4 x 10 cm; loading capacity, not determined; feed, 1×10^{-6} M I_2 in aqueous; temp, 21°C

Ref.	Sorbent	DF	Superficial velocity (m/min)
132	20 to 50 mesh, Fisher 5-685-A activated coconut charcoal	10^4	0.15
	Silver zeolite, 20 to 50 mesh	33	0.016
	Amberlite XAD-12	143	0.08

It has previously been noted that for 10^{-6} $\underline{M}$ I_2 in H_2O, most of the iodine will exist as elemental I_2, but there may be small quantities of ionic species such as I_3^- and I^- (Table 9). Thus the achievement of the highest DF for iodine on the activated coconut charcoal may have occurred because the charcoal had a similar capacity for elemental I_2 as did zeolites and XAD-12; however, it had a greater capacity for I^- species.

When an aqueous solution of 1×10^{-6} $\underline{M}$ I_2 was fed to a 0.4 by 15-cm-long column of XAD-12, a DF of about 50 was obtained for 1700-bed volumes of feed. Methanol did not show much promise as a column regenerating solution.[133]

Various polymeric and anion exchange resins have been screened to determine their capability of removing iodine species from simulated fuel reprocessing plant low-level aqueous effluent streams.[134-136] The following operational characteristics for long-term column tests with the Amberlite XAD series of macroreticular resins were observed:

1. The column efficiency obtained for iodine removal was negatively affected by intermittent operation.
2. In beds preloaded with iodine in continuous flow operation, more iodine was eluted from the XAD-7 and XAD-8 resins than from XAD-2 and XAD-4 resins. This result was somewhat at variance with the batch distribution results of Moore and Howerton[130] in which the amount of iodine sorbed from aqueous solution per gram of resin was about the same for the four resins XAD-2, XAD-4, XAD-7, and XAD-8.

3. Only partially successful regeneration of the Amberlite XAD-resins could be obtained with solutions of 0.1 M Na_2SO_3 and 0.1 M NaOH. In the most successful regeneration test, 85% of the sorbed iodine was removed from a preloaded XAD-2 resin bed. Moore and Howerton[131] had obtained recoveries of 85 to 94% of the iodine loaded onto Amberlite XAD-12 beds. However, using 0.2 M NaOH, they obtained recoveries of only 53 to 65% of preloaded iodine from Amberlite XAD-4 beds.[132] In general, the elemental iodine sorbed on macroreticular resins should be reduced by NaOH to I^-, which has very little affinity for the resin and thus is eluted from the bed.
4. Prewashing of the XAD-4 resins with organic solvents prior to loading could enhance the removal efficiency of molecular iodine.
5. The elemental iodine removal efficiency of the XAD-resins was enhanced by adding H_2O_2 to the feed to oxidize any iodide ion to elemental iodine.[136] It was previously reported in the discussion of Moore's work[129-133] that macroreticular resins had much greater attraction for elemental iodine than for iodide ions in aqueous solutions. Swanson[136] concluded that some chemical grouping in the commercial Amberlite XAD-resins exerted a reducing effect on the elemental iodine in the dilute acidic feeds. The nullifying effect of H_2O_2 on this reductant is shown

in Table 14. It was concluded that there was little possibility of achieving high DFs for elemental iodine on macroreticular resins for peroxide concentrations substantially below 0.3 M; in fact, the addition of 0.3 M H_2O_2 to the entire low-level aqueous waste stream from a large-scale LWR fuel reprocessing plant would carry a severe economic penalty. The reductant effect on I_2 apparently exerted by the macroreticular resins could possibly be counteracted by adding a low concentration of ferric ion and H_2O_2 to the feed, or by adding a trace of nitrite to the feed. The reduction in DF for removal of iodine from dilute acidic solutions using macroreticular resins may also be attributed to the dissociation of iodine in acidic solutions. Davis and Kibbey[114] (also see Table 9) reported that the equilibrium quantity of I_3^- is 1.65% of total iodine for 10^{-3} M I_2 in 0.025 M HNO_3, and up to 2% of iodine for 10^{-3} M I_2 in 0.1 M HNO_3. Thus for a sorbent that is reactive with primarily elemental iodine I_2 but not ionic iodine I_3^-, the maximum DF that could be achieved for the concentrations of 0.025 to 0.1 M HNO_3 would be ≤ 50 (without the presence of an oxidizing agent).

6. Preliminary results suggested that the DF for molecular iodine removal on XAD-4 was reduced slightly by dissolved organics (TBP and NPH diluents were used).

Table 14. The effect of hydrogen peroxide concentration on the sorption of iodine from a dilute nitric acid solution[a]

Column conditions: Aqueous flow rate, 2 column vol/hr; column dimensions, 0.9 by 19 cm; temp, 20°C; feed, 1 x 10^{-5} M I_2, 0.05 M HNO_3, H_2O_2 as indicated

Total column volumes applied	H_2O_2 conc in feed (M)	DF for iodine on XAD-4[b]
65	0.3	350
125	0.1	32
175	0.03	6
220	0.3	120

[a] This information was taken from ref. 136.

[b] DF = iodine concentration in feed/(iodine concentration in effluent). The data were obtained by applying the following feed schedule: 65 column volumes containing 0.3 M H_2O_2; 60 column volumes containing 0.1 M H_2O_2; 50 columns containing 0.03 M H_2O_2; and 45 column volumes containing 0.3 M H_2O_2.

4.3.4 Present applications

All utilizations of macroreticular resins for removing iodine species from aqueous waste streams have been experimental and are conclusively summarized above.

4.3.5 Process capacity

The maximum loading obtained by Moore and Howerton[132] for removal of molecular iodine from 0.5 M HNO_3 solutions with Amberlite XAD-4 macroreticular resin was about 60-mg I_2/cm^3 XAD-4. The iodine loading obtained by Swanson[136] when XAD-4 was used to remove iodine from 0.05 M HNO_3, 0.3 M H_2O_2 solutions was only 0.5-mg I_2/cm^3 XAD-4. The differences in the loading capacities can be partly attributed to the differences in operating conditions:

	Ref. 132	Ref. 136
I_2 feed conc	10^{-4} M	10^{-5} M
Flow rate	0.04 m/min	0.0063 m/min
Loading capacity	60 mg I_2/cm^3	0.5 mg I_2/cm^3
DF maintained	<100	>100
Bed size	3 cm^3	12 cm^3

Perhaps the loading capacity of XAD-4 for iodine obtained by Swanson[136] would have equalled that obtained by Moore[132] if the run time in Swanson's tests had been extended to supply the same quantity of iodine per cm^3 of bed as that attained by Moore.

4.3.6 Process advantages

1. If operated in ascending flow, the macroreticular resins have good flow characteristics. The beads maintain their physical integrity, should be thermally resistant to 250°C, and are acid resistant, particularly to HNO_3 which is the acidic component of actual low-level liquid wastes from reprocessing plants.
2. The macroreticular resins may be sufficiently stable to be considered for burial when they become excessively contaminated from unregenerable iodine.

3. The macroreticular resins offer some promise of regneration, because they are compatible with solutions of methanol, Na_2SO_3, and NaOH.

4.3.7 Process disadvantages

1. The low density of the macroreticular beads requires careful hydrodynamic control, and there may be some problems involved with in situ regeneration of the resins in columns.
2. Further tests of the competitive effect of organics on iodine binding should be pursued because macroreticular resins are primarily noted for their capacity to sorb organics.
3. The performance of the macroreticular resins has not been established as a function of temperature.
4. Resins that perform well for iodine removal from dilute nitric acid streams usually lose iodine when washed with neutral solutions.
5. All studies made with the macroreticular resins were to ascertain their efficiency for removal of iodine from neutral and dilute nitric acid aqueous streams, but no studies have been directed toward determining the capability of the resins to sorb organic iodides from the aqueous feeds. However, due to their lack of solubility in aqueous solutions, such low levels of organic iodides may be present that they may not

constitute a serious problem. Removal of organic iodides could probably best be handled by volatilizing and then sorbing them from humid vapors on silver-exchanged mordenites or the German Ag-KTB (AC-6120) material.

