DOCUMENT NO.	RHO-CD-1400
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C. J. Evoniuk

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Document Number RHO-CD-1400

Issue Approval:

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3/26/81

Date

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Concurring Approval

3/27/81

Date

W. B. Barton for GR Wilson

Concurring Approval

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A-6000-054 (R-7-79)

RHO-CD-1400

PUREX PLANT GASEOUS IODINE 129 CONTROL CAPABILITY AND PROCESS DEVELOPMENT REQUIREMENTS

C. J. Evoniuk

January 1981

EXECUTIVE SUMMARY

Based on historical evidence, the current Purex Plant iodine control system appears capable of meeting the goal of limiting gaseous iodine-129 emissions at the point of discharge to levels stipulated by the Department of Energy (DOE) for an uncontrolled area. Expected decontamination factors (DF's) with the current system will average about 100 and will be above the calculated DF's of 2.2 and 87 required to meet DOE yearly average concentration limits for controlled and uncontrolled areas respectively, but below the calculated DF of 352 required for meeting the proposed Environmental Protection Agency (EPA) mass emission limit. Chemical costs for maintaining compliance with the DOE limits will be approximately $166 per metric ton of fuel processed (based on a silver nitrate price of $12.38/oz). Costs will increase in proportion to increases in silver prices.

The expected DF's for Iodine-129 are based on limited historical plant data for controlling Iodine-131 emissions. Differences between DF's for ^{129}I and ^{131}I can be expected due to the short half life of ^{131}I and the occurrence of isotopic exchange. Therefore, laboratory studies are being directed to provide data for evaluation of alternatives or modifications to the present system. Modification or alternatives may be needed in the event any of the following occur:

- The stability of the absorbed iodine and/or the performance of the silver reactors is less than expected.
- Operating costs for the silver reactors increase significantly.
- The emission averaging period changes from a yearly basis to an actual operating time basis. This would require that the overall Iodine-129 DF's be increased from 87 to 177.
- EPA's emission limits are imposed on Purex and N-reactor operations.
- A criteria is developed requiring that the iodine in the silver reactor and the iodine recovered in the solvent wash cycle be removed and immobilized for long-term storage. The current practice is to bury the silver reactor without removing the iodine and to dispose the iodine from the solvent wash to tank farms.

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INTRODUCTION

This report provides current information on the Iodine-129 emission limits, the capability of the Purex Plant to control the emissions, and alternative control technologies. Information in the report is organized into the following major areas:

1. The basis for controlling Iodine-129 and the expected emission limits to which Purex Operations will have to comply.
2. A description of the current iodine control equipment, how it worked for Iodine-131 and what its predicted performance for Iodine-129 may be.
3. Current Laboratory studies on the behavior of iodine in the Purex Process.
4. Alternatives for improving iodine control.
5. Recommendations for studies in the area of Iodine-129 control.

Historical Background on Iodine-129 Emissions

Iodine-129 is a radionuclide fission product of nuclear reactor fuel. It is a relatively weak radiation source having a specific activity of 1.63×10^{-4} Ci/gram and maximum particle radiation energies of .15 MEV for β and .04 MEV for γ radiation. Concern over the release of Iodine-129 to the environment stems from its relatively long half-life of 1.7×10^{7} years and the possible long term health hazard it may have on the public.

Possible release points of Iodine-129 from the nuclear fuel cycle to the environment are shown in Figure 1. The point which has the greatest potential of releasing iodine to the environment is the fuel reprocessing plant.

Studies were performed from 1964 to 1969 to determine the amount of Iodine-129 present in the environment relative to natural Iodine-127 (Reference 1). Figures 2 and 3 taken from Reference 1 show the average number of Iodine-129 atoms per 10^{9} atoms of Iodine-127 in bovine thyroids found in the United States and Washington State, respectively.

The IAEA-SM-180/34 report (Reference 1) addressed the problem of Iodine-129 in the environment and came to the following conclusion:

> "The current levels of ^{129}I in the environment throughout the United States are higher than can be explained by natural processes and are the result of man-produced ^{129}I being released to the environment. The areas adjacent to the AEC reservations at Hanford, Washington and Savannah River, South Carolina were found to contain levels of ^{129}I higher than found in most other areas of the United States. Above background levels of ^{129}I also exist in the environment of the nuclear fuel reprocessing plant at West Valley, New York. The radiation doses to human thyroids projected from this study are 0.4 mrem/yr in the vicinity of the Hanford Reservation and 3×10^{-4} mrem/yr in the Olympic Peninsula in Western Washington. Such doses are substantially below established limits and are insignificant in comparison to the 100 mrem or more the thyroid receives each year from natural radiation."

Though the radiation doses from ^{129}I are small the concern over long-term effects of accumulated radiation dosages from different sources has led to a policy of limiting emissions of ^{129}I.

Emission Limits for Iodine 129

Based on the premise that any ingested iodine would become concentrated in the thyroid, The Department of Energy (DOE) recommended the guidelines shown in Table 1 for ^{129}I emissions. Recently the Environmental Protection Agency has set forth an additional emission limit of 5 millicuries of ^{129}I per gigawatt-year of electric power produced from Nuclear Power Operations (Dcoument 40 CFR 190 effective December 1, 1979). At the present time the EPA limit is not applied to reprocessing materials for national defense, however, the limit might be imposed on future operations.

Application of the gaseous and liquid emission limits to Purex Operations are defined by the following statements (Reference 2 and 3). "Beginning with the site boundary and moving in towards the point of discharge the following criteria is to be applied:

a) At the site boundary both liquid and gaseous effluents must meet Table II limits;

b) Within a restricted area the radionuclide concentrations must meet Table I limits;

c) The design objective of meeting Table II limits at the point of discharge is a goal.

