DOE/SR/11036--T13

DOE/SR/11036--T13
DE84 025616

DOE/3144/LR-05
Contract DE-AC09-83SR11036

OFF-GAS ALTERNATIVES FOR THE BRET PROJECT

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July 1983

DISCLAIMER

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1.0 INTRODUCTION

The purpose of this study is to review alternate methods of iodine removal to the selected approach presented in the BRET preconceptual design process flowsheets. The Iodox process was selected for removal of iodine from the dissolver off-gas (DOG) in the BRET Flowsheet. In this process, the off-gas is contacted with hyperazeotropic nitric acid in a scrubbing tower. The various iodine species are oxidized to iodic acid, which collects as a solid in the tower bottoms. The iodic acid is subsequently separated from the nitric acid for waste disposal.

Other methods investigated for iodine removal include both solid adsorbers and liquid absorbers. (For a brief summary, see Reference 1.) The AGNS Fuel Reprocessing Plant has installed mercuric nitrate scrubbers for primary iodine removal and silver zeolite beds for final polish.[2]

In this report, two alternate methods for primary iodine removal are evaluated. One system is a caustic scrubber backed by a silver zeolite bed. When the caustic, which also removes CO_2 and some NO_X, is spent, it is transferred to waste disposal. The second system is comprised of two silver zeolite beds in series. When the first bed is loaded, it is removed to waste; the secondary bed is moved to the first position and a new bed is installed in the secondary position. Silver zeolite has excellent adsorption properties for both organic and inorganic iodides. Caustic scrubbing removes inorganic iodides but is not effective for organic iodides. However, the amount of organic iodides in the DOG should be small, so this should not be a deterrent.

The use of silver zeolite for treating the vessel off-gas for iodine removal was also evaluated at the request of ORNL.

Costs were estimated for these systems, including fabrication, replacement, and operation.

2.0 SUMMARY AND CONCLUSIONS

A caustic scrubber and a silver zeolite adsorber systems were evaluated for iodine removal from the BRET DOG. Both systems, backed by a silver zeolite adsorber, could perform the required iodine removal. The I-129 release from the caustic scrubber/AgZ treatment system is conservatively estimated to be 1.64×10^{-4} Ci for one FFTF campaign. For the twin AgZ adsorber system, the release is estimated to be 1.64×10^{-5} Ci per FFTF campaign. The release through the VOG system via one silver zeolite bed is estimated to be 8.63×10^{-5} Ci/FFTF campaign.

For the BRET facility operating on FFTF fuel or FFTF fuel and CRBR fuel, the dissolver off-gas system using two silver zeolite beds is the least expensive. This would not be the case for a larger facility where iodine removal requirements increase the silver zeolite usage significantly.

3.0 PROCESS SYSTEM DESIGN

3.1 Design Bases

- DOG flow to iodine recovery is 9 acfm.*
- Of the iodine in spent fuel, >95% enters the DOG.
- The VOG flow rate is 800 cfm.
- Iodine in the VOG is 5% of the input.
- FFTF fuel, 60,000 MWd/MTHM
  iodine - 550 g/MT or 1.33 kg/core, 411 g/MT I-129
- Silver zeolite capacity 150 mgI/gm zeolite
- Off-gas composition

O_2	-	53.40 w/o
N_2	-	43.21
H_2O	-	1.90
NO	-	1.26
CO_2	-	0.043
I_2	-	0.014
Xe	-	0.164
Kr	-	0.009

3.2 Caustic Scrubber System

The preliminary process design of a caustic scrubber for iodine removal is based on a column packed with Raschig rings with NaOH solution as the absorbent. For Raschig rings of the following parameters:

Size - 0.95 cm dia. x 0.95 cm x 0.04 cm
Specific surface - 518 m^2/m^3
Porosity - 0.81

and 0.7M NaOH solution, a parametric equation for the minimum column diameter (at flooding) is**

$$D_{C(f)} = 1.8 \exp(0.158L^{0.25})$$

where $D_{C(f)}$ is the minimum column diameter at flooding (inches). L is the flow rate of the absorbent in lbs/hr.