6. The process DFs and loading capacities obtained for iodine from low concentration feeds ($<10^{-4}$ $\underline{M}$ I_2) appear to be strongly related to the presence of iodides (and the resultant loss of elemental iodine) in the feeds and while exposed to the resins in the column. Unless this loss of process DF for total iodine can be solved simply without extensive and expensive chemical oxidant addition, the use of macroreticular resins for iodine removal from dilute acidic streams with very low iodine concentrations may remain too inefficient to compete with sorption on charcoal or anion exchange resins.
7. Any additional studies should be conducted in engineering-sized equipment.

4.4 Removal of Iodine Species from Aqueous Streams by Utilizing Anion Exchange Resins

4.4.1 Background

The treatment of aqueous streams for removal of iodine by ion exchange is a process widely used by operators of nuclear power plants to minimize the environmental impact of radionuclides that could be discharged into surface waters. Because there are many cationic and anionic radionuclides in the primary and secondary coolants, coolant condensates, and liquid wastes in nuclear power plants, iodine removal has generally not been studied as a specific problem. However, based on the information derived from the utilities using nuclear power generation, general information concerning the interaction of iodine with ion exchange resins can be obtained. Only a few laboratory studies, primarily in relation to removal of iodine from liquid wastes associated with nuclear reactors, have been conducted. In general, the best iodine removal efficiencies were found for anion exchange resins at neutral or slightly acidic pH. Competitive anions reduced the DF and loading capacity which could be obtained for iodine and, in many cases, an increase in acid concentration reduced the quantity of iodide sorbed. These results appear to be consistent with the studies reported by Davis and Kibbey[114] (also see Table 9) describing the iodine species that apparently exist in HNO_3 solutions. In general, when iodide (I^-) is dissolved in HNO_3, it is oxidized to elemental iodine. Thus, for I^- in HNO_3 solutions (or any other strongly acidic solution), as the concentration of acid is increased, the amount of iodine as elemental I_2 will increase and iodine as I^- or I_3^- will decrease. Therefore, the amount of iodine removed by an anion exchanger should decrease as the acid concentration increases (pH decreases).

Apparently, very little consideration has been given to using anion exchange resins for iodide removal from liquids by designers of nuclear fuel reprocessing plants.

4.4.2 Chemical mechanism

Although no references satisfactorily described the specific chemical kinetics and stoichiometry of the interaction between iodide and anion exchange resins, useful mechanistic information may be gleaned from the following studies.

Ivanov[137] studied the sorption of molecular iodine from aqueous solutions in batch equilibrations with various salt forms of the highly basic anion exchanger AV-17. The iodine concentrations were 5 to 50 millimolar (in excess KI) in aqueous solution at pH 6.4. Thus the iodine was available in both the iodide and elemental I_2 forms. The differences in the iodine sorption capacities of the various forms of the resin were attributed to the affinities of the ions to the sorbent and their redox potentials with respect to iodine. The amounts of iodine sorbed as iodide by the exchanged resin were in the range 3 to 7 millimoles of iodine/g resin, or 0.38 to 0.90-g I^-/g resin. For the halide forms of the resin, sorption of iodine varied according to the sequence AV-17 Cl^- > AV-17 Br^- > AV-17 I^-. That is, of the halides, iodide had the greatest affinity for the resin. Among a wide range of salts tested, the largest amount of iodine was sorbed by the AV-17 resin in the SCN^- form, and the smallest amount was sorbed by the IO_3^-, I^-, and $[Fe(CN)_6]^{-4}$ forms. Among the proposed reactions were:

$$2SCN^- + I_2 = 2I^- + (SCN)_2 \tag{38}$$

$$IO_3^- + 5I^- + 6H^+ = 3I_2 + 3H_2O \tag{39}$$

$$2[Fe(CN)_6]^{-4} + I_2 = 2[Fe(CN)_6]^{-3} + 2I^- . \tag{40}$$

The reducing agents SCN^- and $[Fe(CN)_6]^{-4}$ were oxidized, which resulted in a decrease in the amount of elemental iodine in the aqueous solution and a corresponding increase in iodide sorption. Iodine was normally desorbed from the resin with 10% KOH solutions. The iodine was desorbed least from the SO_4^{-2}, CO_3^{-2}, CH_3COO^{-2}, and PO_4^{-3} forms of the resin.

In summary, to maximize the absorption of iodine from aqueous iodide solutions at pH = 6.4, the highly basic anion exchanger AV-17 was most efficient in either the chloride form or with a highly active reductant group such as SCN^-. The sorption capacity obtained for iodide depended on the affinity of the resin for the counter ion of the original resin form, the species of iodine present in the solution, and the side reactions accompanying the absorption of iodide ion.

4.4.3 Experimental results and engineering data useful for process design

Laboratory tests of iodine species removal from aqueous streams with ion exchange materials. To determine the applicability of gel-type ion exchange resins for the decontamination of radionuclides in cooling water of nuclear reactors, Yokotsuka et al.[138] studied the distribution of 42 inorganic ions, including $Na^{131}I$, between neutral or acidic solutions and several gel types of Diaion and Amberlite ion exchangers. For batch equilibration tests with $Na^{131}I$, the anion exchange resins (in gel form) Diaion SAN-1 and Amberlite IRN-78 (for resin properties, see Table 15) showed good removal efficiency (distribution ratio of 10^1 to 10^2) for iodide ion in hydrochloric acid solutions varying from 0 to 12 M.

In a related study to determine the relative merits of the gel and porous forms of the resins for use in filtering nuclear reactor coolants,

Table 15. Properties of anion exchange resins of the tetramethylammonium chloride form

Resin	Particle size	Divinylbenzene (%)	Weight exchange capacity (meq/g)	Volume exchange capacity (meq/ml)
Diaion SAN-1	20 to 50 mesh	8	2.61	1.07
Amberlite IRN-78	20 to 50 mesh	8	2.77	1.09
Diaion PA-316	0.35 to 0.55 mm	8	3.91	1.46
Amberlite IRA-900	NS[a]	10	3.80	1.03

[a] NS, not specified.

Akatsu[139] investigated the iodide removal efficiencies and flow properties of porous forms of the Diaion and Amberlite series. Good distribution ratios[*] were determined for batch equilibration of iodine as $Na^{131}I$ in acidic solutions and the anion exchangers Amberlite IRA-900 and Diaion PA-316. For both of these anion exchangers in the chloride form, the distribution ratio decreased from 10^3 to 10^2 when the concentration was increased from 0.1 to 1.0 N HCl. The iodide distribution ratios between water and the anion exchangers Diaion PA-316 and Amberlite IRA-900 were 1×10^3 and 2×10^3 respectively. Skorokhod[140] had also reported good iodine removal efficiencies with another Amberlite resin, the strongly basic anion polystyrene ion exchanger IRA-410. In the studies described

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[*] Batch distribution ratio, Kd(ml/g), was

$$\mathrm{Kd} = \frac{\text{volume of aqueous phase}}{\text{weight of air dried resin}} \times \frac{\begin{array}{c}\text{counting rate of initial soln (per ml)}\\ \text{minus that of final soln (per ml)}\end{array}}{\text{counting rate of final soln (per ml)}}$$

in refs. 138 and 139, none of the cation exchangers used showed any iodine adsorption from aqueous or acidic solutions of 0 to 1.0 N HCl. This result had already been shown in tests of Dowex cation exchange resins for removing radionuclides from 0 to 12.0 N HCl solutions.[141]

A rather unique application of ion exchange resins for iodine sorption involved experiments to develop methods of purifying milk containing radionuclides.[142] Radionuclides such as ^{90}Sr and $^{131}I^-$ could be introduced into milk from nuclear weapons fallout. Studies were conducted at both the pilot plant and on a commercial scale to determine the efficiency of sequential anion and cation exchange beds for removing ^{90}Sr and $^{131}I^-$. Operating conditions included a temperature of 10°C, a pH of 5.3 adjusted with either citric acid or hydrochloric acid, the anion exchanger DOWEX 2X8, 20 to 50 mesh, equilibrated primarily with the chloride and citrate anions, and the cation exchanger IR-120 equilibrated primarily with the calcium cation, and to a lesser capacity with the potassium, sodium, and magnesium cations. Flow rates for the 65- by 224-cm anion exchange bed were in the range 0.05 to 0.1 m/min (1/16 to 1/8 resin-bed volumes/min). For three commercial-scale runs with series operation of the anion-cation exchange resin beds, an average of 99.3% of ^{131}I was removed by the anion exchanger.

