FLUORINE DISPOSAL PROCESSES
FOR NUCLEAR APPLICATIONS

By

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Environmental Control

April 8, 1977

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ABSTRACT

A study was performed to determine the best method for disposing of waste fluorine in the effluent from a uranium oxide conversion facility. After reviewing the fluorine disposal literature and upon considering the nuclear safety constraints, it was determined that the two most promising processes were the fluidized alumina bed and the caustic scrubber. To obtain more design data for the latter process, a 3-stage, 5-inch inner diameter spray tower was constructed and operated. This unit used a 10 weight percent potassium hydroxide solution at flows of 1.5 to 3 gpm and achieved a 90 percent fluorine efficiency at fluorine flowrates as high as 4 scfm. However, two toxic by-products, oxygen difluoride and nitroxy fluoride, were detected in the effluent gases. After considering the relative merits of both disposal processes, it is concluded that the fluidized bed is superior, especially if the contaminated waste material were salable.

INTRODUCTION

A series of investigations have been made at the Goodyear Atomic Corporation (GAT) to determine a safe, economical method of fluorine disposal for a uranium oxide conversion facility. The facility, shown in Figure 1, produces uranium hexafluoride by reacting uranium oxides with fluorine in a "flame tower" at 1100^o F. The uranium hexafluoride product then may be fed to a gaseous diffusion cascade for enrichment.

The uranium oxides are introduced into the 5-inch I.D. flame tower by a feed screw. The reaction with fluorine as the oxide particles fall produces uranium hexafluoride, oxygen, and a small quantity of solid "ash". The gaseous products and unreacted fluorine flow to cold traps where the uranium hexafluoride is collected as a liquid. The last traces of uranium hexafluoride are removed by

FIGURE 1: SCHEMATIC REPRESENTATION OF OXIDE CONVERSION FACILITY

sodium fluoride traps, and the remaining fluorine-oxygen mixture is exhausted to the atmosphere through an air jet. However, equipment failures can produce a temporary flow of pure fluorine to the air jet.

Because the oxide conversion facility frequently processes high assay materials, the design of a pollution abatement process is complicated by the geometry constraints imposed by nuclear safety requirements. The design of any fluorine system is impeded by explosion and fire hazards, corrosion problems, and the toxicity of fluorine and some fluorine reaction products.

A review of the literature revealed that more than 30 different methods of fluorine disposal have been investigated. However, the only method that had been used successfully in an industrial-sized installation was the caustic scrubbing process developed by Landau and Rosen^{1,2} in the 1940's. Unfortunately this process used a large packed tower that could not meet modern nuclear safety standards because of the unsafe geometry of such large equipment.* However, because caustic scrubbing was the only proven method of fluorine disposal, it was decided to investigate other types of scrubbers in order to develop nuclearly-safe apparatus. Therefore, a study of geometrically-safe caustic spray towers was initiated, and a full-scale pilot plant was built and successfully operated.³

While the caustic scrubber experiments were in progress, the GAT Chemistry Department started a complementary investigation of packed bed fluorine disposal methods. During the course of these studies, it was discovered

*A brief summary of some of the more common nuclear safety constraints is presented in Appendix C.

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that a process involving a fluidized bed of alumina was going to be used for fluorine disposal at the new Midwest Fuel Recovery Plant operated by the General Electric Company ⁴ at Morris, Illinois. A tour was made of this plant, and it was decided that the fluidized bed process was a viable alternative to caustic scrubbing and that a cost study should be made to determine the more economical process.

The remainder of this paper will deal with a review of the literature, the caustic scrubber studies, and a comparison of the caustic scrubber and fluidized bed processes.

A LITERATURE SURVEY OF FLUORINE DISPOSAL METHODS.

A. Miscellaneous Methods: Various fluorine disposal methods have been investigated on a world-wide basis since fluorine became commercially available in the 1940's, and reviews of these methods have been prepared recently by Navratil⁵ and by Reiter and Saraceno⁶. All of these processes were reviewed for possible application at the oxide conversion facility; however, few of the processes could be used safely and economically.

For example, a process for reacting fluorine with superheated steam was developed by Smiley and Schmitt⁷; later this process was used to dispose of excess fluorine from a uranium hexafluoride feed plant at the Portsmouth Gaseous Diffusion Plant. This reactor never worked properly; small explosions⁸ occurred each time the operating conditions were changed, and when the insulating material was first removed from outside the reactor for maintenance, it was discovered that most of the metal (Monel) had been destroyed by corrosion.

Table 1

PROBLEMS AND ADVANTAGES OF SEVERAL FLUORINE DISPOSAL METHODS

Process	References	Problems/Advantages
1. Packed Bed Reactors (alumina, soda, ash, lime, etc.)	5,9,10	The beds frequently plug, and considerable manpower is required to empty and refill the reactors. If the internal diameter of the reactors is limited to 5 inches by nuclear safety constraints, several reactors will be required for even small fluorine flows.
2. Packed Charcoal Bed Reactors	11,12,13,14,15, 16	There is the possibility of explosion if the proper type of charcoal is not used. The charcoal is consumed almost completely reducing manpower requirements. However, polymerized fluorocarbons may cause plugging, and with oxygen present in the reactant gas, the toxic gas carbonyl fluoride is formed. ¹⁶
3. Burning with Hydrogen or Hydrocarbons	17,18,19,20	20 There are corrosion and explosion problems, and toxic gases may be formed. If oxygen is present in the reactant gases, water is formed making it uneconomical to recover the H ₂ O-HF mixture by cold trapping and/or adsorption; therefore, the product gases must be scrubbed.
4. Reaction with Ammonia	21	The highly toxic gas nitrogen trifluoride is formed in the reaction.
5. Reaction with Steam	7,22	This reaction presents severe corrosion problems, and sudden changes in operating conditions may result in explosions. The hydrogen fluoride formed in the reaction presents a secondary disposal problem.
6. Reaction with Uranium Tetrafluoride	23,24,25	Intermediates in the reaction may cause plugging (or bridging) even when a fluidized bed is used; the plugging is even more severe when small diameter beds are used, such as those required for high assay uranium compounds.