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*It is assumed the DOG has been through a condenser and knockout pot prior to iodine recovery.[3]

**This equation is based on the development in Reference 4.

For a flow rate of 220 pounds per hour, $D_{C(f)}$ is approximately 3.5 inches. The optimal column diameter usually is 30 to 40% greater than minimum. Therefore, a five-inch diameter column is of sufficient capacity for the BRET DOG.

Normally, four to six transfer units are required for efficient absorption, assuming no chemical reaction.[5] Obviously, there will be chemical reactions between the iodine species and NaOH which would reduce the number of required transfer units. However, for purposes of design, a range of four to six transfer units was chosen.

Based on the equations developed by Vivian and Whitney[6], $(HTU)_G$ was calculated to be approximately one foot. Therefore, a six-foot column is more than adequate to provide for efficient absorption.

A sketch of an absorption column is shown in Figure 3-1. The column includes the bottom gas inlet section, a top disengaging section, and a cooling jacket. The working section is packed with Raschig rings. A pump tank and metering pump are also included. An alternate design (not shown) includes two tanks, one feed and one receiving.

A cost estimate for the Figure 3-1 design is as follows: (See Section 4-1)

Absorption column plus x-ray	$ 8,500
Pump tank plus x-ray	6,000
Interconnecting piping	200
Metering pump	500
Jets, two	600
LL transmitter and DR	4,000
	$19,800

These costs do not include design, delivery, or installation.

The cost estimate for a two tank system is $30,000. The difference is the second tank and additional instrumentation.

The production rate of liquid waste is controlled by the rate at which NaOH is converted to a salt. This rate is primarily dependent on the amount of NO_2 in the off-gas. The CO_2, if totally absorbed, would require only 414 gm NaOH per day and the iodine even less.

The dry off-gas is shown as being devoid of NO_2; however, it is highly unlikely the NO_2 absorber will remove all the NO_2 from the gas stream. NO does not react with caustic[7]; however, NO_2 reacts as follows:

$$2\ NaOH + 3NO_2 \rightarrow 2NaNO_3 + NO + H_2O$$

For purposes of calculating waste loading, it was assumed that 50% of the NO_x (shown as NO) is converted to $NaNO_3$.

On this basis, a 25-day campaign would result in 13.7 kg Na_2CO_3, 236 kg of $NaNO_3$ and approximately 1.5 kg of NaI. Total NaOH utilized would be approximately 122 kg. This material would be in the form of spent scrubber solution which for purposes of calculation is assumed to be 0.1M NaOH, i.e., scrubber solution is replaced when it reaches 0.1M NaOH.

The volume of liquid waste depends on the initial concentration of NaOH. On the assumption that the amount of NaOH used is 122 kg, the volume of solution, V, is

$$V = \frac{3050.75}{\underline{M} - 0.1}$$

where M is the molarity of the NaOH solution. If the NaOH was 2M initially, the waste volume would be 1605.6 liters, at 1M NaOH waste volume would be 3389.7 liters, etc. If the spent caustic was converted to concrete without further concentration, the number of 55-gallon drums of concrete as a function of caustic molarity is as follows:

NaOH M	No. 55-Gallon Drums
2.0	8
1.3	12
1	16
0.7	23

If the waste was concentrated to 6.2M $NaNO_3$ (the maximum concentration without precipitating $NaNO_3$), the concentrate could be contained in three 55-gallon drums of concrete.

A 55-gallon stainless steel drum with liner is \$500. Deep repository charge is \$4936/drum.(8) Shipping charge is \$1400/load(9) (1000 miles - one way). However, one load can include 30 drums so that the shipping charge to the repository is not a consideration. Thus, the total savings per drum not used is \$5436.

Utilizing a design similar to the AGNS service concentrator, which would be more than adequate for this service, costs are \$26,000 in 1983 dollars. Supporting tankage, piping, and installation would probably double this cost. Even so, it would appear cost effective to concentrate the spent caustic prior to solidification. It is estimated one eight-hour shift would be required for the concentration step. At \$40/hr, the labor cost would be \$320. Labor cost to prepare the drummed waste is estimated to be \$320.