Apparently, one workable method of removing iodine species from aqueous process streams would be to first reduce the iodine species to iodine ions and then remove them on anion exchange resins. Anion exchangers such as Amberlite IRN-78, Amberlite IRA-900, Amberlite IRA-410, and Diaion PA-316 have shown promising affinity for iodide. Swanson[143] has recently studied the removal of iodide from 1×10^{-5} M I^- in HNO_3

solutions on small columns ($\sim$12 cm^3) of the Rohm and Haas anion exchange resins: Amberlyst A-26, Amberlite IRA-910, Amberlite IRA-900, Amberlite IRA-94, and Amberlyst A-21. The best DFs (>10) and iodide loading capacities were obtained for the first three anion exchangers. The iodide removal from nitrate solutions using the IRA-900 increased when the nitrate concentration of the feed solution was decreased; for example, the iodide capacity of IRA-900 increased by a factor of 5 when the nitrate concentration was reduced from 0.05 to 0.01 M. This effect appears to be consistent with a reduction in oxidation of I^- to elemental I_2 as shown in Table 9. That is, when nitrate concentration is decreased from 0.05 to 0.01 M, relatively more of the total iodine is found as the iodide ion rather than in elemental form. Subsequently, the capacity of the anion exchange resin for iodine as I^- should be increased. It is possible that one method of regenerating the iodide-loaded anion exchangers would be to elute them with 2 to 3 M HNO_3 solutions.

Other less orthodox adsorbents have been suggested for removal of iodine species from aqueous solutions. In general, these sorbents are not likely to be considered as viable alternatives for low-level radwaste streams, because either additional definitive experiments are necessary or preliminary efficiencies were not promising. Zuljevic[144] reported that iodide ions are partially sorbed to ferric hydroxide precipitates prepared by mixing $FeCl_3$ and NH_3 solutions. Poor loading capacity and undefined sorbent hydrodynamics appear to limit further application of this adsorbent. Brevnova et al.[145] investigated the utilization of isotopic exchange for isolating iodine from fission products in a 1.5-cm-ID column containing fibrous sulfonate ion exchangers treated with 10% solutions of $AgNO_3$ and KI. For a solution containing 1 x 10^{-5} Ci ^{131}I/liter (6.2 x 10^{-13} M I^-), >95% of the radioactive iodide could be collected on the sulfonate sorbent when 1 N H_2SO_4 and 5% sodium hexametaphosphate were added to the feed solutions to allow for selective sorption of only the radioiodine. Although this appears to be a promising adsorbent, more study is needed to elucidate the hydrodynamic properties and firmly establish the relative contributions of both isotopic exchange and ion exchange to the total binding mechanism. Swanson[146] has also studied the removal of iodine species (both as I_2 and I^-) from dilute HNO_3 with manganese dioxide (MnO_2)-impregnated porous materials. Results were promising, but more study is needed concerning the selection of substrate material for optimization of MnO_2 impregnation and improvement in DFs for high feed rates (DFs were near 100 only for flows less than one column volume per hr).

Large-scale operations for removal of iodine species from aqueous streams with anion exchange resins. Very early in the operation of power reactors, ion exchange resins were introduced to remove fission products from circulating coolant streams. The cleanup and filtering operations for purification of liquid streams in Boiling Water Reactor (BWR) and Pressurized Water Reactor (PWR) power plants have many similarities. Most of the differences arise because there are more circulating chemicals in the primary and secondary coolants of the PWR.

One of the early studies[147] to determine the possibility of utilizing mixed anion and cation exchange beds to both control pH and remove fission products in sidestream coolant purification systems was in the NRX reactor at the Chalk River Nuclear Facility, Ontario. For in-pile loop tests at Chalk River, a column 2.54 cm ID and 91 cm long with a bed volume of 465 cm^3, was operated at a superficial velocity of 0.71 m/min. The resin was 223 dry g of mixed bed, with anion exchanger IRA-400 in the hydroxyl form and IRA-120 in the lithium form. For ^{131}I and ^{133}I, a DF of 10^4 was obtained after 46 days of operation with very dilute iodide feeds. Mixed beds of the IRA-400 and IRA-120, in a 1/1 equivalent ratio, were suggested for effectively controlling pH and radionuclides in PWR coolant streams.

Anion exchange resins in combination with charcoal beds were also tested to determine the feasibility of treating low-level radioactive liquid streams to recycle the purified water for reuse at nuclear installations.[148] Iodine was specifically removed in two stages of the micropilot plant: one stage consisted of a 750-ml bed of the strong-base anion exchange resin Dowex 1-X8 (20 to 50 mesh), and the second stage consisted of a 1200-ml bed of granular activated charcoal. For a flow rate of 150 ml/min and a feed concentration of 1×10^{-10} g $^{131}I^-$/liter, DFs $\geq 10^3$ were obtained for radioactive iodine. Fletcher[149] conducted a comprehensive study to determine mass transfer coefficients and equilibrium constants for ion exchange sorption of radionuclides (such as cesium and iodine) contained in aqueous coolants and liquid wastes from such nuclear installations as the Shippingport Atomic Power Station, Apollo, Pennsylvania. This paper is an excellent reference for those interested in theoretical analysis of ion exchange. Experimentally, the DF for $^{131}I^-$ was determined at a flow rate of 0.114 m/min through the anion exchanger XE-78 (20 to 30 mesh) packed in a 1.75-cm-ID column.

Resin properties were 20 to 30 mesh, with exchange capacities of 4.0 meq/dry g and 1.07 meq/wet cm^3. The resin was converted to the borate form and the feed contained 10^{-10} $\underline{M}$ $Na^{131}I$. The variation of DF and mass transfer rate with concentration of KOH indicated both competition of the OH^- with I^- for exchange sites and an effect of solution total ionic strength on DF. The data concerning the effects of pH and borate concentration on the DF for iodide was limited, but for XE-78 in the 1.75-cm-ID bed with 1000-ppm boric acid (no alkali), a ^{131}I DF of 14 was obtained for 28 hr of operation. In studies of the purification demineralizer in the Saxton reactor,* Weisman[150] observed a reduction in iodide DF from 10^4 to 10^2 when the anion exchanger was converted to the borate form from the hydroxyl form. Again, the reduction was attributed to competition between borate and I^- for exchange sites.

Theoretical derivations useful for analysis of ion exchange processes. Drawing from several theoretical discussions of the ion exchange process, expressions were derived for both the steady state and transient ion exchange reaction for the cases of mono-monovalent exchange and monopolyvalent exchange.[151] The basic assumptions were that (1) the process involved exchanging radionuclides in trace concentrations that undergo decay; and (2) mass transfer was controlled by transfer of ions through the liquid film around the resin particle. Because of the complexity of these derivations, the resultant expressions will not be summarized here. Another derivation involved the expression for the mass transfer coefficient for ion exchange of a radionuclide undergoing decay from a trace concentration in a liquid feed. Those

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*The Saxton nuclear power facility was a closed-cycle PWR operated in an experimental program conducted jointly by the Westinghouse Atomic Power Division and the Saxton Nuclear Experimental Corporation, a subsidiary of General Public Utilities Corporation of Pittsburg, Penn.

interested in the mechanism of ion exchange should consult these derivations because of their considerable value in providing guidelines for the acquisition, analysis, and presentation of experimental data for the packed-bed ion exchange process.

Lin[152] has also discussed the ion exchange mechanism in relation to the interpretation of operating data obtained from utilities for the removal of trace radionuclides from liquids in commercial nuclear power plants. Specific aspects of ion exchange were those affecting ionic selectivity, reversibility of ion exchange reactions, exchange capacity, swelling equilibrium, and degree of cross linking. Because the rate of exchange reaction is generally so high, the rate-controlling step in the overall process is normally diffusion, mass transfer in either the solution film (at low ionic concentration) or through the resin particle (at high ionic concentration). Expressions were presented that were useful for (1) evaluating the rate-controlling step, and (2) evaluating the instantaneous rate of the overall ion exchange process.