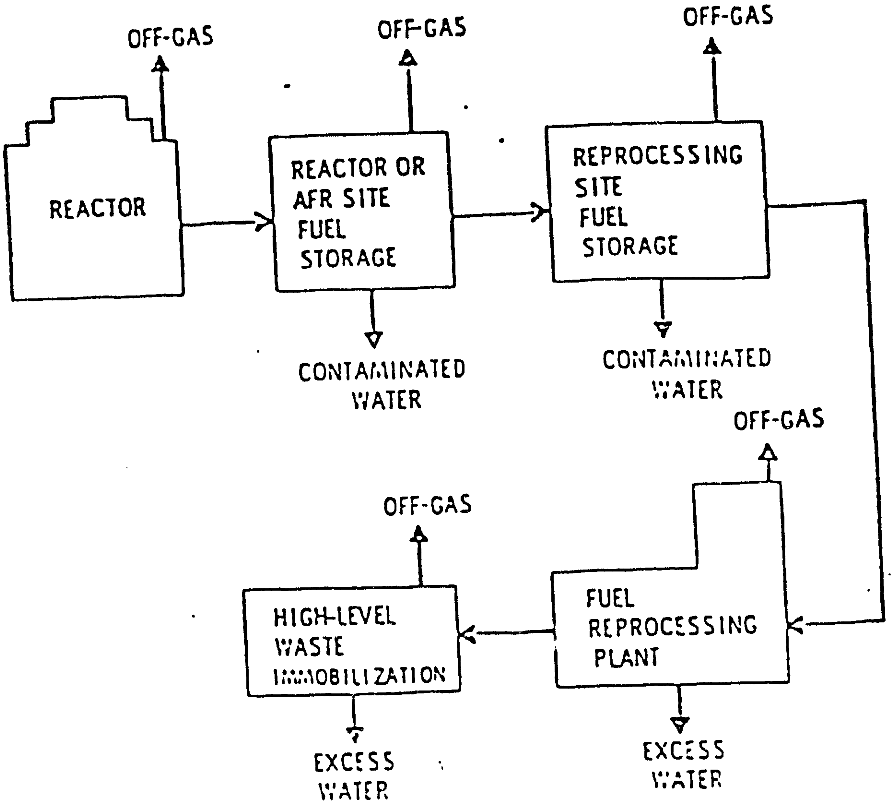


FIGURE 1. Release Points for Iodine

FIG. 2 Average ratio by states of ^{129}I atoms per 10^9 atoms of ^{127}I in bovine thyroids collected between 1964 and 1969. (From IAEA-SM-180/34)

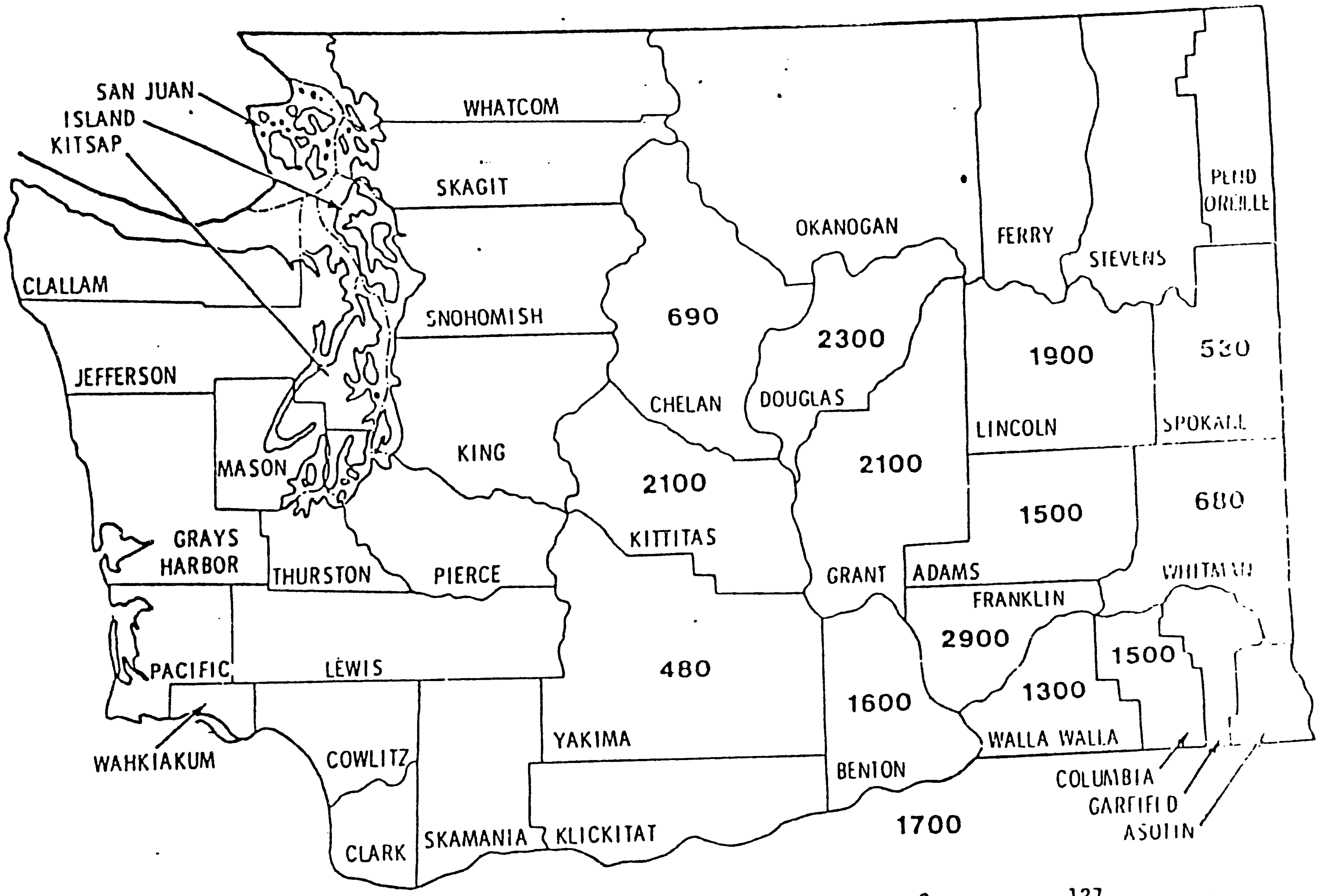


FIG. 3 Average ratio by Eastern Washington counties of ^{129}I atoms per 10^9 atoms of ^{127}I in bovine thyroids collected between 1964 and 1966. (From IAEA-SM-180/34)

New facilities should be designed with the objective of meeting Table II limits. The operational objective for old facilities should also be Table II limits, however, the As Low As Reasonably Achievable (ALARA) concept must be applied to ensure that meeting these limits is in fact reasonable. If it is not reasonable to meet these limits then the mandated goals of meeting Table I within the restricted area and Table II at the area boundary become the limiting bases.
(Note, Table I and II mentioned in the statements refer to DOE Manual Chapter 0524 Appendix A, Standards for Radiation Protection.)

Based on the DOE guideline, the EPA limit, and the quantities of ^{129}I present in the fuels to be processed at Purex (shown in Table 2), the required DF's (Decontamination Factor = amount in/amount out) were determined for controlling ^{129}I emissions from the Purex Plant. The DF's which are shown in Table 3 were calculated under the following assumptions:

a) The stack gas flow rate is 100,000 scfm (4.078×10^{12} ml/day).

b) The 12% Pu-240 fuel contains 2.6×10^{-3} Ci of I-129 per metric ton and the 6% Pu-240 fuel contains 1.3×10^{-3} Ci I-129 per metric ton of fuel.

c) N-reactor generates 0.51 gigawatt-yr of energy with 346 metric tons of fuel;

d) Stack gases are diluted by a factor of 1000 by the time they reach ground level. This is based on conservative engineering calculations.

e) Purex will be reprocessing 1000 MT's of 12% Pu-240 fuel or 2000 MT's of 6% Pu-240 fuel per year. Actual reprocessing rates for 6% Pu-240 may be 1000 MT's/yr or less. However worst case analysis is based on 1000 MT's/yr of 12% Pu-240 (equivalent to 2000 MT/yr of 6% Pu-240).