Table 1 (cont'd)

Process	References	Problems/Advantages
7. Caustic Scrubbing	1,2,9,20,26, 27,28,29	This process produces large quantities of calcium fluoride that are essentially worthless and that require long-term storage. The water used in the process is a moderator and could present nuclear safety problems. However, the process has been investigated thoroughly and was used in an industrial-sized installation.
8. Fluidized Bed Reaction with Alumina, Sodium Carbonate, etc.	30,31	Optimal design of a fluidized bed is difficult because of nuclear safety constraints. However, there are no excessive manpower requirements or problems with plugging as there are with fixed bed reactors.

The advantages and shortcomings associated with several of the disposal processes reviewed by Navratil and others are presented in Table 1. It should be noted that some of the other processes reviewed by Navratil as fluorine disposal methods were actually intended for the control of hydrogen fluoride or particulate fluoride emissions. Care should be used when consulting the literature published by the phosphate and aluminum industries because the term "fluorine" is used synonymously with "fluoride".

In addition to the public literature, approximately 24 cu. ft. of old documents belonging to the Atomic Energy Commission were examined to find if work had been done on other fluorine disposal processes during the early years of the Manhattan Project. These documents had been sealed in boxes at an AEC repository in Georgia for almost 30 years. Most of the material had been the office files of Rosen and Landau who were employees of the Kellex Corporation and were responsible for the process chemicals used in the first gaseous diffusion plant at Oak Ridge, Tennessee.

Examination of the documents revealed that an organized search for a reliable fluorine disposal process had been started by Kellex in 1943 and that the DuPont, Chrysler, Hooker, and Harshaw Corporations and the Johns Hopkins and Columbia Universities had taken part in the study. Several disposal methods were considered by Kellex, including the reaction of fluorine with sulfur, mercury, sodium chloride, cobaltous fluoride, and caustic solutions.^{20,32,33}

The use of either mercury or cobaltous fluoride is impractical because of the high costs for these materials. The reaction of fluorine with sulfur produces a useful product, sulfur hexafluoride, that is used in modern electrical

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equipment as a dielectric.³⁴ However, a very toxic biproduct, disulfur³⁵ decafluoride, is formed in the reaction,³⁶ and costly equipment is necessary to pyrolyze the S_2F_{10} and to purify the product.³⁶ Also, the high concentration of oxygen in the oxide conversion vent gases would reduce the yield of SF_6 by promoting the formation of sulfuryl fluoride, SO_2F_2 .

The two disposal processes most favored by Kellex were the reaction of fluorine with sodium chloride and caustic scrubbing.³⁷ However, the caustic scrubbing process was chosen finally because there were problems with plugging in sodium chloride beds, and the chlorine liberated from this reaction would have had to have been destroyed, probably by caustic scrubbing or by reaction with soda ash in a packed bed.

B. Caustic Scrubbing Processes: Scrubbing with water alone is unsuitable for²⁰ fluorine disposal. Early experiments at the DuPont Jackson Laboratory showed that two types of reaction may occur when fluorine is contacted with a water spray:

- (a) A smooth "burning reaction" characterized by a purple-blue flame and near stoichiometric production of hydrogen fluoride or,
- (b) the more common "inhibited reaction", manifested by violent explosions in which only a small portion of the fluorine is consumed.

However, the addition of a caustic to the water was reported to prevent the explosions and also destroyed the hydrogen fluoride produced in the reaction. In 1944 a large caustic scrubber was designed and successfully operated for the^{1,2} Manhattan Project by the Kellex Corporation.

In the Kellex installation the fluorine was scrubbed with a 100 gal./min. flow of 5 to 10 weight percent sodium hydroxide solution in a packed tower

approximately 20 feet high and four feet in diameter. The spent caustic solution was reacted with slaked lime, regenerating the caustic and precipitating calcium fluoride in a settling tank as shown in Figure 2. The regeneration process required two to three times the stoichiometric amount of lime, but resulted in a cost savings because lime is much less expensive than caustic. The regeneration process also had environmental advantages, because it removed the potentially toxic fluoride ion from the scrubbing solution. The overall chemical reactions involved in the plant were as follows:

Scrubbing Reaction:

Regeneration Reaction:

The large packed tower was very efficient. The scrubber was operated at an average fluorine feed rate of 2.5 pounds per hour for several months with no fluorides detected in the effluent gases. It was operated for several hours at a feed rate of 500 pounds per hour, and the fluoride concentration in the effluent did not exceed 3 ppm. The tower was built with such large dimensions to give the gas stream a minimum contact time of one minute. It was thought that this contact time was necessary in order to absorb any oxygen difluoride formed in the scrubbing reaction. It was necessary to remove the OF_2 because it is even more toxic than fluorine; for example, the threshold limit values³⁸ for fluorine and OF_2 are 1.0 and 0.05 ppm, respectively.³⁹

The one-minute contact criterion for the scrubber was derived from kinetic data presented by Simons, et.al.⁴⁰ Simons' experiments were performed at several different caustic concentrations and temperatures, and the OF_2 "gas" concentrations used in the analyses were the averages of results obtained both

FIGURE 2: SCHEMATIC REPRESENTATION OF CAUSTIC REGENERATION SYSTEM

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gasometrically and by titration. More recently, Misra and Cady also determined the kinetics of OF_2 hydrolysis. However, their rate expressions were based upon the OF_2 concentrations in the liquid phase. Therefore their results are not directly comparable, but a brief summary of the results of both experiments is presented as Table II.