Some of the experimental studies describing iodine species removal from liquids with anion exchange resins are summarized in Table 16.

4.4.4 Present applications

The following summation of the status of the technology (to 1973) of ion exchange resin utilization for treatment of nuclear power plant coolants was taken from Lin's excellent review[152] of 24 nuclear power plants in the United States. The primary coolant streams in PWR and BWR power plants contain levels of radioactivity that vary from 10^{-7} to

Table 16. Removal of iodine species from liquids by treatment with anion exchange resins

Ref.	Resin form[a]	Feed composition	Bed size	Retention time	Loading capacity	DF	Batch distribution ratio
137	Strongly basic anion exchanger AV-17 in about 10 different anion forms.	Aqueous iodine-KI solutions 0.005 to 0.05 M	NA[b]	Batch equilibration	0.38-0.9 g iodine	ND[c]	ND
138	Diaion SAN-1, Amberlite IRN-78, resin gel and chloride form.	Aqueous or acidic (0-12 M) HCl with tracer $Na^{131}I$	NA	Batch equilibration	ND	ND	10-100
139	Anion exchangers Diaion PA-316, Amberlite IRA-900, resin porous structure, chloride form.	Aqueous and acidic (0-1 M) HCl with $Na^{131}I$ tracer	NA	Batch equilibration	ND	ND	10^2-10^3
142	Anion exchanger Dowex 2X8, 20-50 mesh, chloride and citrate forms.	Milk at 10°C and pH 5.3 ^{131}I tracer	65 cm ID x 224 cm	8-16 min	ND	143	NA
143	Anion exchangers Amberlite IRA-910,	1×10^{-5} M I^- in 0.05 M NO_3^-	0.9 x 19 cm	30 min	<0.07 mg I^-/cm^3	>10	NA
	IRA-900, Amberlyst A-26.	1×10^{-5} M I^- in 0.01 M NO_3^-	0.9 x 19 cm	30 min	<0.35 mg I^-/cm^3	>10	NA
148	Anion exchanger Dowex 1-X8, 20 to 50 mesh.	Simulated low-level radioactive aqueous wastes	750-ml bed	5 min	ND	$>10^3$	NA

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[a] For resin properties, see text or Table 15.

[b] NA - Not applicable.

[c] ND - Not determined.

1 μCi/ml; for ^{131}I, 3.8 x 10^{-3} μCi/ml (or 1 x 10^{-13} $\underline{M}$ $^{131}I_2$) in a representative BWR, and 10^{-5} μCi/ml (or 1 x 10^{-15} $\underline{M}$ $^{131}I_2$) in a representative PWR. Performance data with reference to removal of a specific radionuclide from the coolant and liquid waste streams are not normally available for individual power plants. Most removal efficiency data are based on gross ($\beta + \gamma$) radioactivity measurements that do not provide identification of individual radionuclides. However, some plants do determine radioiodine removal efficiency as a measure of the nominal function of the ion exchangers.

The resins used most frequently by nuclear power plants are strong acid cation exchangers (because most of the radionuclides are cations) and strong base anion exchangers. The resins are generally synthetic organic resins with a polystyrene backbone. In conventional operation, resins with a particle size range of 0.4 to 0.7 mm are packed into beds that are 0.60 to 2.4 m (2 to 8 ft) in diam, 0.91 to 1.8 m (3 to 6 ft) deep, and contain 0.85 to 6.0 m^3 of resin. Large powdered resin units that function as both filters and demineralizers are often used in BWRs. Flow rates for various ion exchange systems are: (1) 1 to 50 gpm/ft^2 of bed cross section (4 to 200 cm/min) for BWRs; and (2) 5 to 20 gpm/ft^2 (20 to 80 cm/min) for PWRs. Feed stream temperatures are usually below 60°C. Feed streams in BWRs are near neutral, but the pH in PWRs may vary widely from 4 to 10.5.

So that the high quality of water required in light-water-cooled power reactors can be maintained, "nuclear grade" ion exchange resins must be employed. These nuclear grade resins are superior to regular grade because (1) they contain much smaller quantities of leachable organic impurities, (2) they have a more uniform particle size, and (3) they have a higher degree of conversion to ionic form. The physical and chemical properties of these nuclear grade resins are listed in Table 17. The operational parameters affecting the removal efficiency of these resins are: (1) chemical and physical forms of contaminants in the feed, (2) temperature, (3) pH, (4) flow rate, (5) design and dimension of beds, and (6) degree of resin regeneration.

The ion exchange arrangement most frequently used in treatment of primary and secondary coolants and waste liquids is the mixed-bed system, which consists of a stationary bed containing mixed anion and cation exchange resins. The iodide species are removed primarily by the anion exchange resins. Under normal conditions, the concentrations of radioiodine species in liquid streams at nuclear power plants are much less than parts per billion. For example, in the primary coolant of a BWR the radioiodine concentrations are in the ranges as specified: (1) ^{131}I, 1×10^{-7} to 3×10^{-2} μCi/ml; (2) ^{132}I, 10^{-2} to 4×10^{-1} μCi/ml; (3) ^{133}I, 5×10^{-5} to 10^{-3} μCi/ml; (4) ^{134}I, 4×10^{-2} to 4×10^{-1} μCi/ml; (5) ^{135}I, 1×10^{-4} to 2×10^{-1} μCi/ml. For the primary coolant in a PWR, the radioiodine concentrations are in the ranges: (1) ^{131}I, 10^{-5} to 10^{-4} μCi/ml; (2) ^{133}I, 6×10^{-4} to 3×10^{-3} μCi/ml; (3) ^{135}I, 10^{-3} to 10^{-2} μCi/ml.

The DFs shown in Table 18 represent time-average values over the operating life of the resin beds. They were derived from water treatment experience, ion exchange fundamentals, laboratory data, and plant operating experience. They are considered to be attainable for treatment of aqueous solutions containing radioactivity less than 0.1 μCi/ml,

Table 17. Characteristics of typical anion exchange resins (OH^- form) used in treatment of liquids in nuclear power plants

Resin type	Functional groups	Typical regenerant	Regeneration level (%)	Theoretical capacity (meq/ml wet resin)	pH range	Max operating temp (°C)
Strong base, Type 1	Quaternary ammonium, Type 1	4% NaOH	80	0.5-1.0	1-14	60
Strong base, Type 2	Quaternary ammonium, Type 2	4% NaOH	80	0.5-1.0	1-14	38
Weak base	Primary, secondary, and/or tertiary amine	4% NH_4OH	95	1.5-2.5	1-7	93

Table 18. Decontamination factors for radioiodine species that can be attained with various ion exchange systems[a]

	DF (average over the system life-time)
PWR	
Mixed bed, Li^+-BO_3^{3-} form	10
Cation bed, H^+ form	1
Mixed bed, H^+-OH^- form (radioactive waste)	10^2
Anion bed, OH^- form	10^2
BWR	
Mixed bed, H^+-OH^- form	
Primary coolant	10
Steam condensate	10^3
Clean waste	10^2
Dirty waste	10^2
Cation bed, H^+ form (dirty waste)	1
Powdex in any system	10
PWR and BWR	
Mixed bed, H^+-OH^- form (evaporator condensate)	10

[a] The information for this table was taken from ref. 152.

provided that (1) a sufficient amount of ion exchange resin is available, (2) the concentrations of dissolved and suspended solids are less than 1000 ppm, and (3) the systems are well-designed and effectively operated.

Both the primary and secondary coolants in PWR plants contain additives, with hydrogen and hydrazine in the primary system for oxygen scavenging, enriched ^{7}LiOH for pH control to reduce corrosion, and H_3BO_3 for control of core reactivity. The secondary coolant may contain Na_2HPO_4 to render the water alkaline. The effect of these additives is to shorten the service life of resins for PWR coolant filtration, primarily by reducing the DFs and loading capacities of the resin beds. Because the liquid waste streams from LWR fuel reprocessing plants will also contain acid organic contaminants and perhaps other inorganics, some of the information gained in years of operating resins for cleanup of power plant coolants may be applicable to the treatment of fuel reprocessing liquid wastes.