In Table 3 the DF required under the EPA limit is constant for all conditions because the limit is associated with the electrical output produced by the fuel which is predetermined by the reactor efficiency. The DOE limit is on a time average concentration basis therefore the required DF's are affected by the averaging time period and the concentration of the ^{129} I coming out of the stack. If the averaging time was reduced to a value corresponding to the actual operating time, or the reprocessing rate doubled, the DOE required DF's would then be proportionally increased. The current interpretation of the DOE limit is that they be based on a yearly time average.

TABLE 1

IODINE-129 CONCENTRATION GUIDELINES FROM DOE MANUAL CHAPTER 0524

		Table I Controlled Area		Table II Uncontrolled Area	
		Air Ci/ml	Water Ci/ml	Air Ci/ml	Water Ci/ml
Iodine-129	Soluble*	8×10^{-10}	5×10^{-5}	2×10^{-11}	6×10^{-8}
	Insoluble	7×10^{-8}	6×10^{-3}	2×10^{-9}	2×10^{-4}

---

* In the derivation of the concentration guides for soluble forms of iodine in Table I, a 2 gram thyroid (infants) and daily intakes of 3×10^6 ml of air and 1×10^3 ml of water (fluid water plus water contents of foods was assumed).

TABLE 2

IODINE-129 FISSON ACTIVITY IN THE FUELS TO BE PROCESSED CURIES/METRIC TON

240 Pu %	12		9		6
Fuel 235 U Enrichment % Exposure MWd/T, MW/T	Mark IV .947 2435, 11	Mark IA 1.25 - .947 2903, 11	Mark IV .947 1670	Mark IA 1.25 - .947 2[illegible]	Mark IV 1.25 - .947 1200
Cooling Time	5 years	5 years	5 years	5 years	180 days
I-129 Ci/MT	2.2×10^{-3}	2.6×10^{-3}	1.5×10^{-3}	1.8×10^{-3}	1.01×10^{-3}
grams/MT	13.5	16.0	9.2	11.0	6.2

TABLE 3

DECONTAMINATION FACTORS (DF's) REQUIRED FOR CONTROLLING IODINE-129 EMISSIONS TO DOE AND EPA LIMITS

	DF's For DOE Limits			
	Table I Applied At		Table II Applied At	
	The Stack	Ground Level	The Stack	Ground Level
180 Days Averaging	4.4	*	177	*
365 Days Averaging	2.2	*	87	*
	DF's For EPA Limits			
	352 For All Cases			

* - no DF required

DESCRIPTION OF THE IODINE REMOVAL SYSTEM IN THE PUREX PLANT

Figures 4 and 5 are process flow diagrams of the Purex off-gas system in which silver reactors have been used as the primary means of radioiodine control since startup in 1956. Off-gases from the cladding removal process pass from the dissolver through a down-draft condenser to a knockout pot and then to the in-cell ammonia scrubber. The residual gas from the ammonia scrubber is routed to the steam off-gas heater, then to the electrical off-gas heater and the silver reactor. The off-gas is heated to 380°F prior to entering the silver reactor. After leaving the silver reactor the off-gas passes through two glass fiber filters and then to the ventilation stack. Off-gases from the dissolution of uranium follow the same path with the exception that the ammonia scrubber is not operated during uranium metal dissolution, and the gases are routed to the stack through the acid absorber and scrubber.

The Purex nitric acid recovery and iodine back-up facility, was put in service during 1957. The 293-A Building contains the 8-tray acid absorber and a caustic scrubber together with supplementary equipment. Valving is provided to permit dissolver off-gases to bypass the acid abosorber and caustic scrubber on their way to the ventilation stack. Shortly after the acid and iodine absorbers were put in service, Purex laboratory data indicated that greater than 90 percent of the radioiodine entering the acid absorber was retained in the recovered acid. Since the caustic scrubber removed so little iodine and presented waste disposal and operating problems, it was converted to an acid absorber in April 1958, and operated in series with the first absorber.

The other off-gases from the Purex concentrator, condensers, columns, and tanks are routed through a steam off-gas heater and then through the vessel vent silver reactor. The reactor is of the same design as those used in the dissolver cells but is operated at a temperature of 300°F instead of 380°F. After passing through the silver reactor, the gases are routed through an in-cell glass fiber filter, blended with canyon cell ventilation air and then pass through a final filter on their way to the ventilation stack.