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The DuPont Corporation performed several experiments for Kellex and their own purposes to determine if there were any reagents suitable for scrubbing OF_2 from a gas. A 300 ml Orsat apparatus was used as a "scrubber", and 12 to 20 ml of gas containing 50 percent OF_2 was forced through the apparatus for several passes. Fifteen different scrubbing solutions were used including several bases, acids, and reducing and oxidizing agents. The acids and oxidizing agents had no effect, but practically all of the reducing agents aided in the decomposition of OF_2 , particularly those in alkaline solution. However, none of the solutions were significantly more effective than a sodium hydroxide solution. Potassium hydroxide solutions were not used in the experiments.

In addition to the Kellex packed tower and the DuPont bubbler, there have been several other spray scrubbers used for fluorine disposal investigations. The first of these was built by Burford and Hamilton at Johns Hopkins University. This caustic scrubber was built from a vertical Monel pipe approximately 7 feet tall and 7.75 inches ID. The caustic solution was introduced at the top of the scrubber through a spray-head. The spray-head was merely a flat plate with about 200 $\frac{5}{64}$ -inch holes drilled in it.

Table II

KINETICS OF THE HYDROLYSIS OF OXYGEN DIFLUORIDE
IN CAUSTIC SOLUTIONS

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A. The Results* of Simons

Caustic Concentration:	Temperature	First Order Rate Constant
10 wt.% NaOH ($[\text{OH}^-] = 2.8 \frac{\text{g.moles}}{\text{L}}$)	29°C	0.34 min. ⁻¹
1 wt.% NaOH ($[\text{OH}^-] = 0.25 \frac{\text{g.moles}}{\text{L}}$)	59°C	0.10 min. ⁻¹
1 wt.% NaOH	21°C	0.045 min. ⁻¹

*Oxygen difluoride concentrations were measured in the gas phase.

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B. The Results** of Misra and Cady

Caustic Concentration	Temperature	First Order Rate Constant***
10 wt.% NaOH	29°C	0.13 min. ⁻¹

**Oxygen difluoride concentrations were measured electrometrically in the caustic solution.

***The first order constant, k' , was derived from the published rate equation:

$$\frac{d[\text{OF}_2]}{dt} = -k[\text{OF}_2] \left([\text{OH}]^{\frac{1}{3}} - 0.0105 \right), \text{ yielding}$$

$$k' = k \left([\text{OH}]^{\frac{1}{3}} - 0.0105 \right) \text{ at constant pH.}$$

The fluorine was introduced through a pipe entering the scrubber about 12 inches below the spray-head and extending downward to the centerline of the scrubber about 18 inches below the spray-head. The caustic flowrate was maintained at 5 gpm, and the liquid and gases flowed cocurrently down the scrubber and exited through a 2-inch horizontal pipe at the bottom. The liquid then poured into a 50-gallon Monel tank and was recycled to the spray-head; the gases also flowed through the 2-inch pipe and were released into the work area.

Five to ten percent sodium hydroxide solutions were used in most of the experiments, and up to 3 lbs./hr. (0.472 scfm) of fluorine was disposed of with no fluorides detected in the outlet gases. The detection method was reported to be sensitive to fluoride concentrations of 5 ppm or greater in the gas phase.

No quantitative data were available to show the effect of diluting the fluorine with inert gases. Although the maximum fluorine flow was diluted with as much as 5 lbs./hr. (1.06 scfm) of nitrogen, no fluorides were detected in the effluent gases. However, lowering the caustic concentration produced drastic effects. As the concentration was lowered, the scrubber continued to absorb the fluorine quantitatively until a concentration of 0.02 weight percent NaOH was reached. At lower concentrations the operation of the scrubber became erratic, and several small explosions occurred.

This scrubber was also used to dispose of waste gases from a small pilot plant that produced experimental fluorocarbons. Over four months of

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operating experience were accumulated with the scrubber, and several operational problems were solved.

The fluorine inlet pipe was the only portion of the scrubber that suffered extensive corrosion. When the tower was first built, it was used as a counter-current scrubber. However, the metal (Monel ?) gas inlet tube had a "prohibitively short life.... believed due to the high concentrations of corrosive gas and caustic alternately reacting with the exposed metal parts."⁴² This problem was solved by converting the tower to a cocurrent flow pattern. In addition to the corrosion problem, the pump used to recirculate the caustic solution was replaced several times because of erosion failures. Because the scrubber had no caustic regeneration system, the fluoride concentration in the caustic solution slowly increased until sodium fluoride precipitated. Fine particles of sodium fluoride circulating through the pump caused the parts to erode.

Other spray scrubber experiments were performed by Liimatainen and Levenson.⁹ Low concentrations of fluorine (less than 0.5 mole percent) were used in a single-stage, cocurrent spray tower. The tower had an inner diameter of 5 in., making it nuclearly safe for high assay uranium compounds (A brief summary of some of the more common nuclear safety constraints is presented in Appendix C.). A hollow cone (60°) spray nozzle was used, unlike the coarse spray used by Burford and Hamilton. Also, lower liquid flow rates of 1.7 to 0.88 gal./min. were used, and potassium hydroxide was used instead of sodium hydroxide.