The caustic scrubber would require a back-up iodine removal system. Using a silver zeolite bed as discussed in Section 3.3.1 would be adequate for this service. Assuming the caustic scrubber was 90% efficient, the back-up adsorber would function for 10 FFTF campaigns (or less if CRBR fuel is also reprocessed). Thus, there would be a disposal charge at 10 years or less (~4 if reprocessing one FFTF core and one CRBR core per year).

3.3 Silver Zeolite Systems

3.3.1 Design Criteria

Fully exchanged silver zeolite can adsorb approximately 150 mg per gram of zeolite. The adsorber beds for the DOG system were sized on the basis of iodine content in the off-gas. The adsorber bed for the VOG system was designed to accommodate the volume of gas, the iodine content being incidental.

3.3.2 Dissolver Off-Gas System

The dissolver off-gas system consists of two silver zeolite beds in series. On the assumption that 95% of the iodine in the spent fuel reaches the adsorbers, the input to the beds is 2.2 grams per hour. Sizing the bed to adsorb the iodine in one core of FFTF fuel (1.3 kg of iodine) requires 20 pounds of fully exchanged silver zeolite. Using a nominal 10-inch diameter bed, the bed depth for 20 pounds of packing would be seven inches (assumed packing density of 62.4 lbs/ft^3). The face velocity would be much less than 1 ft/sec.

The secondary bed is the same size as the primary. It serves as the back-up to the primary bed and in turn is moved to the primary position following each reprocessing campaign.

A sketch of the adsorber is shown in Figure 3-2. The adsorber housing is fabricated into the off-gas piping. The cover is flanged for remote disassembly and the piping run from the cover is fitted with a Hanford connector. The basket which contains the silver zeolite is sealed into the housing by means of O-rings.

At the end of a campaign, the flanges and Hanford connectors would be remotely disassembled. The cover and connecting piping would be removed by means of the lifting bale. The primary bed would be transferred to waste disposal, the secondary bed moved to the primary position and a fresh bed placed in the secondary position. The system would then be reassembled for the next campaign.

FFTF fuel irradiated to 60,000 MWd/MTHM contains 4.11×10^2 gms of I-129 per tonne. The specific activity of I-129 is 1.75×15^{-4} Ci/gm so that the activity in a spent bed from one FFTF campaign would be slightly less than 0.17 Ci. The spent bed could be cast in a 55-gallon drum of concrete for disposal. In the event that other fast reactor fuels are available for reprocessing in the BRET facility, the spent silver zeolite could be stored temporarily and the beds from more than one campaign could be cast in one drum of concrete.

It is estimated that eight man-hours would be required for changing beds, and an additional eight hours would be required for waste disposal, i.e., casting into concrete. In addition, there would be shipping charges to the repository and repository changes. Costs are estimated to be:

Labor (16 hrs. @$40/hr)	$ 640
Silver zeolite (20# @ $150/lb)	3000
55-gallon drum	550
Shipping @ $1400/load ÷ 30 drums/load(9)	~50
Repository charge(8)	4936
	$9176

As can be seen, the repository charge is the largest item. If more than one spent bed could be disposed of in a drum, or the spent bed could be consolidated with other waste, considerable savings could result.

3.3.3 Vessel Off-Gas System

The design of a silver zeolite bed for iodine removal from the vessel off-gas is based on a volumetric flow rate of 800 cfm. At this flow rate, face velocity through the bed is the limiting parameter for design purposes. A bed three feet in diameter would have a face velocity of 1.8 ft/sec while a four-foot diameter bed would have the recommended value of 1 ft/sec. A 4-foot bed seems excessive for the BRET project (for space and handling considerations) so the design basis was three feet in diameter.