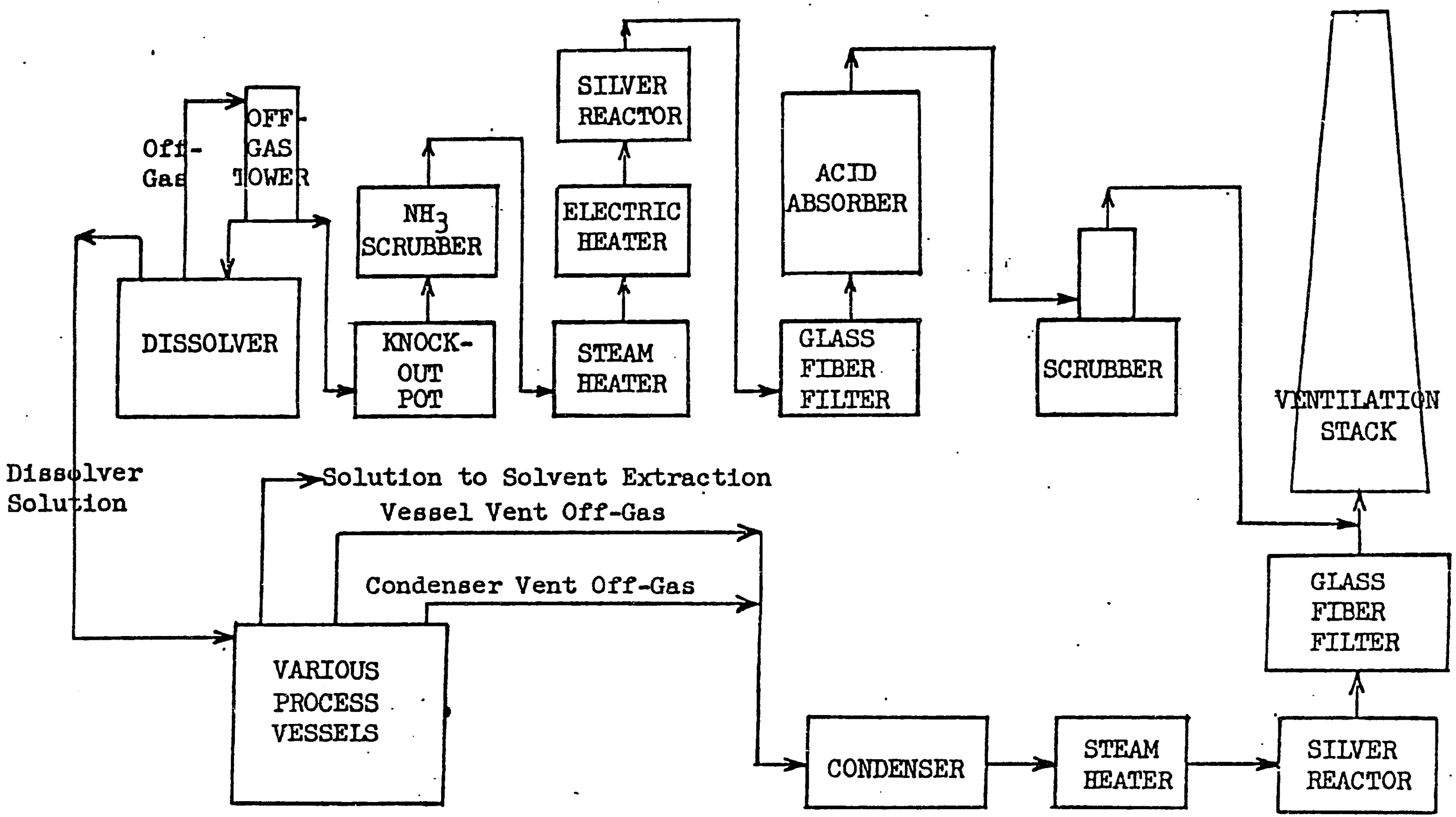
Description of the Silver Reactors

The Purex Plant contains 3 dual bed silver reactors of the type shown in Figure 6 and one older model single bed reactor. The heart of the reactors are the unglazed ceramic Berl Saddles (or Intalox saddles) which have been coated with silver nitrate. Removal of iodine from the gas

FIGURE 4

PUREX PLANT

OFF-GAS PROCESS FLOW DIAGRAM



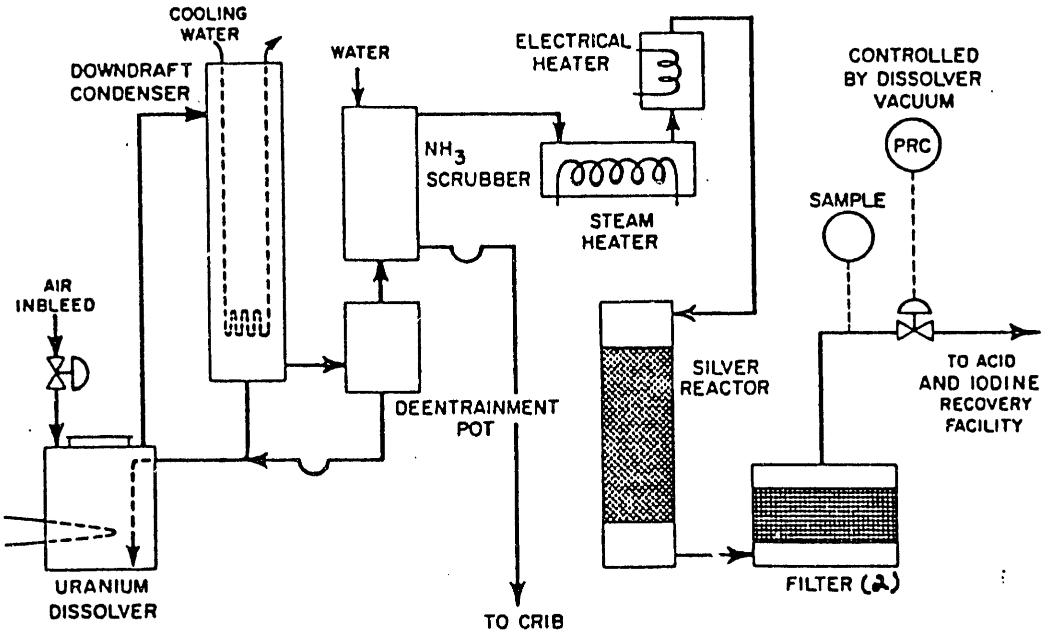


Figure 5. Hanford Purex Dissolver Off-Gas Train

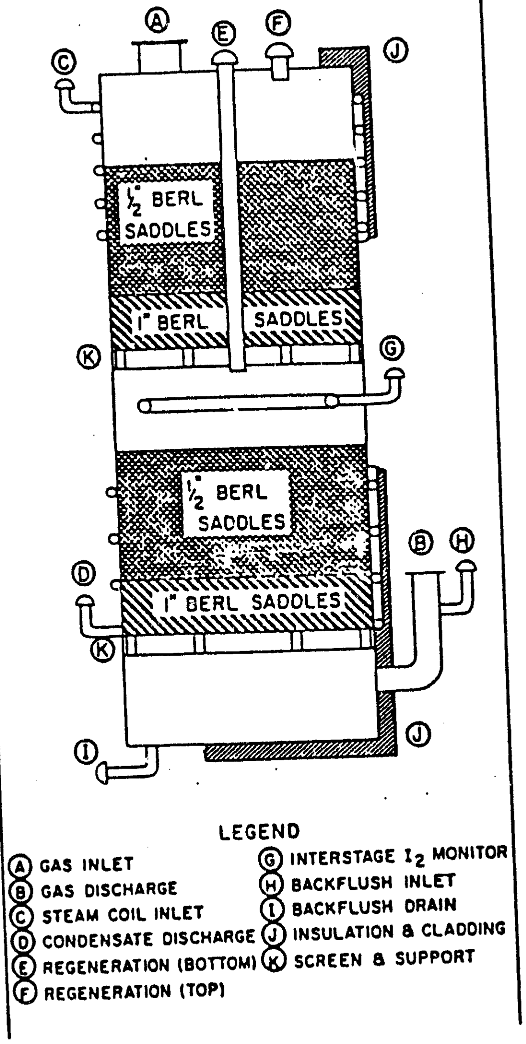


Figure 6. Improved Silver Reactor

which passes through the reactor is performed through the reaction of iodine with silver nitrate to produce nonvolatile silver iodide or silver iodate (References 4 and 5). The bed of saddles provide a fairly large surface area for the gas-solid reaction to occur while maintaining a very low pressure drop across the reactor. The procedure used for coating the unglazed saddles was to put them in a wirebasket, dip the basket in hot (180°F) 5-7 molal silver nitrate solution, swirl the basket in the solution for approximately one minute, remove the basket and allow the saddles to drip dry and then bake them for 4 hours at 220°F. The Berl saddles were satisfactory for reactor packing if they picked up 7-9 pounds of silver nitrate per cubic foot of saddles. Laboratory work indicated that coating of the unglazed Berl saddles in 5-7 molal silver nitrate gave saddles of equal or better quality than those coated in the original 18-24 molal silver nitrate solution.