FIGURE 3:
ABSORPTION OF FLUORINE IN A SPRAY COLUMN

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Liimatainen and Levenson found that the efficiency of absorption appeared to be independent of both the gas flow rate and the concentration of fluorine in the gas phase. The efficiency of absorption was a function of the liquid flow rate only (liquid resistance controlled). By moving the spray nozzle, the height of their tower was varied from 3.4 to 2 ft. with little effect on the absorption efficiency. It was concluded that most of the absorption occurred in the first several inches of spray from the nozzle.

A brief summary of the Liimatainen and Levenson data is presented as Table III, and a correlation they presented between the height of a transfer unit and the liquid rate is shown as Figure 3. Only four runs were made, but there appears to be very little scatter in their data. Decreasing the caustic concentration was reported to give a reduction in absorption efficiency. Run 4 in Table III was made with five percent KOH and shows a 0.6 percent reduction in efficiency from Run 3 where 10 percent KOH was used.

Note that almost complete absorption took place in all of the runs, and although the contact times were all lower than two seconds, no oxygen difluoride was detected in the outlet gases from their scrubber. Liimatainen and Levenson offered two possible explanations for the lack of OF_2 :

- (a) Oxygen difluoride may be formed more readily in dilute sodium hydroxide solutions than in dilute potassium hydroxide solutions, and

Table III

A SUMMARY OF FLUORINE ABSORPTION DATA FROM THE
EXPERIMENTS OF LIIMATAINEN AND LEVENSON ⁹

Run No.	Height of Tower (ft)	KOH Concentration (wt%)	Gas Rate (lb/hr-ft ²)	Liquid Rate (lb/hr-ft ²)	Gas Inlet Concentration (ppm)	Gas Outlet Concentration (ppm)	Efficiency of Absorption (percent)	HTU (ft.)
1	3.5	10	215	6750	1850	30	98.4	0.85
2	2.0	10	208	5800	952	7	99.3	0.41
3	2.0	10	344	3460	4510	74	98.4	0.49
4	2.0	5	353	3460	2510	56	97.8	0.53

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- (b) The fine spray used in their experiments gave a rapid fluorine absorption which may not have favored the formation of oxygen difluoride.

Liimatainen also performed experiments with a horizontal spray
scrubber. This design was later used for an emergency vent system
at the Oak Ridge National Laboratory. However, the design incorporated
a scrubber with a 4 X 4 foot cross section which could not meet
nuclear safety criteria for highly enriched uranium.

C. The Fluidized Alumina Bed: Using the caustic scrubbing process for fluorine disposal presents a nuclear safety problem because the scrub solution acts as a moderator. Reacting the fluorine with solids with low scattering cross sections alleviates this problem, but packed bed reactors are impractical for continuous operation because the beds frequently plug and because emptying and filling the beds require considerable manpower. However, by using a fluidized bed instead of a packed bed, the plugging problem is solved. Also, the filling and emptying operations may be simplified by using fluidized feed and withdrawal operations.

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Holmes, Koppel, and Jonke performed fluorine disposal experiments with a 2-inch fluidized bed of activated alumina, and a considerable amount of design data was published. The data show the effects of bed size, temperature, and particle size on the efficiency of the reactor. The alumina was consumed as shown in the following reaction:

Their reactor gave up to 84 percent conversion of alumina at breakthrough (0.1 percent fluorine leakage). Single runs were also made with limestone and sodium carbonate as reactants. Conversion of the limestone at breakthrough was only 12 percent; this poor performance was thought to be due to poor diffusion through the calcium fluoride ash. However, the conversion of the sodium carbonate was 90 percent, and this material is a promising substitute for alumina because it is much less expensive.

At the start of the GAT fluorine disposal studies, it was decided that a fluidized bed system would be difficult to design properly; no one at GAT had any practical experience with fluidization. Also, it was desired to find a disposal system of proven capability, but no industrial-sized fluid bed system was found in the search of the fluorine disposal literature. However, after the GAT caustic scrubber experiments were started, a phone call to Jonke revealed that the new General Electric Fuel Recovery Plant at Morris, Illinois would use a fluidized bed of alumina for fluorine disposal.

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A trip was made to the General Electric Plant to inspect the system shown in Figure 4. At that time the unit had not yet been placed onstream. This unit was designed for a maximum flow of 2 scfm at a maximum fluorine concentration of 20 mole percent. When there would not be enough process flow to maintain the minimum fluidization velocity (0.2 ft./sec), a supplemental makeup stream of air was planned.

Figure 4

GENERAL ELECTRIC FLUIDIZED ALUMINA BED

The alumina feed was to be Alcoa, grade F-1, 100 mesh particle size, and it was hoped that an 80 percent conversion of the alumina could be realized. The maximum assay of the uranium compounds that could accidentally be introduced to the bed was 5 wt. percent U-235.

Depleted alumina was to be removed while the bed was operating by manually opening a valve to a 1-ft³ free volume. When this volume was filled, other valves were to be opened, and the depleted alumina was to be carried pneumatically to an underground storage vault. At approximately the same time, a fresh 1-ft³ charge of alumina was to be added to the bed by a gravity feed system. There were four banks of four sintered metal filters at the top of the 3-ft. ID settling section of the reactor to remove the "fines" generated in the reaction. The filters were equipped with a sequential blowback system that was to clear one bank of filters with high pressure air each five minutes.

During the visit to the General Electric Plant, it was discovered that a paper³¹ had been published discussing their fluidized alumina bed and describing the relative advantages of the bed over caustic scrubbing. The capital costs for the alumina system were estimated to be approximately \$10,000 less than for the scrubber system, but the direct material costs favored the scrubbing system by about \$10 per day. Presented in Table IV are several other factors which favored their use of the fluidized bed.