The sketch of an adsorber bed for the VOG is shown in Figure 3-3. The adsorber is quite similar to that for the DOG, except larger dimensions. An eight-inch bed depth is approximately 300 pounds of silver zeolite. On the assumption that 5% of the input iodine enters the VOG, this would be equivalent to 65 grams per campaign of FFTF fuel. The capacity of a 300-pound bed is 20 kg of iodine, so one adsorber bed could operate for 300 FFTF campaigns before changeout.

As can be seen, waste disposal for the VOG adsorber bed will occur at the end of life of the facility. The housing would be remotely disassembled and the basket removed to waste disposal. The bed would be mixed into three 55-gallon drums of concrete. Each drum would contain approximately 0.085 Ci of I-129.

The cost estimate for the adsorber unit is $8100. The initial charge of silver zeolite would be $45,000. Amortized over the life of the plant this is not an excessive cost.

3.4 Decontamination Factors

The caustic scrubber is assumed to give a decontamination factor of 10 and a silver zeolite adsorber a factor of 100. Both of these decontamination factors are conservative; however, they are used for illustration.

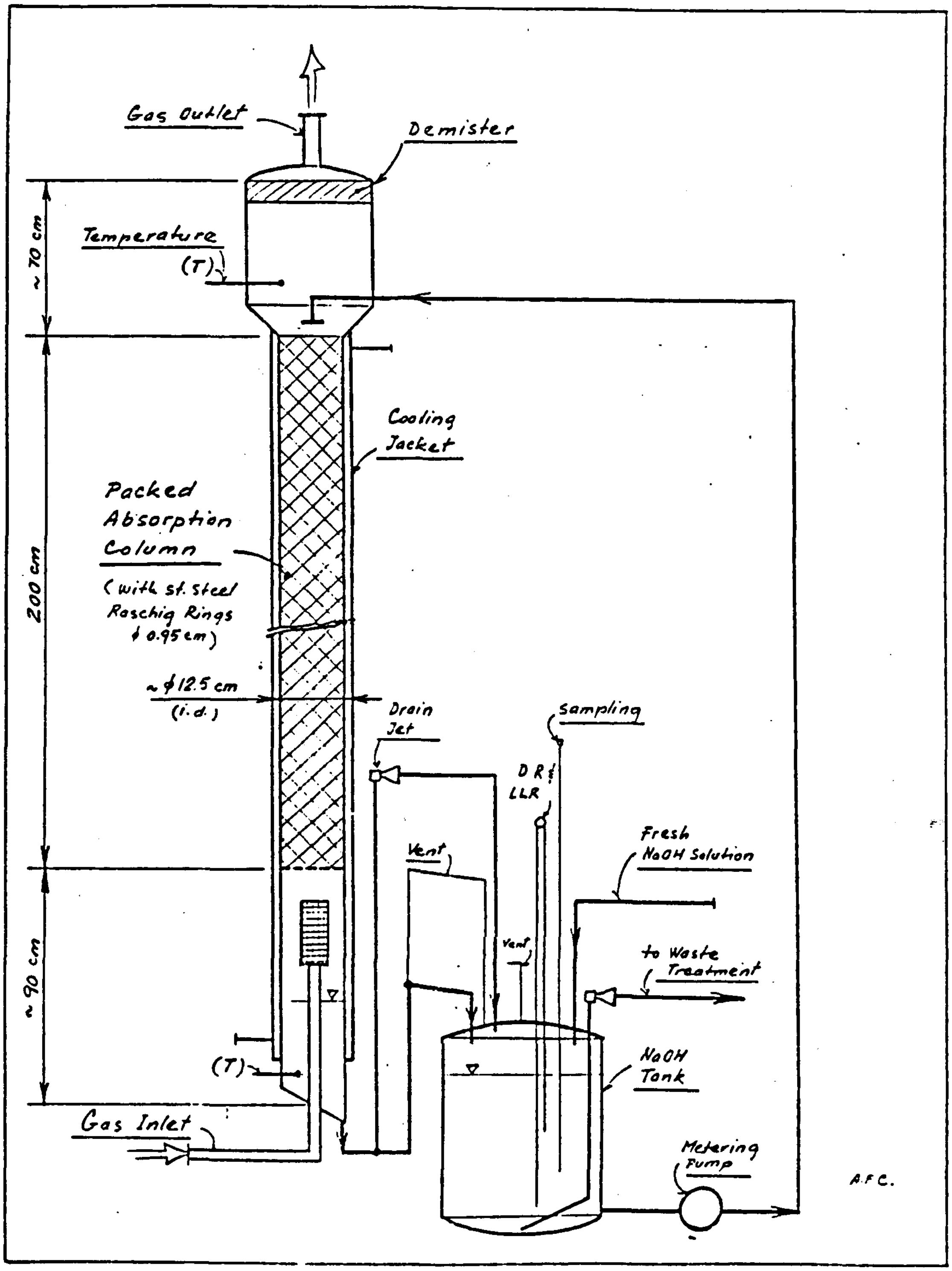
At 0.1 tonne per day, the iodine input to the process is 8×10^{-8} Ci/sec or 7.6×10^{-8} Ci/sec to the DOG system. The total df for a caustic scrubber and silver zeolite bed in series is 10^3 for a release rate of