Weisman and Bartnoff[150] had reported that the DF for radioiodine removal from a PWR coolant utilizing a KOH-form resin was decreased from 10^4 to 10^2 when a boric acid shim was added to the coolants. In another investigation to determine the effect of competitive anions on the iodide DF, Dickinson and Higgins[153] conducted a study to determine the efficiency of intermediate-base and weak-base anion exchange resins for the removal of nuclides from boric acid shims in the presence of extraneous ions. Anion exchange resins were Duolite A-30R (an epoxy intermediate base), A-101D (styrene matrix, type 1 basicity), and DS-4155 (aliphatic weak base). Feed solutions for the anion exchangers contained 17,000-ppm H_3BO_3, 2.54×10^4-ppb ^{131}I, and 100-ppm Na_2SO_3. The addition of Na_2SO_3 served to both maintain ionic iodide and provide extraneous ions. For sorption of $^{131}I^-$, only the intermediate-base resin A-30R was effective in removing iodide from a solution containing Na_2SO_3. The iodide DF for A-30R was 10^4 with a loading of 0.017-Ci/liter resin.

It has been discussed at several points in this review that for the composition and pH ranges which are predicted to exist in low-level radwaste liquid streams, it is highly probable that iodine will exist in both elemental and anionic forms. It thus follows that one logical approach to the treatment of such a stream would be to utilize series operation of two sorbent beds, chosen so that one has a high affinity for anionic species while the other has high affinity for elemental iodine. Alternately, a packed bed containing mixtures of sorbents having affinity for both elemental iodine and anionic iodine species could be utilized. Based on the sorbents discussed in this review, it is suggested that perhaps the most effective process for removal of iodine from low-level radwaste liquid streams would be operation of a bed of activated charcoal (highly impregnated with K^+) in series with a bed of the appropriate strongly basic anion exchanger.

Shown in Figure 7 is a photograph of a bench-scale experimental facility employed at ORNL[154] to test various types of impregnated charcoal, macroreticular resins, and anion exchangers for their ability to remove iodine from simulated low-level radioactive liquid wastes (with compositions similar to those discussed in Sect. 4.1 or those utilized by Moore and Howerton in their studies[129-133]). Iodine containing 10^{-4} to 10^{-5} $\underline{M}$ I_2 (with ^{131}I tracer) in aqueous or dilute

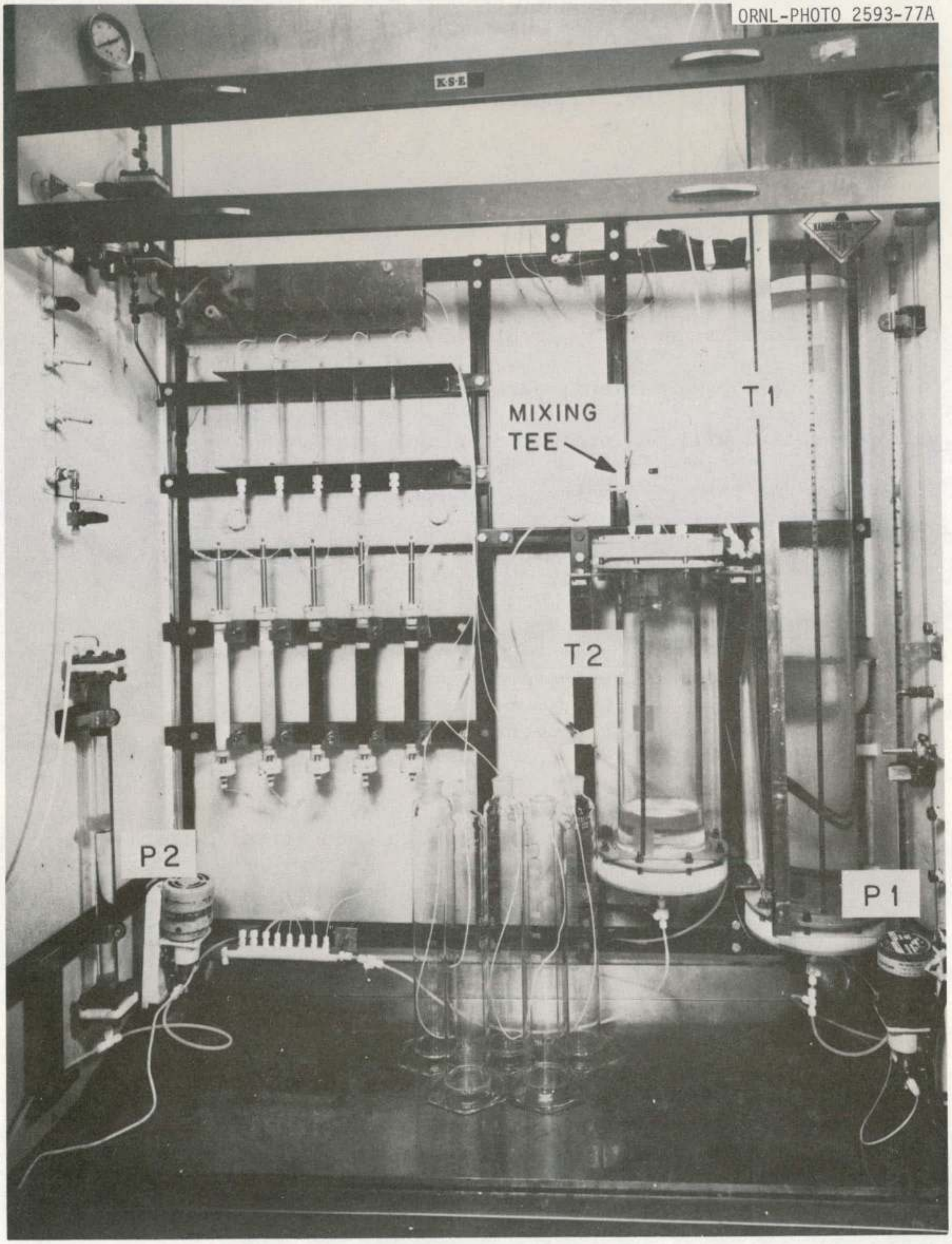

Fig. 7. Photograph of equipment used to screen candidate sorbents for removing iodine from aqueous solutions.

nitric acid solutions was pumped by pump 1 from tank 1 to be mixed with distilled water in tank 2. From pressurized tank 2, the simulated low-level radwaste liquid was supplied to the various columns through a manifold.

4.4.5 Process capacity

The theoretical capacity of the anion exchangers for iodine in the iodide form is generally about 0.5 to 2 meq/g (or 63 to 254 mg I^-/g of resin). Although various operators establish different limits at which operation will be terminated because of decreasing removal efficiency and loss of loading, a standard discard limit would be when only 33% of the original theoretical capacity remains unused.

4.4.6 Process advantages

1. Anion exchange resins are capable of removing iodide from streams with concentrations ranging from 10^{-19} $\underline{M}$ to 10^{-5} $\underline{M}$ iodide.
2. Anion exchange resins have a high theoretical capacity for sorption of iodine species. However, loading capacity must always be considered to be a function of the DF delivered.
3. The loading capacity should not be seriously reduced by low-level organics in liquid radwaste streams.
4. Operation of anion exchangers in treating PWR and BWR coolants was successful to 60°C.

4.4.7 Process disadvantages

1. The capability of removing organic iodides from waste streams has not been shown.
2. The effect of competitive anions on loading capacity of anion exchanger for iodide must be established. The efficacy of the NO_3^- form of various anion exchange resins would have to be established.
3. The effect of temperatures in excess of 60°C would have to be established.
4. The effect of pH and other ionic species on the disproportionation of iodine to elemental I_2 and ionic species would need to be established for the particular liquid waste stream to be treated. The presence of some of the iodine as elemental I_2 would probably reduce the overall DF to be achieved for iodine on an anion exchanger.