Table IV

GENERAL ELECTRIC COMPARISON OF FLUORINE
DISPOSAL METHODS : CAUSTIC SCRUBBING VERSUS
ALUMINA FLUID BED*

<u>CHARACTERISTIC</u>	<u>CAUSTIC SCRUBBING</u>	<u>Al₂O₃ Fluid Bed</u>
Maintenance demands	Moderate	Anticipated to be low
Confinement of radioactivity	Fair	Good
Efficiency	90% expected	99% assured
Nuclear safety	Uranium precipitation problem	System is safe
Manpower requirements	Filter changeout problem	Solids handling problem
Previous experience	Moderate	Very little
Control requirements	Requires liquid sampling system. Responds poorly to surge or upset.	Easily controlled. Handles surge or upset smoothly.

*Reproduced from a table prepared by Lambert and Dotson.³¹

SCRUBBER EXPERIMENTS

A. Initial Considerations: After the literature search was completed, the fluidized bed was considered briefly as a fluorine disposal method for the oxide conversion facility. However, GAT personnel lacked experience in fluid bed design, and at that time it was not known that a fluid bed had been used in an industrial-sized disposal system. Caustic scrubbing was a proven process, and it appeared that no special engineering training would be necessary to design the equipment. Therefore, it appeared that caustic scrubbing was the more attractive disposal process, and preliminary work was started to develop a scrubber design for the oxide conversion facility.

Because of the possibility of high-assay uranium fluorides accidentally entering the scrubber, it was necessary to limit the design geometry to a 5-inch ID column. A 5-inch column was chosen because this geometry is nuclearly safe even when 100 percent U-235 is contained with a moderator; such columns are used frequently in the nuclear industry.

A packed bed scrubber design was considered and then rejected because of the high pressure drop and because of possible plugging problems. Plugging was a distinct possibility because some calcium would always be present in the scrub solution, especially if the caustic regeneration system were used. Also, there was again the possibility that uranium could be introduced accidentally into the column. The calcium would form the precipitate CaF_2 , and the uranium would precipitate as $\text{K}_2\text{U}_2\text{O}_7$. Therefore, a spray column was chosen as the unit most likely to meet the necessary design criteria; such columns had been used before at GAT for

other applications and to determine the effect of these conditions.

It was also decided that pilot plant studies would be required to determine the performance of the spray tower. The Burford and Hamilton experiments had shown that an 8-inch spray column could dispose of up to 0.472 scfm of fluorine with no detectable fluorine in the effluent gases. However, their column had a cross-sectional area about 2.5 times larger than the area of the proposed GAT column. Also, there was interest in attempting higher mass transfer rates in the GAT column.

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The Liimataninen and Levenson data were more applicable to the GAT scrubber, because a 5-inch column was used in the experiments and because a correlation (Figure 3) was presented which gave the height of a transfer unit for a 2-foot spray stage. However, their data were taken at very low fluorine flow rates (~ 0.03 scfm) and low fluorine concentrations (~ 0.005 mole percent). Therefore, because mass transfer coefficients decrease substantially with increasing mass transfer rates, it was possible that the use of the Liimataninen and Levenson correlation would be overly optimistic. It was also feared that oxygen difluoride might be produced at higher mass transfer rates.

B. Apparatus and Procedure: The spray tower was fabricated from sections of 5-inch inner diameter Monel pipe and was 8-feet tall. The top section of the tower contained several pieces of Monel screen to act as a demister. Three spray nozzles were located at 2-foot intervals down the tower, and the bottom 4-inch section of the tower was kept full of caustic solution.

The nozzles (Model 3/8 GA 15) were manufactured by the Spraying Systems Company of Bellwood, Illinois. The nozzles had a flow range of 0.5 to 1 gal./min. of caustic solution per nozzle, and the flow was monitored by a rotometer at each nozzle.

Both pure fluorine and fluorine-nitrogen mixtures were used in the spray tower. The fluorine was metered through a flat plate orifice calibrated by measuring nitrogen and carbon dioxide flow rates with a wet test meter and determining the equivalent fluorine flow by interpolation. The diluent nitrogen flow was monitored through a similar orifice calibrated directly with a wet test meter. The inlet fluorine line entered the tower about 6 in. from the bottom of the tower. The gases flowed upward through the tower, counter-current to the caustic spray, and were vented to the building exhaust header through a copper tube fitted with a sample tap. The pressure at the outlet of the tower was maintained within 1 psi of atmospheric pressure.

Ten weight percent caustic solution was prepared by mixing technical grade potassium hydroxide with sanitary water in one tank and decanting the solution into the 250-gallon tank that fed the spray tower. This procedure was used to avoid plugging the spray nozzles with the calcium hydroxide formed when mixing the caustic and water. After flowing through the tower, the spent caustic solution was fed through a valve and a leveling tank that was calibrated to maintain the 4-inch level of caustic solution at the base of the spray tower. The solution then was pumped to two sealed 55-gallon drums. The leveling tank was vented into the side of the spray tower, and the 55-gallon drums were vented to the building

exhaust header.

The caustic solution was isolated from the working environment after passing through the tower to avoid possible outgassing of entrained fluorine or oxygen difluoride to the air. This precaution was justified because an oxygen difluoride concentration of 2.8 mole percent was detected once in the leveling tank during a preliminary experiment, when the bottom of the tower went dry due to the miscalibration of the leveling system. The oxygen difluoride was probably formed in the leveling tank by fluorine bubbling through the caustic solution.

The skin temperature of the tower and the inlet and outlet caustic and gas temperatures were monitored from chromel-alumel thermocouples with leads running through a rotary switch to a digital thermometer. These measurements were made during only three runs.