7.6×10^{-11} Ci/sec for I-129. The release for one FFTF campaign would be 1.64×10^{-4} Ci.

The I-129 release rate for two silver zeolite beds in series would be 7.6×10^{-12} Ci/sec for an overall release (via the DOG) of 1.6×10^{-5} Ci.

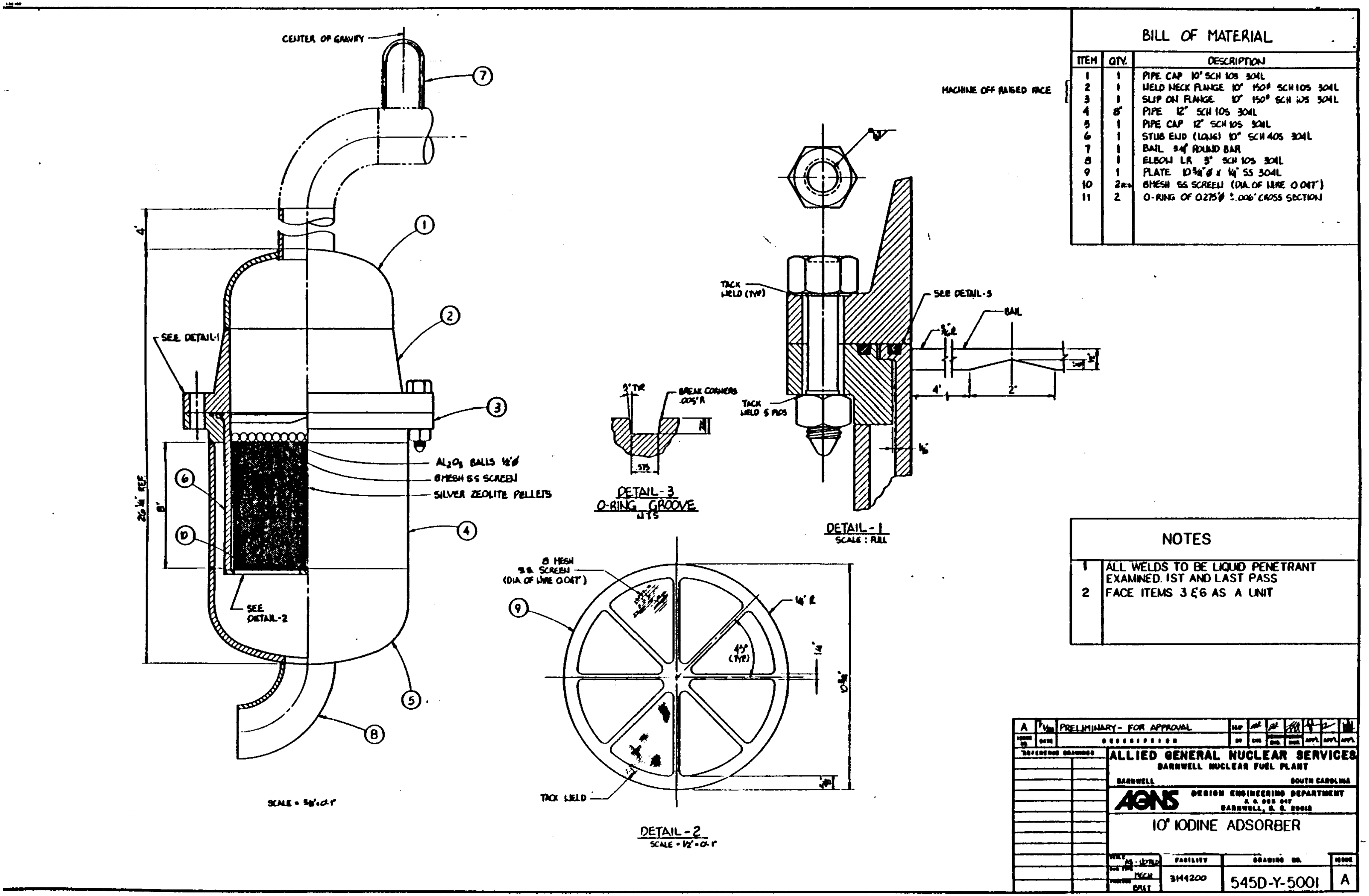
For the VOG system, the iodine input is 4×10^{-9} Ci/sec. The release would be 4×10^{-11} Ci/sec or a release of 8.63×10^{-5} Ci per FFTF campaign.