Regeneration of the Purex Plant silver reactors was scheduled when scintillation type monitors on the off-gas stream indicated an apparent radio-iodine breakthrough. The procedure used for regeneration of the Purex silver reactors was to cool the reactor to 150°F and then spray the packing with 0.3 gallons of 5 molal silver nitrate solution per cubic foot of Berl saddle packing. After baking for four hours at 230°F, the reactor was again cooled and sprayed as before. After the second spraying the reactor was heated to 230°F for six hours and returned to service.

When repeated regenerations (6 to 10) caused excessive differential pressure in the silver reactors, the reactor was replaced or flushed. The flushing consisted of filling the reactor with aqueous 2 $\underline{M}$ sodium thiosulfate and 0.2 $\underline{M}$ sodium hydroxide solution and steam sparged for 24 hours. The flushed solution was removed and the procedure was repeated, after which the unit was thoroughly flushed with water. After drying at 220°F for four hours, the reactor was ready for a normal regeneration.

The average life of a silver reactor varys between 200 and 600 tons of metal dissolved. Work done by McClanahan and Barton plus observations made by Hanson (Reference 4) at Redox indicated that some of the available silver was combining with the ammonia from the aluminum decladding process. An explosion of the A-Cell silver reactor was attributed to flushing of the reactor with an ammonia solution to remove silver salts. After the explosion the flushing of the silver reactors with an ammonia solution was discontinued.

Past Performance of the Dissolver Off-Gas Silver Reactors

Past development data and subsequent plant operation indicated that the silver reactors should remove radio-iodine from the dissolver off-gas streams with an efficiency of at least 99.9 percent (DF = 1000).

The efficiency of new reactors or successfully regenerated units has been measured at greater than 99.99 percent for removal of ^{131}I. The over-all efficiency of the Purex Iodine control facilities was determined on a daily basis, for 1959 and 1960 (Reference 4) by determining the total amount of ^{131}I charged to the Purex dissolvers and the total ^{131}I emitted to the atmosphere. With the 293-A back-up facility in operational as an acid absorber, the overall radio-iodine removal efficiency was between 99.5 and 99.9% (DF's between 200 and 1000) at Purex. A review of these figures indicates that, with few exceptions, periods of high emission (greater than one curie per day) are associated with high radio-iodine inputs to the dissolvers. Periods of high emission have also been repeatedly traced to the inefficiency of the vessel vent silver reactor.

Vessel Vent Silver Reactor Performance

The silver reactor in the Purex vessel vent system has never operated at peak efficiency. This poor performance has been attributed to operating the reactor at 320°F instead of 380°F. Increasing the reactor operating temperature would increase the reactor performance. Economic and safety concerns have prevented modifications to the vessel vent system that would increase the operating temperature of the reactor. The available plant steam for heating the vessel vent gases is at 180 psia and 370°F, and this limits the operating temperature of the vessel vent silver reactor to 320°F. Costly modifications would be necessary to increase the steam temperature and the heat exchanger size for heating the vessel vent gases to 380°F. An alternative is to install an electric heating system. But, this is also expensive and poses a safety hazard. The presence of organic vapors in the vessel vent gases plus a chance spark from a malfunction in the electrical heaters could cause an explosion.

If the temperature of the vessel vent reactor was increased, the over-all DF may increase significantly. Data taken from the Purex Technical Manual showed the following relationship between reactor temperature and the iodine concentration leaving a silver reactor.

Reactor Temperature (°F)	284	320	368	420
Concentration (ppm) of Iodine Leaving the Reactor	1.8	.187	2.42×10^{-3}	4.35×10^{-5}

(Note: the gas entering the reactor was composed of 10% NO_2 and 90% air)

Care should be exercised in use of the data on the exit iodine concentration. Both chemical equilibrium and reaction rates are highly dependent on temperature and on other gaseous components. Exiting iodine concentrations have been noted to be highly dependent on NO_2 concentration and therefore the data presented is applicable only under the stated conditions.

The strong dependency of the iodine exit concentration on temperature indicates either reaction rate or chemical equilibrium is the limiting factor in the absorption of iodine rather than mass transport. If chemical equilibrium is limiting removal, than the concentration of iodine entering the reactor must be greater than the equilibrium exit concentration for absorption to occur. The calculated concentration of iodine entering the dissolver off-gas silver reactor is 2.8 ppm (This is based on off-gas flow of 250 scfm a dissolution rate of 13.9 Kg Uranium/min and a fuel which contains .0165 grams of iodine per kilogram of uranium.). For an inlet concentration of 2.8 ppm and an equilibrium exit concentration of 2.42×10^{-3} ppm the theoretical maximum DF attainable on this stream is 1157.

If 1% of the iodine went to the vessel vent system and was diluted to 9.3×10^{-3} ppm the maximum DF attainable on this stream would be 3.9 (assuming an equilibrium exit concentration of 2.42×10^{-3} ppm). No DF could be attained on the vessel vent system if the equilibrium exit concentration was equal or higher than the entering concentration.

A consequence of an equilibrium controlled absorption process is that material would desorb off the the bed if the inlet concentration fell below the equilibrium concentration. In order to minimize emissions the equilibrium exit concentration and the gas flow rate through the reactor would have to be kept as low as practicable.

If chemical reaction rates were limiting iodine absorption then increased absorption can be achieved through an increase in temperature or an increase in the gas residence time in the reactor. Gas residence time in the reactor could be increased by decreasing the air leakage into the system.

To determine what modification should be done to increase the absorption efficency of the silver reactors, laboratory studies should be conducted to determine the controlling phenomena. Alternatives other than temperature increases may prove more cost effective and have more of an effect under different off-gas conditions.

Service Life and Operating Costs of the Silver Reactors

The useful life of a silver bed reactor is determined by its ability to remove radio-iodine from the dissolver off-gases. The efficiency for removing radio-iodine decreases as the silver nitrate coating on the Berl saddles is converted to silver iodide, silver chloride, or other silver compounds formed by reaction with the dissolver off-gases.

Low-melting eutectics such as $AgI-AgNO_3$ are formed which are fluid at normal silver reactor temperatures. Abnormal operation of the reactor at temperatures above the melting point of silver nitrate (414°F) can quickly decrease the efficiency of the reactor by allowing the coating to flow off the packing. Also, successive regenerations can eventually fill the void spaces of the reactor bed with silver salts to the point where the flow of dissolver off-gases is so restricted that operations must be stopped. Plugged reactors can be reclaimed by flushing and regeneration.