Fluorine and oxygen difluoride samples were collected in evacuated glass bulbs and in preconditioned, evacuated metal sampling bombs, respectively. None of the glass bulbs showed evidence of frosting although some were used over 20 times. The amount of fluorine contained in the bulbs was determined by reacting the gas sample with a 10 percent potassium iodide solution and titrating with sodium thiosulfate; the oxygen difluoride concentrations were determined by infrared spectroscopy. The limit of detection for fluorine was 0.05 mole percent, and the limit of detection for oxygen difluoride was between 0.01 and 0.11 mole percent, depending upon the pressure and composition of the sample.

The mole fraction of fluorine in a bulb was determined by dividing one-half of the fluoride moles, found by titration, by the total moles of material in the bulb. The total moles of material in a bulb was calculated from a pressure measurement in a constant temperature bath, assuming ideal gas behavior.

The spray tower was operated over a rather narrow range of flow conditions. During the experiments the fluorine flow was set at values that ranged from 1 to 4 scfm and the nitrogen flow was varied from 0 to 4 scfm. The flow of potassium hydroxide solution was varied from 0.5 to 1.0 gallon per minute per nozzle, and the three nozzles were always adjusted to produce identical flows during each run. The capacity of the caustic feed tank limited each experimental run to an operating time of about 20 minutes, and during that time, flow rates were monitored carefully to assure uniform operating conditions.

C. Results: Typical fluorine concentrations found in the outlet gases from the spray tower are presented in Table V, and a more complete listing of the experimental data is presented in Appendix A. Considerable scatter is apparent in the data, and each concentration shown in Table V is the average of several data points. At least part of this scatter may have been caused by changes in operating conditions within the spray column. This interpretation was supported by the observed variation in the skin temperature of the scrubber during the experiments; somewhat cyclic temperature variations of about 3 to 11°F were measured near the principal reaction zone at the base of the scrubber. It also should be

Table V

SUMMARY OF SCRUBBER EFFICIENCY RESULTS

<u>Total Caustic Flow (Gpm)</u>	<u>Inlet Fluorine Flow (scfm)</u>	<u>Inlet Nitrogen Flow (scfm)</u>	<u>Average Fluorine Removal Efficiency (%)</u>	<u>Number of Data Points</u>	<u>Standard Deviation</u>
3	4	0	96.1	2	2.83
3	3	3	89.7	23	4.86
3	3	0	95.6	4	2.55
3	2	2	90.2	4	2.13
3	2	0	98.1	4	1.39
3	1	1	95.2	6	3.44
2.25	3	3	88.4	4	2.57
2.25	3	0	96.2	4	1.77
1.88	3	0	91.8	8	3.54
1.5	3	3	90.0	4	4.13
1.5	3	0	90.8	8	6.10

noted that a muffled explosion always occurred when the fluorine flow was first introduced at the start of each run.

A few typical operating temperatures are presented in Table VI.

Average temperatures were used to make several enthalpy balances around the scrubber as a check of the fluorine flow instrumentation. The results were within ± 10 percent of the value of - 5,500 BTU/lb. fluorine calculated from heat of reaction data. Temperatures were recorded during only three experimental runs; all of them at a caustic flow of 3 gal./min.

Oxygen difluoride was detected in 20 of 55 outlet gas samples; the highest concentration detected was 5.7 mole percent. No definite correlation was found between operating conditions and the OF_2 concentration. However, OF_2 usually was detected in high concentrations only at the start of a run, and usually disappeared after the spray tower had been operating for a few minutes. Oxygen difluoride was detected only in six of the 32 samples that were collected after the scrubber had been operating for more than ten minutes, and the maximum concentration detected, after ten minutes, was 0.3 mole percent.

After the experiments had been in progress for about a month, a close examination of one of the infrared spectra indicated the presence of another fluoride compound in the outlet gases. The compound was identified as nitroxy fluoride, NO_3F . Subsequent infrared spectra were analyzed more closely, and NO_3F was detected in 31 out of 36 samples of the scrubber

Table VI

TYPICAL OPERATING TEMPERATURES
IN CAUSTIC SPRAY TOWER*
SPRAY TOWER SKIN TEMPERATURES (°F)

<u>Location of Thermocouple (ft. from bottom of tower)</u>	<u>8 min.**</u>	<u>10 min.</u>	<u>12 min.</u>	<u>14 min.</u>	<u>16 min.</u>	<u>18 min.</u>
0.9	145.4	149.6	151.4	149.9	148.8	146.7
1.1 (F inlet flange)	168.8	169.6	170.2	168.0	167.2	167.3
2.	119.1	120.0	120.3	120.0	118.9	117.3
3.	109.3	111.2	113.0	111.6	107.2	106.1
4.	106.2	107.6	108.8	108.1	104.8	103.7
5.	104.9	105.7	106.3	106.0	103.9	102.8
6.	101.8	102.3	102.9	102.7	101.4	100.4
7	DEFECTIVE THERMOCOUPLE					
8	102.8	103.6	104.6	105.6	104.7	103.4

*The values in the table are a portion of the temperature data collected during the experiment of August 7, 1972. The fluorine and nitrogen flows were both set at 3 scfm, and the total flow of caustic solution was 3 gpm.

**These values represent the time elapsed from the instant the fluorine flow was introduced into the scrubber.

outlet gases. The average concentration detected was about 0.4 mole percent; the maximum concentration was 1.3 mole percent. Because NO_3F is not only toxic, but explosive^{46,47}, tests were made to determine whether the compound were explosive at the concentrations found in the spray tower. During the tests, several attempts were made to detonate samples of the tower outlet gases with a spark. No explosion occurred, and subsequent analyses of the gases in the spark chamber showed that more NO_3F ⁴⁸ had been produced in the test chamber by the electrical discharges.