These results are below the limits of 5×10^{-3} Ci/GWe yr given in 40 CFR-190 for I-129. Although the FFTF does not produce electricity, it can be estimated at 100 MW.[10]



CAUSTIC SCRUBBER FOR IODINE ABSORPTION

FIGURE 3-1



BILL OF MATERIAL

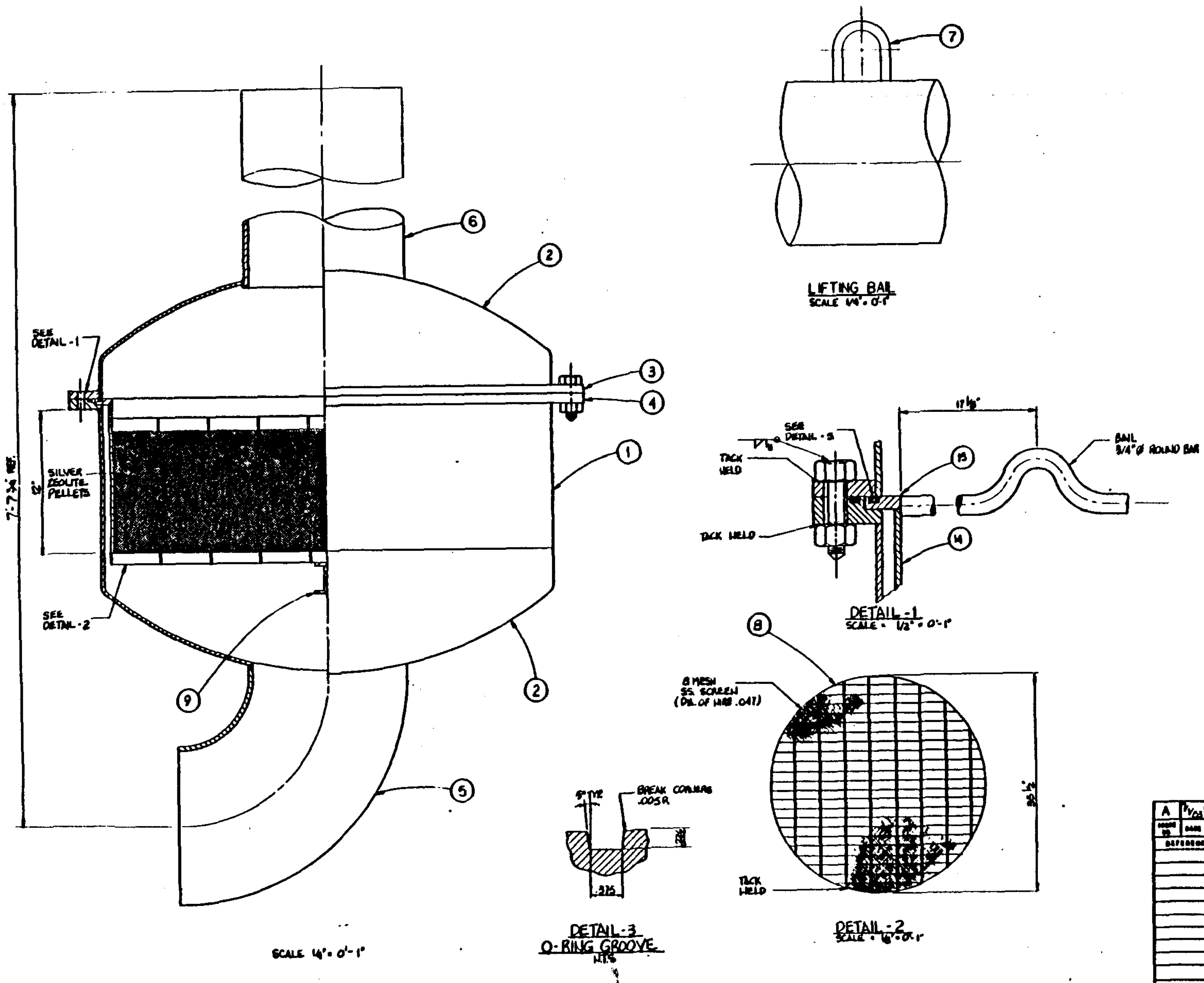
ITEM	QTY.	DESCRIPTION
1	1	PIPE CAP 10" SCH 10S 304L
2	1	WELD NECK FLANGE 10" 150# SCH 10S 304L
3	1	SLIP ON FLANGE 10" 150# SCH 10S 304L
4	8"	PIPE 12" SCH 10S 304L
5	1	PIPE CAP 12" SCH 10S 304L
6	1	STUB END (LONG) 10" SCH 40S 304L
7	1	BAIL 3/4" ROUND BAR
8	1	ELBOW LR 3" SCH 10S 304L
9	1	PLATE 10 3/4"Ø x 1/4" SS 304L
10	2 pcs	8 MESH SS SCREEN (DIA OF WIRE 0.047")
11	2	O-RING OF 0.275"Ø ±.006" CROSS SECTION

NOTES