5. SUMMARY

A literature survey was conducted to provide information for the assessment of the various processes now available to remove iodine species from simulated LWR fuel reprocessing off-gases and low-level radwaste aqueous streams. The candidates for off-gas treatment included: two acid-scrub processes, Iodox and the mercuric nitrate--nitric acid scrubbing technique, and several processes based on solid sorbents such as silver zeolites; silver mordenite--lead mordenite sorbents in tandem; the proprietary Ag-KTB (AC-6120) material consisting of $AgNO_3$-substituted silicic acid; and macroreticular resins. The candidates for low-level liquid waste treatment included: (1) activated charcoal, (2) macroreticular resins, and (3) anion exchange resins in general. These processes are summarized in the following sections.

5.1 Methods for Removal of Iodine Species from Off-Gases

The processes for iodine species removal from off-gases that have been most extensively investigated are the Iodox acid-scrubbing process (iodine scrubbed into hyperazeotropic nitric acid in bubble-cap columns), the mercuric nitrate--nitric acid [$Hg(NO_3)_2$-HNO_3] scrubbing process, and sorption on the solid sorbents (silver zeolite, silver mordenite--lead mordenite, and the Ag-KTB proprietary material). Specifically, these processes have been studied with the most accurately simulated fuel reprocessing off-gases, and in some cases have been utilized in actual pilot plant demonstration. The operating parameters that were considered to exert the most extensive effects on the iodine removal capabilities of the candidate processes are summarized in Table 19. Table 20 summarizes the experiments with each candidate process for those cases where the conditions most clearly simulated the treatment of LWR fuel reprocessing off-gases.

The Iodox process, which is excellent for off-gas treatment, should be applicable to both primary and secondary iodine removal, because acceptable DFs for CH_3I of 10^5 to 10^6 can be obtained for feed concentrations of 200 to 0.02 mg I_2/m^3. The Iodox process is capable of processing feed gases containing high concentrations of H_2O and NO_x species at ambient temperatures and still deliver DFs $>10^4$ for I_2 and CH_3I.

Table 19. Comparison of systems for trapping iodine species from gaseous streams

Affecting process variable	Iodox	Mercuric nitrate-nitric acid	Silver zeolite	Regenerable silver mordenite-disposable lead mordenite	Macroreticular resins	Silver nitrate impregnated silicic acid, AC-6120, West German material
Water vapor	Dilutes acid, decreases process DF and capacity	Minimal effect	Reduces loading[a] capacity and DF	6% H_2O and 250°C[a] negligibly affected capacity of Ag°Z	High relative humidity decreases capacity and DF	Relative humidity >70% affects capacity[a] and DF
NO	Reacts to NO_2, reduces DFs on lower trays	Unknown, but possibly similar to NO_2	Unknown	2% NO increased capacity of Ag°Z	Unknown	Unknown
NO_2	Reduces DFs on lower trays	Eliminates iodate formation, improves process performance	2% NO_2 and 200°C greatly reduces loading capacity and DF	Negligible effect of 2% NO_2	Unknown for gas but resins are stable in HNO_3 solutions	Prevents oxidation of Ag, enhances performance
CO_2	None	None	None	None	Unknown	Unknown, probably none
Temperature	Unknown, to be determined	Normal operation at 40°C for $Hg(NO_3)_2$; higher temp (80°C) reduces capacity	DF and loading capacity for CH_3I and I_2 vary directly and inversely with temperature (respectively)	No effect to 250°C unless saturated with H_2O	Reduces capacity	No effect to 150°C unless H_2O saturated
Organics and other poisons	May exclude aromatic iodides; hexane affects process DF and capacity	Aromatics drastically reduce process DF and capacity; other aliphatics detract to a lesser extent	Not affected by propane, hexane;[a] affected by dodecane, H_2S, SO_2	Not determined; probably same behavior as AgX, $AgNO_3$-impregnated German material	Organics in general reduce capacity (e.g., dodecane)	Unaffected by a wide range of cyclic and aliphatic organics
Other limitations	Requires hyper-azeotropic nitric acid	Mercury disposal	Cost, heat transfer, solids handling, affected by prolonged exposure to steam	Heat transfer, solids handling	Heat transfer, solids handling, poor hydrodynamic properties	Cost, heat transfer, solids handling
Construction material	Zircaloy[b]	Stainless steel	Stainless steel	Stainless steel	Stainless steel	Stainless steel

[a] In general, sorption of I_2 is less affected by process variables (such as humidity and organics) than is the sorption of CH_3I.

[b] Recent studies have indicated that other alloys may have to be considered for construction of Iodox.

Table 20. Maximum decontamination factors obtained for iodine species removal from the feed-gas compositions that most accurately simulated LWR fuel reprocessing off-gas

Operation	Concentration of iodine species		Gas feed rate	NO conc[a] (%)	NO_2 conc (%)	H_2O conc[a] (%)	Column or bed temp (°C)	Feed gas temp (°C)	Loading capacity[a]	Decontamination factor	Effect of organics[a]
	I_2 (mg/m^3)	CH_3I (mg/m^3)									
Iodox 10.2-cm-ID, 8 bubble-cap plates, 15-cm spacing	233 (22 ppm)		96 slm (1.2 m/min)	None	2	2.4	Plate 1 - 23 Plate 6 - 27	∿21	ND	5 x 10^5	ND
		264 (46 ppm)	98 slm (1.2 m/min)	None	7.6	1.9	Plate 1 - 24 Plate 6 - 27	∿21	ND	3.2 x 10^5	ND
Mercuric nitrate-- nitric acid, 2.54- cm-ID simulated bubble-cap column, 8 stages	600 (57 ppm)		2.5 slm (5 m/min)	None	N_2O_3 @ 1	ND	25	∿25	ND	5 x 10^4	No effect of octane, dodecane; xylene, diethylbenzene reduced DFs to 100
		40 (7 ppm)	2.5 slm (5 m/min)		N_2O_3 @ 0.4	ND	25	∿25	ND	8 x 10^4	
Silver zeolite[b] 2.54 x 5.08-cm beds	500		60 m/min	None	2	5	ND	100	42 mg I_2/g	2 x 10^2 (breakthrough)	I_2 and CH_3I loading not affected by O_2, CO_2, H_2, propane, hexone, kerosene, but CH_3I affected by H_2S, SO_2
	∿9		19 m/min	None	None	2.3	∿200	200	6 mg I_2/g	2 x 10^5	
		∿816	19 m/min	None	None	2.3	∿200	200	74 mg CH_3I/g	>10^4	
		∿785	19 m/min	None	None	2.3	∿200	200	178 mg CH_3I/g	10^2	
Ag-KTB (AC-6120/H_1)[c] $AgNO_3$ impregnated amorphous silicic acid, 2.34 x 10-cm beds	4000 (∿380 ppm)		15 m/min	ND	2-20	4.2	150	150	>50 mg I_2/g	>10^4	With the beneficial presence of NO_2, removal of I_2 was not affected by alkyl iodides, secondary and tertiary alkyl iodides, alicyclic and aromatic cyclic iodides
		100-150 (17-26 ppm)	15 m/min	ND	10	4.2	150	150	5 mg CH_3I/g	>10^3	
Silver mordenite-- lead mordenite tandem beds, 5 x 15 cm	1500 (∿143 ppm)		15 m/min	2	2	5.6	150	150	Saturation zone, >150 mg I_2/g	10^3 to 10^4	ND
		d	d	d	d	d	d	d	Overall average >120 mg I_2/g	d	d
Macroreticular resins Amberlite XAD-4 0.5 x 10-cm columns	3000		7.65 m/min	None	None	0	25	25	218 mg I_2/g	>10^4	Preloading XAD-12 with 20% (w/w) of dodecane reduced removal efficiency for I_2
	400		12.2 m/min	None	None	1.8	25	25	>50 mg I_2/g	>10^3	
		1 x 10^3 to 4 x 10^3	7.65 m/min	None	None	0	25	25	12 mg CH_3I/g	>10^2	

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[a] ND, not determined.

[b] The DFs for CH_3I removal with AgX are affected much more by low feed-gas temperatures and high humidities than are the DFs for I_2.

[c] Available from Bayer in Leverkusen, Federal Republic of Germany.

[d] No data were taken for CH_3I.