A recent analysis of the dissolver silver reactors showed that the material on the Berl saddles was primarily silver chloride (Reference 5). Since silver chloride is more thermodynamically stable than silver iodide, any chloride that would enter the reactors is capable of converting the silver iodide or silver nitrate to silver chloride. Analysis of available chemicals used in the dissolution process indicated that less than 34 grams of chloride per metric ton of fuel would be available for converting the silver reactor material to silver chloride. Assuming that all the chloride is absorbed in the silver reactor, that the fuel contains 19 grams of iodine/MTU, and the silver reactor charge is 250 lbs. of silver nitrate of which 50% is utilized before breakthrough occurred a silver reactor would have to be regenerated after 300 MTU have been processed. Chemical costs for regenerating a reactor would be $166.00/MTU (based on a silver nitrate cost of $12.38/oz. August 1980, Chemical Marketing Report).

The initial DF for iodine-129 with a new or regenerated reactor should be similar to DF's for iodine-131. However, the effective lifetime of a silver reactor for maintaining an iodine-129 DF will be less than that experienced for iodine-131. This is due to iodine-131 decay in the bed (due to its short half life) plus subsequent isotopic exchange occuring to replace the decayed iodine.

Figure 7 shows the increase in iodine-131 DF's as compared to DF's for stable or long half life iodine-129 (Reference 18). The ratio of the DF's is a function of the amount of isotopic exchange taking place and the time an absorber has been in operation. Data on iodine-131 control during past operations indicated that a silver reactor was effective in maintaining DF's of 200 to 1000 during the time 400 to 600 tons of fuel were processed and the reactor was being rejuvenated about every 100 days. The DF for iodine-129 could have been a factor of 7 lower than the DF for iodine-131 at the end of the 100 days. Past laboratory data indicated that the fraction of iodine-131 exchange with iodine from silver iodide coated Berl saddles would be greater than 0.99 (Reference 19). The actual lifetime of a silver reactor for iodine-129 control will have to be determined from further laboratory and engineering studies, and ultimately, from actual plant operations.

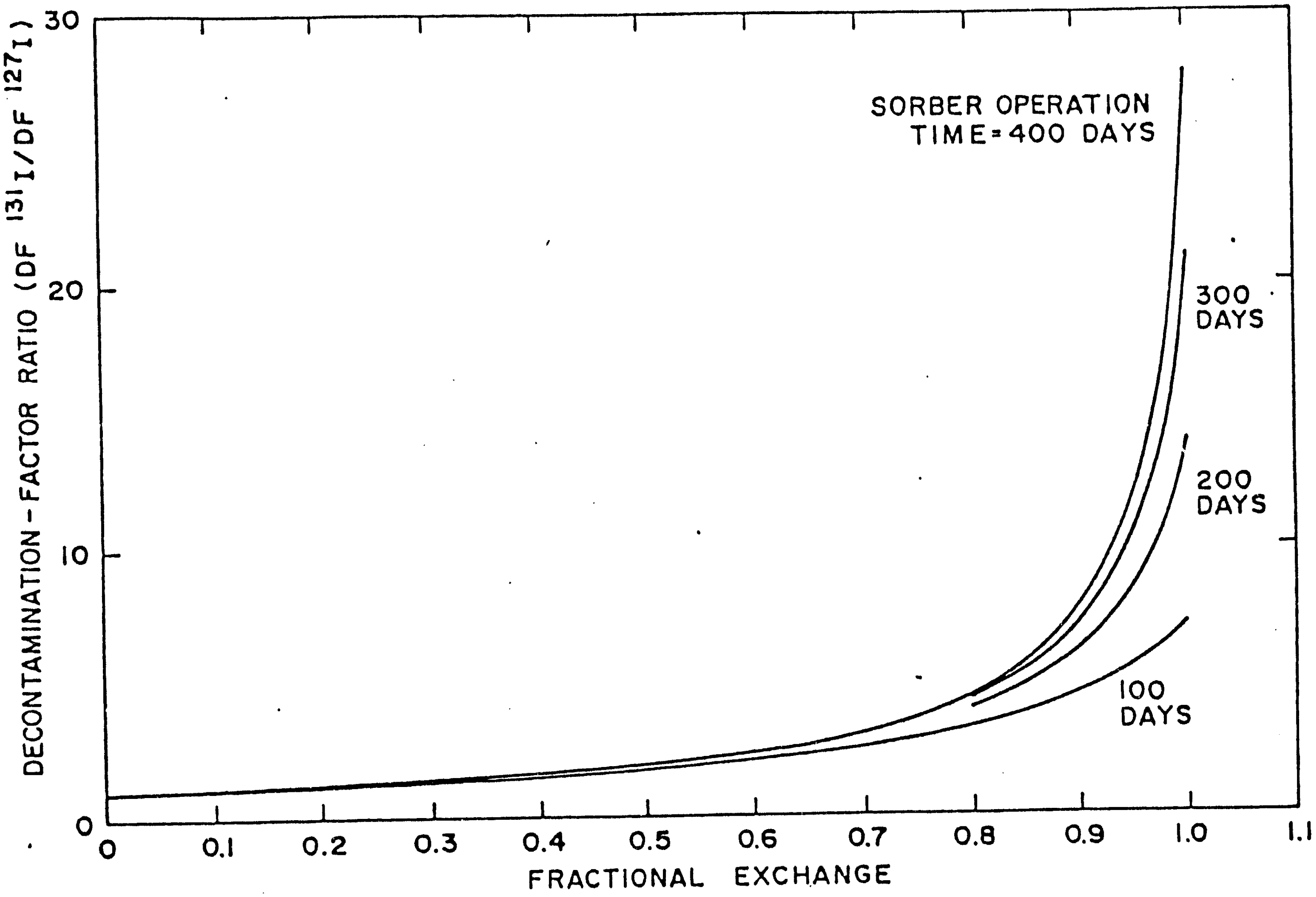


Figure 7. Effects of fractional exchange and time on the ratio DF ^{131}I/DF ^{127}I.
(taken from Reference 18, ORNL 5060)

STUDIES CHARACTERIZING IODINE BEHAVIOR IN THE PUREX PLANT

There are three major reasons for characterizing the behavior of the iodine in the Purex Plant. First, data is necessary to determine the amounts of iodine that are evolved to the dissolver off-gas system and to the vessel vent system. The vessel vent reactor absorbs very little iodine and any iodine entering the system can be assumed to escape to the environment. On the other hand the dissolver off-gas system is believed to absorb greater than 99% of the elemental iodine entering the system. Therefore as much volatile iodine as possible should be evolved to the dissolver off-gas system. If we assume that 99% of the iodine-129 has to be recovered (DF = 100), then less than 1% of the initial iodine can be allowed to escape to the environment.