1	ALL WELDS TO BE LIQUID PENETRANT EXAMINED. 1ST AND LAST PASS
2	FACE ITEMS 3 & 6 AS A UNIT

SILVER ZEILITE ADSORBER FOR DOG

FIGURE 3-2



BILL OF MATERIAL

ITEM	QTY.	DESCRIPTION
1	1	S.S. PLATE 304L 9.425" x 12" x 1/4" THK.
2	2	TANK HEAD (HI-CROWN) 304L 36" x 1/4" THK.
3	1	S.S. PLATE 304L 41"Ø x 3/4" FACE TO 5/8" AFTER WLDG.
4	1	S.S. PLATE 304L 41"Ø x 1 1/8" FACE TO 1" AFTER WLDG
5	1	90° ELBOW 304L 12" SCH 10S
6	FIELD	PIPE 12" 304L 12" SCH 10S
7	1	ROUND BAR 3/4"Ø x 24" LG 304L SS
8	2 PCS	SUBWAY GRATING 35 1/2"Ø
9	1	I BEAM 3" x 7.5 304L
10	2 PCS	8 MESH S.S. SCREEN (DIA. OF WIRE .047")
11	2	O-RING 0.275"Ø
12	1	ROUND BAR 3/4"Ø x 35" LG. S.S
13	1	S.S. PLATE 304L 36 3/4"Ø x 5/8" FACE TO 1/2" AFTER WLDG
14	1	S.S. PLATE 304L 9.032" x 12" x 1/4" THK.