The combined effects of high relative humidity and high NO_x concentration of feed gases at ambient temperature constitute one of the most severe tests of any system for removing iodine from off-gases. The major disadvantages of the Iodox process are probably the complexity of the system and the necessity of using costly, highly corrosive resistant construction materials to tolerate the severe effects of >23 M hyperazeotropic nitric acid. The effect of organics such as dodecane, kerosene, and aromatic hydrocarbons on the Iodox process should be investigated further. There is evidence that aromatic iodides may escape the system.

For the $Hg(NO_3)_2$-HNO_3 scrubbing process at ambient conditions, good DFs ($>10^3$) were obtained for CH_3I and I_2 removal from off-gases containing high concentrations of NO_x (high concentration of H_2O should not significantly affect the wet-scrub process). The presence of NO_x's actually benefits the scrubbing system by eliminating iodate formation. However, the DFs obtained for iodine in the $Hg(NO_3)_2$-HNO_3 scrubbing process are severely reduced from 10^4 to 10^2 when aromatics are included in the feed gas. The DFs for the $Hg(NO_3)_2$-HNO_3 system varied little for feed concentrations of 0.5 to 500 mg/m^3.

Among the first solid sorbents that showed promise for off-gas treatment were the silver-exchanged zeolites (AgX). Silver zeolites are very efficient for iodine species removal at high off-gas temperatures and are able to adsorb iodine to 500°C and retain iodine to 1000°C. However, when off-gases are treated at ambient conditions, the efficacy of AgX for the organic iodides, as represented by CH_3I, is severely reduced by the presence of water vapor. For example, at 25°C, the DFs for I_2 and CH_3I were 10^4 for dry air with loading of $\sim$50 mg I_2/g

AgX. However, the introduction of H_2O to 90% relative humidity resulted in a severe reduction in the DF for CH_3I to $\sim$20. The DF for I_2 is much less affected by H_2O and can remain at 10^4 with only a small loss in loading capacity. To retain high trapping efficiencies for CH_3I as well as I_2 in the presence of water vapor, it has been necessary to heat AgX beds and the incoming feed gas to as high as 100 to 200°C, at which temperatures the effects of water vapor are negated (and the attraction of CH_3I for AgX is apparently enhanced). In the absence of NO_xs, AgX can be effectively utilized to achieve DFs $\geq 10^4$ for removing CH_3I and I_2 from off-gases heated to 150°C and containing 70% relative humidity. However, only those zeolites which are acid resistant could be expected to withstand prolonged exposure to NO_xs in a humid atmosphere. Silver zeolites have been shown to be effective in reducing the iodine in off-gases to $\leq 10^{-10}$ mg/m^3.

Recent studies have shown that acid-resistant silver mordenites and the Ag-KTB material ($AgNO_3$-impregnated material used in the Federal Republic of Germany for iodine removal from fuel reprocessing off-gases) are able to tolerate 4 to 5% H_2O and 2 to 10% NO_x when the beds are operated in the 100 to 150°C range, while still delivering very acceptable DFs of 10^4. Both sorbents should be capable of processing feed containing I_2 varying from 100 to 10^{-3} ppm. The Ag-KTB material is actually beneficially affected by NO_2, which apparently prevents oxidation of the Ag. The silver mordenite--lead mordenite tandem system (Ag°Z-Pb°Z) compares favorably in all respects to the Ag-KTB and may offer the advantage of a reduction in cost because the Ag°Z bed can be recycled. However, the ultimate application of the Ag°Z-Pb°Z system will be dependent on determining if it can retain CH_3I removal efficiency for high-humidity feed gases. A wide range of organics that might be found in actual off-gas should also be studied to determine how they might affect the DF and loading capacity of both I_2 and CH_3I in the Ag°Z-Pb°Z system. The effects of organics on DF and loading capacity have been well-defined for Ag-KTB.

There have been insufficient studies to allow for the full characterization of the capability of macroreticular resins to remove iodine species from off-gases. Based on the initial studies, the macroreticular resins appear more promising for operation at ambient conditions than for temperatures $\geq 100°C$. For CH_3I feed concentrations of 1×10^3 to 4×10^3 mg/m^3, the best removal efficiency was obtained with Amberlite XAD-12. The loading capacity for a flow rate of 7.65 m/min at 50°C was 84-mg CH_3I/g with a maintained DF of 10^4. However, the feed was bone-dry air; it is therefore likely that with the introduction of H_2O, the loading capacity and DF would decrease considerably (e.g., the I_2 loading for XAD-12 was 1390-mg I_2/g at 25°C and 0% relative humidity, but 60-mg I_2/g resin at 25°C and 60% relative humidity). Generally, the loading capacity and DF for CH_3I of XAD-12 at 25°C and $\sim$0% relative humidity were comparable to the best data obtained for silver zeolites or mordenites under similar operating conditions. However, experiments should have been conducted to determine the interrelated effect of high humidity and high NO_x content on the DFs that could be obtained for CH_3I removal at ambient conditions. No studies have been made with the resin for dilute feeds (<1.0 mg/m^3).

Due in part to the lack of sufficient data for the macroreticular resins, the silver mordenite--lead mordenite system and the Ag-KTB sorbent must be considered more promising than the macroreticular resin because: (1) those sorbents retain their performance for humid feeds if the beds and feed are heated, and (2) those sorbents are less likely to be fouled by organics than are the macroreticular resins. All three systems (silver mordenite--lead mordenite, Ag-KTB material, and macroreticular resins) would appear to have comparable tolerance for high-NO_x concentrations.

Activated charcoal was not considered as a candidate for removing iodine species from nuclear fuel reprocessing off-gases because: (1) it is deleteriously affected by nitrogen oxides (with possible generation of explosive compounds); (2) it desorbs iodine readily at high temperatures; (3) it has a low ignition temperature; (4) it is unsatisfactory as a solid for long-term burial.

Based on the ranges of superficial velocity presented in Table 20 for the sizes of contactors indicated, the acidic solution-scrub processes [Iodox and $Hg(NO_3)_2$-HNO_3] would apparently require considerably larger equipment than would the solid sorbents for treating the same full-scale volumes of off-gases for iodine removal.

In summary, the Iodox system has produced iodine removal DFs that are as good or better than those obtained by any other process used for off-gas treatment. However, there are legitimate concerns about the operational complexity of Iodox, the difficulty in maintaining plumbing integrity in view of the corrosive scrubbing solution employed, and the full-scale process size and the capital costs. These concerns may lead to adoption of either the Ag-KTB sorbent system or the silver mordenite--lead mordenite regenerable system for iodine species removal from fuel reprocessing off-gases. All necessary experiments and complete cost analyses have not been conducted, however, so that a carefully considered selection cannot yet be made.

5.2 Methods for Removing Iodine Species from Dilute Aqueous Solutions

A summary of the principal process parameters and their major effects on the candidate processes for removing iodine species from low-activity-level aqueous and acidic solutions is shown in Table 21. Activated charcoal is a possible candidate for this process, because the operating conditions would be in a wetted phase well-below the ignition temperature. There would still be questions, however, about the ultimate disposal of charcoal that had been in prolonged contact with nitrates. In studies of the candidate processes to remove iodine species from liquids, activated charcoal, macroreticular resins, or silver zeolite, Moore[132] has shown that activated coconut charcoal was the most efficient for removing iodine from a 1×10^{-6} $\underline{M}$ I_2 aqueous feed solution. The DFs for I_2 and the flow rates for each of the three sorbents in 0.4- by 10-cm columns were: (1) 10^4 at 0.15 m/min, activated charcoal; (2) 142 at 0.08 m/min, Amberlite XAD-12; and (3) 33 at 0.016 m/min, silver zeolite. Charcoal has been used to achieve DFs of 10^3 for feeds as low as 10^{-13} $\underline{M}$ I_2. Details of specific studies with the various sorbents are shown in Table 22.