Second, studies have indicated that the iodine escaping from the plant may be distributed in several chemical forms. Perkins (Reference 10) measured the ratio of organic iodide to inorganic in the stack discharge and found it to very from 0.12:1 to 1.45:1. The quantities of the various iodine species and the ability of the current silver reactor to absorb the various species need to be known in order to evaluate the overall performance of the iodine-129 controls.

Third, estimates on the overall plant capability for iodine-129 control have been derived from past data for iodine-131 control. The estimates for iodine-129 control may be in error due to reasons discussed in the previous section.

Laboratory Studies on Iodine Evolution to the Dissolver Off-Gas System

Pacific Northwest Laboratories (PNL) performed tracer and hot cell studies for determining the amounts of iodine evolved during dissolution of the uranium metal (Reference 6). The hot cell tests with spent N-reactor fuel indicated that approximately 8% of the initial Iodine-129 remained in the dissolver solution, while tracer studies with unirradiated fuel indicated that 10% to 30% of the iodine remained in solution. Additional sparging tests on the dissolver solution with air, nitric oxide (NO), and the addition of hydrogen peroxide to the solution were not effective in reducing the amount of iodine remaining below the 8% level (Reference 7). However, continued sparging with air or NO was effective in reducing the remaining iodine from a 30% level to a 8% to 12% level. The studies with unirradiated fuel also indicated that a significant fraction of the iodine evolved would be recycled back to the dissolver via the down draft condenser.

Behavior of Iodine in the Dissolver Solution

Iodine which remains in the solution is transferred along with the dissolver solution to the uranium and plutonium extraction cycles. During the process of transferring the dissolver solution, a significant fraction of iodine has been noted to evolve to the vessel vent. A study which was performed in 1955 on the effects of process variables on Iodine-131 emissions from the Purex Plant came to the following conclusions (Reference 8):

> "The majority of Iodine-131 emissions are released through the F Cell vessel vent and condenser vent system. The approximate percentages of Iodine-131 released from each of the main off-gas outlets are: 80% through F Cell vessel vent and condenser vent systems; 19% through the dissolver off-gas system; and 1% from U and R Cells vessel vent systems. The primary sources of Iodine-131 emissions into the F Cell vessel vent and condenser vent systems are solutions being transferred by jet and centrifuged in head-end. Also, overheating (140°F) the metal solutions in F Cell has resulted in Iodine-131 evolutions. The No. 1 solvent recovery system (G Cell), however, has never been known to cause Iodine-131 emissions."

The iodine remaining in the dissolver solution will be extracted into the organic solvent and remain there until the solvent treatment cycle (Reference 8). In the solvent treatment cycle most of the iodine is scrubbed out of the solvent and sent with the solvent wash waste to the waste storage tanks. Any iodine that is not removed in the solvent wash is recycled to the extraction process with the solvent. Both the amount of iodide recycled with the solvent through the process and the amount evolved to the vessel vent system are unknown and are currently being investigated.

In past Purex Plant operations mercuric nitrate was successfully used to reduce the radio-iodine emitted from the vessel vent system. Mercuric nitrate was routinely added to the metal solution from the dissolvers after transfer of the metal to solution storage tanks. A concentration of 0.0005 $\underline{M}$ Hg^{++} in the solution of short-cooled metal (less than 120 days cooling) suppressed the evolution of radio-iodine to the vessel vent off-gases so that the total radio-iodine emitted from the Purex Plant was reduced by a factor of two to four. The cost effectiveness of using mercury to suppress iodine emission as compared to alternatives has not been fully explored. Mercury is known to cause problems in the area of waste management and from this standpoint it is undesirable to add it to the process solutions.

Behavior of the Organic Iodides

Laboratory data suggests that if the methyl iodide (which was one of the organic iodides found in the stack discharge) is passed over the silver reactor material or is present with NO_x and water vapor, decomposition of the organic iodide to form elemental iodine and organic products will occur (References 11, 12, 13 and 14). Tests showed that in a contact time of 1.5 seconds and at temperatures of 212°F to 302°F, 30% to 50% of the methyl iodide (original concentration equal to 1000 ppm) was recovered by a bed of silver nitrate coated Berl saddles. At 374°F, 95% of the methyl iodide decomposed upon contact with the bed and the decomposition products were CH_3ONO_2 and I_2. However, essentially all of the I_2 produced during the decomposition at 374°F passed through the bed unrecovered. It appeared that at lower temperatures the CH_3I decomposed less efficiently, but a more favorable loading of iodine from decomposed CH_3I was obtained. A preliminary test was conducted to evaluate the iodine recovery efficiency of $AgNO_3$ coated Berl saddles exposed to CH_3I, NO_x and H_2O at 378°F. The results indicated that at this temperature and in the presence of the other gases, the CH_3I decomposed prior to exposure to the bed of material and none of the iodine was absorbed.

Other studies performed with the gas mixture alone in a glass vessel indicated that the time required to decompose 30% to 40% of the methyl iodide at 302°F would be on the order of 20 to 30 minutes. From this result it would appear that in the other studies the decomposition reaction was accelerated by the silver nitrate and/or by other materials used in the packed bed studies. Further laboratory studies will be required to clarify these results, if organic iodides prove to be an emission problem.

ALTERNATIVE IODINE-129 CONTROL PROCESSES

A literature survey was conducted by Halladay (Reference 16) on the status of current processes for controlling Iodine-129 emissions. The candidates for off-gas treatment included: two acid-scrub processes, the 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 German manufactured material (Reference 17) Ag KTB or AC-6120 consisting of an $AgNO_3$-substitued 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. The process characteristics of the treatment processes are summarized in Tables 4 and 5.

Of the processes described the silver mordenite and Ag-KTB solid sorbents have the greatest potential for absorbing inorganic and organic iodides and for being substituted for the Purex silver nitrate coated Berl saddles. The cost of using these materials or their performance in Purex type conditions (high NO_x concentrations and low iodine concentrations) has not been determined. Preliminary analysis of the sorbents indicates that their performance is in part related to their small particle size and subsequent high exposed surface area. One drawback of the small size materials would be the high pressure drop they would create across the reactor. However, the required cost of adding more steam jets and other modifications may be less than the savings realized by using these materials.

If iodine recovery is strongly affected by surface area, then it may be possible to reduce the size of the silver reactor packing and still use a silver nitrate coating without increasing the pressure drop significantly.

An analysis of the data in Table 5 indicates that the high DF's provided by the solid sorbents are associated with high input iodine concentrations and/or the absence of high NO_x concentration in the test gases. The Purex dissolver off-gas contains low iodine concentrations ($\sim$ 2 ppm) and high NO_x concentrations (20% to 30%). Therefore the sorbent (like AC-6120) may not be able to provide any higher DF's under these conditions than the current silver reactors. This would be especially true if in the tests the reaction between the iodine and silver reached chemical equilibrum before the gas stream left the sorbent test bed. In which case, the alternative is to either reduce the amount of gas diluting the iodine or use a counter current scrubbing process where mass transfer or reaction rate is controlling absorption.