NOTES

1. LIFTING BAIL TO BE ATTACHED AT CENTER OF GRAVITY
2. ALL WELDS TO BE LIQUID PENETRANT EXAMINED. 1ST AND LAST PASS
3. FACE ITEMS 4 & 13 AS A UNIT.

ISSUE NO.	DATE	DESCRIPTION
A	1/1/02	PRELIMINARY - FOR APPROVAL

ALLIED GENERAL NUCLEAR SERVICES
BARNWELL NUCLEAR FUEL PLANT
BARNWELL SOUTH CAROLINA

AGNS DESIGN ENGINEERING DEPARTMENT

36" IODINE ADSORBER

SCALE	FACILITY	DRAWING NO.	ISSUE
AS NOTED	3144200	545D-Y-5002	A

SILVER ZEOLITE ADSORBER FOR VOG

FIGURE 3-3

4.0 COSTS

4.1 Cost Basis

Rough cost estimates for the equipment items shown in Figures 3-1, 3-2, and 3-3 were based on materials take-off and vendor supplied information for pipe fittings, instrumentation, and equipment items. The weight of the equipment items to be fabricated was taken from the materials takeoff. Assuming $2/lb for stainless steel gave the materials cost. For the 10-inch silver zeolite bed and the caustic scrubber, it was assumed materials cost was 25% of the fabricated cost. For the 36-inch silver zeolite bed, it was assumed that the material cost was 30% of the fabricated cost. X-ray inspection was estimated to be $500 for the caustic scrubber, $300 for the 36-inch bed and $200 for the 10-inch bed. Piping costs were estimated based on length of runs, bends and fittings. Cost estimates do not include design, delivery, or installation as they are expected to be similar for comparable systems.

Waste packaging and repository charges were discussed in Section 3.0.

4.2 Cost Comparison

A comparison of costs between the caustic scrubber and silver zeolite adsorber for the DOG is developed below. The initial costs are as follows:

Caustic Scrubber System

Absorption Column and Auxiliaries	$19,800
Silver Zeolite bed	2,575
Silver Zeolite	3,000
Concentrator	26,000
	$51,375

Silver Zeolite Adsorber

Silver Zeolite beds (2)	5,150
Silver Zeolite (2 charges)	6,000
	$11,150

The incremental costs per campaign are as follows:

Caustic Scrubber

Waste drums (3)	$16,308
Chemicals	200
	$16,508

Silver Zeolite Adsorber

Waste drum (1)	$ 5,436
Replacement bed	3,000
	$ 8,436

4.3 Cost Summary and Findings

Labor charges for the two processes for operations, waste handling, etc., are considered equivalent so are not included in the incremental costs. The waste drum cost includes cost of the drum and repository charge. Shipping is considered a wash.

The silver zeolite system is more economical than the caustic scrubber, both for the initial cost and incremental cost. Engineering design, procurement costs, and installation are not shown in initial costs as they would be expected to be equivalent for both systems.

It has been suggested that lead zeolite might be used as the final form for disposal; however, this would require additional equipment and labor. This is an option which could be explored further. The lead zeolite in concrete does have poor leach resistance.[1]

The waste drum which includes the deep repository charge is the major incremental cost for both systems. An extension of the caustic scrubber system would be to add a barium iodate conversion unit to concentrate the iodine. Conceivably, the iodine from several campaigns could be placed in one drum for disposal. This could cut the incremental cost considerably.

In spite of the high cost of silver, it does not appear unreasonable to use silver zeolite as the first stage iodine adsorber in the BRET process. For a larger scale plant, iodine recovery should be reevaluated.

5.0 REFERENCES

(1) Steindler, M. J., et al, ANL-82-78, "Fuel Cycle Programs Quarterly Progress Report," July-September 1982, pp 102-115, (March 1983).

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(10) Croft, A. G. and Bjerke, M. A., "An ORIGEN 2 Model and Results for the Clinch River Breeder Reactor," NUREG/CR-2762 (July 1982).