Table 21. Comparison of systems for removing iodine species from low levels in liquid streams

Affecting process variable	System		
	Activated charcoal	Macroreticular resins	Anion exchange resins
Nitric acid solution	Effect of <0.5 M HNO_3 on iodine removal efficiency and loading capacity unknown. Possible explosive hazard for flow disruption, or for HNO_3 >0.5 M.	Little effect on styrene-DVB resins, greatly reduced efficiency of acrylic resins.	Limited experiments have been done, but for the Amberlite exchangers, iodide capacity varied inversely with HNO_3 conc.
Neutral aqueous	DFs for I_2 of 10^4.	Greatly reduced I_2 DF and capacity of styrene-DVB resins; highest I_2 DFs for acrylic resins.	For many anion exchangers, maximum iodide capacity (and DF) are achieved in neutral aqueous solutions.
Iodine species	Molecular I_2 has greater affinity for activated charcoal than ionic species. Ionic species may be highly sorbed on K^+ impregnated charcoals.	Some resins may reduce I_2. Molecular I_2 has greater affinity for macroreticular resins than do the ionic iodine species. Addition of H_2O_2 improved iodine sorption.	Iodine preferentially sorbs to anion exchange resins as I^-, I_3^-, IO_3^-, etc.
Organics	High affinity for charcoal.	Prewashing resins with methanol improved I_2 DF, but other organic contaminants might compete with I_2 for sites.	Most serious for low-pH, mixed-bed operation. Reduces ion exchange capacity. Less serious for strong-base anion exchange resins regenerated with NaCl.
Temperature	Unknown effect on DF. Drying of charcoal after prolonged exposure to HNO_3 would introduce explosion hazard.	Resins should be stable at elevated temperature, but the effect on loading capacity and removal efficiency is unknown.	Normal operating temperature for nuclear reactor coolant cleanup is less than 60°C. Higher temp shortens service life.
Other variables	Charcoal is not a suitable solid for long-term burial.	Poor hydrodynamic properties.	Iodide loading capacity and DF reduced by competing anions OH^-, BO_3^{-3}, PO_4^{-3}.

Table 22. Maximum decontamination factors obtained for iodine species removal from aqueous and dilute acidic streams

Operation	Concentration of iodine species	Flow rate (m/min)	Aqueous solution	Acidic solution	Other components	Column temp (°C)	Loading capacity	DF
Activated charcoal, 0.4 x 10-cm column	1×10^{-6} M I_2	0.15	Yes	NA[a]	None	21	ND[b]	10^4
Macroreticular resins:								
Amberlite XAD-12, 0.4 x 15-cm column	5×10^{-4} M I_2	0.04	Yes	NA	None	21	130 mg I_2/cm^3	160
	1×10^{-6} M I_2	0.017	Yes	NA	None	21	ND	50
XAD-4, 0.4 x 25 cm	5×10^{-4} M I_2	0.04	NA	0.5 M nitric acid	None	21	60 mg I_2/cm^3	14-25
	5×10^{-4} M I_2	0.04	NA	3.0 M nitric acid	None	21	50 mg I_2/cm^3	~ 100
XAD-4, 0.9 x 19 cm	1×10^{-5} M I_2	0.006	NA	0.05 M nitric acid	0.3 M H_2O_2	20	1 mg I_2/cm^3	$>10^2$
Anion exchange resins: Amberlite IRA-910 and IRA-900, Amberlyst A-26, 0.9 x 19 cm	1×10^{-5} M I^-	0.006	NA	0.05 M nitrate	None	20	<0.07 mg I^-/cm^3	>10
	1×10^{-5} M I^-	0.006	NA	0.01 M nitrate	None	20	<0.35 mg I^-/cm^3	>10
Anion exchange resins, 0.6 to 2.4 m ID x 0.9 to 1.8-m deep beds. PWR and BWR coolant cleanup	10^{-19} to 10^{-11} M $^{131}I^-$	0.04 to 2.0		Aqueous for BWR; pH varies from 4 to 10.0, may contain from 0.01 to 0.05 M H_3BO_3 in PWRs.	No additives for BWR; PWR coolant contains hydrazine, hydrogen, ^7LiOH, H_3BO_3, Na_2HPO_4; BO_3^- reduces life and capacity of resins; other trace radionuclides also present.	<60	63 to 254 mg I^-/g dry resin	$\sim 10^2$

[a] NA, not applicable.

[b] ND, not determined, but $\sim$100 mg I_2/g for batch distribution.

The manner in which the iodine disproportionates is very critical for all the candidate processes used to treat iodine bearing solution. Because of the nature of their chemical structure, the macroreticular resins have the greatest affinity for molecular compounds, so they would most probably have a greater capacity for organic iodides and molecular iodine than for ionic iodine. Swanson[136] has reported that the loading capacity of resins for I_2 from very dilute acidic solutions can be enhanced by the addition of oxidants such as H_2O_2 and ferric ion to counteract reductant effects on I_2 resulting from the acidic solution interactions with the resin structure. The capacity of activated charcoal for iodine as molecular I_2 or in ionic form is apparently strongly dependent on the degree of hydrolysis of iodine in dilute solutions; it also depends on the metal content (primarily as K^+) of the native and/or impregnated charcoals. In general, charcoal and macroreticular resins have shown comparable loading capacities for I_2 in the 50 to 100 mg/g sorbent range. However, loading capacities are very dependent on flow conditions and thus on the level of DF that is to be established and maintained (capacity increases as DF is allowed to decrease). Of the two sorbents, charcoal and macroreticular resins, charcoal would appear to be preferable in terms of DF and loading capacity delivered for a given flow rate, and also for the capability of maintaining high DFs as flow rates increase (thus effectively reducing contactor size relative to that required for macroreticular resins). A valid question may concern storage capabilities of both kinds of sorbents, particularly as related to their ability to retain sorbed iodine at higher temperatures.

The most promising method for iodine species removal from aqueous and dilute acidic nitrate liquors may well be (from a mechanistic standpoint) the utilization of anion exchange resins. These resins would be employed after the waste solution had been treated to ensure that all the iodine was in the ionic form. Anion exchange resins are widely used in the nuclear power industry to remove radionuclides from reactor coolants, condensates, and dischargeable plant liquor wastes. They are capable of treating waste streams with iodine concentrations ranging from 10^{-5} to 10^{-19} $\underline{M}$ I^-, while delivering DFs of 100 at temperatures to 60°C. The DF for I^- on these resins can be deleteriously affected by other anions (such as BO_3^{-3} and PO_4^{-3}), and also by prolonged exposure to organic-laden solutions. However, a distinct argument for the anion exchanger beds is the long and favorable operating experience gained with their use in the nuclear power industry in a great variety of flow conditions.

Because of the chemical composition and pH ranges which are expected for low-level radwaste liquid streams, it is highly probable that iodine will exist in both elemental and anionic forms. Thus the best approach for removal of total iodine may ultimately be to utilize a bed of mixed sorbents having strong affinity and high loading capacity for both elemental and anionic iodine.

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APPENDIX A: CONCENTRATIONS OF IODINE SPECIES EXPECTED IN LWR FUEL REPROCESSING DISSOLVER OFF-GASES AND LOW-LEVEL LIQUID WASTE STREAMS

A-1. Dissolver Off-Gas Concentration

In this literature survey, several different estimates of the concentration of I_2, I^-, and CH_3I to be expected in dissolver off-gas were encountered. Although there was certainly some disagreement in the estimates of different investigations, the overall comparison of the various estimated levels was fairly good. The estimates of the different experiments are shown below:

Study	Ref.	Head-end dissolver off-gas	Secondary iodine removal
D. Crouse et al.	38	45 ppm I_2, 14 ppm CH_3I	
D. Crouse et al.	39		0.045 ppm I_2
W. E. Davis	4	6 ppm I_2	
B. A. Hannaford	16-20	25 ppm I_2 50 ppm CH_3I	
J. G. Wilhelm	97	13-40 ppm I_2 10-20 ppm CH_3I	
L. P. Murphy et al.	105	36 ppm I_2	

A-2. Low-Level Liquid Waste Stream Concentration

Calculations are based on 20-gpm effluent from a standard large-scale LWR fuel reprocessing plant: DF of 10,000 for I_2.

1.0×10^{-8} $\underline{M}$ in I_2.

Conversion of iodine species concentration can be made utilizing the following factors (based on 1 m^3 at 21°C and 1 atm):

$$\frac{1\ \mu g\ CH_3I}{m^3} = 0.17\ ppb,$$

$$\frac{1\ \mu g\ I^-}{m^3} = 0.19\ ppb,$$

$$\frac{1\ \mu g\ I_2}{m^3} = 0.095\ ppb.$$

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