⁴⁹
Cursory analyses were performed on the scrubber solutions to determine if the nitroxy fluoride were formed from nitrate impurities in the caustic. These analyses showed that the inlet caustic solution contained about 2 ppm nitrate, and the spent caustic solution from one experiment contained about 15 ppm nitrate. However, the Laboratory did not have complete confidence in the analytical method because of possible interference from the caustic⁴⁹, and the scrubber project was terminated before a new analytical method could be found or developed.

No gross evidence of corrosion was found in any of the apparatus during the experiments, and the spray nozzles never plugged. However, the inlet gas line was once found to be plugged with a white material.⁵⁰ Analysis of the material by x-ray diffraction indicated that the only crystalline compound present was $\text{KF} \cdot \text{HF}$, but elemental analysis by x-ray fluorescence methods indicated potassium with traces (≤ 1 percent) of nickel, copper, iron and chromium. Therefore, it is quite possible that the scrubber apparatus was corroding, although corrosion was not detected visually. Small amounts of potassium hydroxide and potassium^{fluoride}_A were found frequently within

the apparatus, and the entrainment separator once plugged with such solids.

D. Discussion.: As shown by the data in Table V, there was little change in the fluorine removal efficiency of the scrubber although the fluorine feed was varied by a factor of four, and the liquid rate was varied by a factor of two. Also, there was much scatter in the data. Much of this scatter undoubtedly was due to uncertainties in the flow measurements and the analysis of the samples, but part of it may be due to random changes in the operating conditions within the scrubber as evinced by the changes in skin temperatures that were observed.

As shown in Table VI, most of the fluorine was destroyed in the lower portion of the spray tower, as indicated by the higher temperatures near the fluorine inlet line. The higher temperature at the 8-foot thermocouple is indicative of the temperature of the outlet gases. That thermocouple was located about one foot above the highest spray nozzle and was not cooled by the caustic spray.

Note that the fluorine concentrations shown both in Table V and in Appendix A were determined, in part, from pressure measurements. That is, before titration the sample bulbs were placed in a constant temperature bath at 25°C, and the pressure of the gases was measured. The total moles of gas in the sample bulb were calculated assuming ideal gas behavior, and the weight of fluoride found by titration was converted to a "mole percent fluorine" value. The vapor pressure of water, or of an HF-H₂O

mixture, was not subtracted from the bulb pressure, although some sample bulbs contained a small portion of liquid.

The fluorine removal efficiency shown in Table V and in Appendix A was calculated on a "dry" basis by the use of the following equation which is derived in Appendix B:

$$E_d = 100 \left[\frac{F - M(N+F)}{F \left(1 - \frac{M}{2}\right)} \right] \dots\dots\dots (1)$$

where E_d = fluorine removal efficiency (percent),
 F = inlet fluorine flow (scfm),
 N = inlet nitrogen flow (scfm), and
 M = mole fraction fluorine in outlet gases.

In deriving this equation, the presence of water in the outlet gases was ignored, and it was assumed that fluorine, not hydrogen fluoride, was contained in the gases. These assumptions are somewhat unrealistic, because the vapor pressure of the caustic solution was significant at the temperatures encountered and because fluorine reacts with water as shown in the following chemical equation:

51

Because HF is absorbed quite easily by water sprays, it is reasonable to assume that a considerable portion of the fluoride collected in the bulbs was initially fluorine. However, by the time the samples were analyzed, the above reaction would have been completed. Note that the presence of water vapor or of hydrogen fluoride would cause some error when Equation 1 was used to calculate the fluorine removal efficiency. The presence of additional moles of gas in the sample bulb

would cause an erroneously high efficiency to be calculated.

Because only cursory temperature measurements were made, the temperatures of the outlet gases at low liquid flows are unknown; therefore, the amount of water vapor in the gases cannot be calculated. However, the error caused by ignoring the effect of water vapor has been calculated at several selected outlet temperatures and is shown in Figure 5. To calculate the error, it was assumed that the outlet gases initially contained fluorine, not hydrogen fluoride, and it was assumed that the gases were saturated with water vapor at the specified temperatures. The equations are derived in Appendix B. The small "kinks" in some of the curves in Figure 5 correspond to the fluorine concentration at which all the water vapor is consumed.

The data in Figure 5 show that the maximum bias caused by water vapor is no greater than 20 percent and that the majority of the efficiency calculations are biased by less than 5 percent. The highest temperature considered was 150°F. It is conceivable that higher outlet temperatures could have been encountered; however, at higher temperatures another type of bias would take effect.

At higher temperatures the amount of water vapor in the outlet gas exceeds the amount of hydrogen fluoride by a considerable margin, and condensation of the HF - H₂O mixture would occur when the sample was cooled. Condensation would reduce the amount of hydrogen fluoride in the gas phase, and, therefore, reduce the effect shown in Figure 5. If a

FIGURE 5
EFFECT OF MOISTURE ON CALCULATION
OF FLUORINE REMOVAL EFFICIENCY

sufficient amount of water were present, the total moles in the gas phase could be reduced below the "dry basis" assumed for Equation 1. That is, condensation could cause an erroneously low efficiency to be calculated. A similar error could result if droplets of caustic solution bypassed the entrainment separator and were collected in the sample bulb. This latter situation would cause the maximum bias of this type, because the reaction of the caustic with the hydrogen fluoride would drastically reduce the vapor pressure exerted by the liquid. The "condensation" error is presented graphically in Figure 6, where it is shown that the maximum bias of this type would be about -6 percent. The data for this figure were derived by assuming that the pressure in the sample bulbs resulted only from oxygen and nitrogen; the derivation is presented in Appendix B.