Table 4

Comparison of Systems for Trapping Iodine Species from Gaseous Streams (from Reference 16)

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 hyperazeotropic 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

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[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 5

Maximum Decontamination Factors Obtained for Iodine Species Removal (from Reference 16)

Operation	Concentration of iodine species: I_2 (mg/m³)	Concentration of iodine species: CH_3I (mg/m³)	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]
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	5×10^5	ND
		264 (44 ppm)	98 slm (1.2 m/min)	None	7.6	1.9	Plate 1 - 26 Plate 6 - 27	~21	ND	3.2×10^5	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	5×10^4	No effect of octane, dodecane; xylene, diethylbenzene reduced DFs to 100
		60 (7 ppm)	2.5 slm (5 m/min)		N_2O_3 @ 0.4	ND	25	~25	ND	8×10^4	
Silver zeolite[b] 2.54 x 5.08-cm beds	500		60 m/min	None	2	5	ND	100	42 mg I_2/g	2×10^2 (breakthrough)	I_2 and CH_3I loading not affected by O_2, CO_2, N_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	2×10^5	
		~816	19 m/min	None	None	2.3	~200	200	76 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/H1)[c] $AgNO_3$ impregnated amorphous silicic acid, 2.34 x 10-cm beds	6000 (~180 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	$>10^3$	
		1×10^3 to 4×10^3	7.65 m/min	None	None	0	25	25	12 mg CH_3I/g	$>10^2$	

[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 following alternatives could also be implemented to increase the performance of the Purex Iodine control system.

1) Route the vapors from the initial solution transfer steps to the dissolver off-gas silver reactor. This would reduce iodine emissions to the vessel vent system.

2) Add mercury to the dissolver solution to reduce iodide evolution to the vessel vent system.

3) Increase the operating temperature of the vessel vent silver reactor to increase the iodine absorption rate and/or to decrease the iodine equilibrium concentration leaving the reactor.

4) Install a sorbent bed to trap the chloride before it reaches the silver reactor. This would extend the life of the silver reactors.

The need and applicability of any of the processes or improvements described will depend heavily on the iodine emission limits, their interpretation and on a cost benefit analysis. In addition a criteria for long-term storage of Iodine-129 could change the overall economics and cost benefit analysis of any recovery process.

CONCLUSIONS

The guidelines for iodine-129 emission limits for the Purex Plant is the Department of Energy's (DOE) manual chapter 0524 "Standards for Radiation Protection". To be in compliance with the guidelines the yearly average concentration of iodine-129 being emitted from the point of discharge (Purex stack) must be less than or equal to 8×10^{-10} Ci/ml for a controlled area (Table I) and 2×10^{-11} Ci/ml for an uncontrolled area (Table II). The Environmental Protection Agency (EPA) has also set forth an emission limit of 5 millicuries of iodine-129 per gigawatt-year of electrical power produced from nuclear power operations. At the present time the EPA limit is not applied to reprocessing materials for national defense. However, the limit might be imposed on future operations.

Based on reprocessing 1000 metric tons of fuel a year which contains 2.6×10^{-3} Ci of iodine-129 per metric ton, the Purex Plant will have to provide decontamination factors (DF) of 2.2 and 87 for meeting the emission limits for a controlled and uncontrolled area respectively.

Data from past Purex operations indicate that overall DF's of 100 for iodine-131 were routinely achieved with the current silver reactors which were used to absorb the iodine. The reactors were recharged approximately after every 100 days of operation. The useful life or the time period between recharging of the silver reactors might be less for controlling iodine-129 emissions. This is due to iodine-131 having a much shorter half life than iodine-129 and isotopic exchange taking place to replace the decayed iodine-131.

Laboratory analysis of the material in the silver reactors has shown that most of the silver material has been converted to silver chloride. The source of the chloride is unknown but the most plausible source is from the chemicals added to the dissolver solution. Based on estimates of the chloride content of the chemicals and the utilization of the silver in the silver reactors, the cost of maintaining a DF of 100 for iodine-129 is approximately $160 per metric ton of fuel processed. This cost is based on the price of the silver nitrate used to recharge the silver reactors.

The data on the Purex plant iodine control capability is primarily limited to iodine-131 control and there are uncertainties in extrapolating the data for evaluating the plants capability for iodine-129 control. A number of laboratory investigations are being undertaken to characterize and understand the behavior of the iodine in the plant. The amount (mass) of iodine-129 in the fuel to be processed is much greater than the amount of iodine-131 present. For short cooled fuel the radiation levels for iodine-131 are higher than for iodine-129, however, the mass of iodine-129 present is still greater than that for iodine-131.

Laboratory tests have shown that 10% to 30% of the iodine in the fuel remains in the solution of dissolved fuel. The iodine remaining in the dissolved fuel solution is thought to be the major source for the iodine emissions. Laboratory studies are underway to characterize the behavior of this iodine and to determine effective methods of removing it from the solution.

In addition studies are being performed to determine the limiting factors for removing the various iodine species evolved to the process off-gas with the existing silver reactors. Alternatives for iodine control are being studied in order to provide a means to control the emissions if the present equipment proves to be inadequate for current or future emission requirements.

RECOMMENDATIONS

The engineering and laboratory studies needed to develop technology for meeting Iodine-129 emission limits and improve process performance are as follows:

1) Determine the capability of the silver reactors to absorb organic iodides and inorganic iodides from different gas compositions. Determine if the removal process is mass transfer limited, reaction limited or thermodynamically limited.

2) Determine the stability of the absorbed iodine under expected Purex process gas compositions.

3) Determine how much iodide is evolved to the vessel vent system.

4) Determine how to enhance iodine evolution from the dissolver solution.

5) Determine the feasibility of increasing the operating temperature of the vessel vent silver reactor; and/or routing off-gases from the first dissolver solution transfer to the dissolver off-gas system and/or adding mercury to the dissolver solution.

6) Determine the source and long-term impact of the chloride which converted the silver reactor material to silver chloride and determine methods of preventing the chloride poisioning.

7) Determine the quantities of the different iodine species in the off-gases.

8) Test alternative sorbent material for iodine control.

9) Determine how to increase iodine removal in the solvent wash cycle.

10) Determine the feasibility and cost of separating and recovering the Iodine-129 for storage or disposal and reusing the silver to regenerate the silver reactors.

11) Determine the effect of regeneration procedures on silver reactor performance.

12) Perform an order of magnitude cost benefit analysis for implementing more stringent iodine controls, including long-term storage of the iodine.

13) Determine the most effective method for disposal and storage of the iodine.

Data gathered from these studies would provide the information needed to evaluate the most reasonable approach for controlling Iodine-129 emissions.

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