A portion of the "dry" efficiency data in Appendix A was examined further using analysis of variance (ANOVA) techniques in an attempt to determine the effects of diluting the fluorine with nitrogen and the effects of varying the flow of caustic solution. The data from the runs where the inlet fluorine flow was 3 scfm were divided into two groups. One group represented the data where no diluent nitrogen was used; the other group consisted of data collected when 3 scfm of nitrogen was used to dilute the fluorine. Each of these large groups then was subdivided further into three smaller groups corresponding to caustic flows of 3, 2.25, and 1.5 gal./min. A total of 47 data points were used; these data are presented in Appendix B.

FIGURE 6 EFFECT OF CONDENSATION OR CARRY-OVER OF WATER ON
CALCULATED FLUORINE REMOVAL EFFICIENCY

The results of the analysis of variance are shown in Table VII. The F tests show that there may be a very slight indication (probability of error = 0.28) of an increase in efficiency with caustic flow, and there is a slight indication (probability of error = 0.082) of a drop in efficiency caused by dilution. However, neither effect could be termed statistically significant. This does not necessarily mean that such effects were not present. Rather, it is more likely that such effects were masked by the error in the measurements, by a natural variation in scrubber performance, and /or by the biases caused by water in the outlet gases.

No good explanation can be offered for the presence of nitroxy fluoride in the effluent gases. This gas was detected in runs where no diluent nitrogen was present in the inlet gases, and infrared analyses of the inlet fluorine stream indicated no nitrate impurities. Chemical analyses of the inlet and outlet caustic solution showed an increase in nitrate concentration upon passing through the scrubber. The possibility of foreign material inside the scrubber also is unlikely. Only Teflon and metal were used as materials of construction. Analyses of the gaseous effluents from the scrubber indicate that about one pound of nitrate radical (as NO_3F) was vented during the experiments, and more nitrate may have been discharged with the spent caustic. Therefore, if foreign material were present within the apparatus, it should have been apparent upon inspection. However, repeated inspections of the interior of the apparatus indicated no contamination.

Table VII

ANALYSIS OF VARIANCE FOR SCRUBBER EFFICIENCY DATA*

Source	Sum of Squares	Degrees of Freedom	Mean Square
Dilution	150.15	1	150.15
Caustic Flow	112.96	4	28.24
Error	879.58	41	21.45
Total	1142.69	46	

F test for caustic flow: $\frac{28.24}{21.45} = 1.316$, $Q(1.316|4,41) = 0.28$

F test for dilution: $\frac{150.15}{28.24} = 5.317$, $Q(5.317|1,4) = 0.082$

*The data are presented in Appendix B.

It is possible that the caustic contained a nitrogen compound that reacted within the scrubber to produce nitrate. It also is possible that the analytical procedure for determining nitrates in the caustic solution was in error. However, there is no direct evidence to support either hypothesis.

Because the OF_2 threshold limit value (TLV) is 20 times more stringent³⁹ than the fluorine TLV, the presence of OF_2 in the effluent gases was a matter of concern. However, OF_2 usually was detected only at the start of each experimental run. Because of this unusual behavior, it is hypothesized that the majority of this gas was produced by the reaction of fluorine with solid deposits of potassium hydroxide within the scrubber. The reaction of solid potassium hydroxide with fluorine has been reported²² to produce a mixture of oxygen and oxygen difluoride. Deposits of hydroxide were to be expected within the scrubber, resulting from traces of caustic solution that had dried since the previous run.

Because both OF_2 and NO_3F are very toxic gases, calculations were performed to compare the relative toxicity of the inlet and outlet scrubber gases. The procedure used, which is described in Appendix B, contains the implicit assumption that the relative environmental toxicity of a substance is³⁹ proportional to its molar flowrate divided by the threshold limit value for that substance*.

*The threshold limit value (TLV) is a quantity defined by the American Conference of Governmental Industrial Hygienists. With some exceptions, it refers to the maximum time-weighted concentration of a substance that can be safely tolerated by a worker for an 8-hour workday and a 40-hour workweek.

This procedure is not recommended by the American Conference of Governmental Industrial Hygienists. Furthermore, the TLV's are based on the effects of a substance upon humans and/or animals, but most ambient fluoride standards were enacted to protect plantlife. However there is no other readily available method to use for such calculations, and the procedure at least provides a cursory overview and can point out potential problems.

The calculation was made by assuming that the concentration of OF_2 and NO_3F in the outlet gases were 0.05 and 0.4 mole percent, respectively. It was assumed that the inlet fluorine and nitrogen flowrates were both 3 scfm and that the fluorine removal efficiency was 90 percent. The calculation, which is presented in Appendix B, indicates that the relative toxicity of the inlet fluorine is reduced by about 80 percent by the scrubber.

This result would indicate that the presence of OF_2 and NO_3F does not drastically impair the effectiveness of the caustic scrubber as a pollution control device. However, for a proper evaluation of the harmfulness of any pollutant mixture, environmental scientists and certified industrial hygienists should be consulted.

E. Conclusions and Recommendations: The large amount of scatter in the scrubber efficiency results precludes any analysis of the data that would lead to correlations for predicting scrubber efficiencies at other operating conditions. However, at a liquid flowrate of 3 gpm and at

fluorine feed rates of 1 to 4 scfm, the scrubber may be relied upon to remove about 90 percent of the fluorine feed — even when the fluorine is diluted by up to 50 percent with inert gases.

If there are to be future caustic scrubber experiments, more precise instrumentation and analytical procedures should be used. Mass flowmeters should be considered for monitoring the inlet gases, and a reliable method should be developed for measuring the fluoride concentration in concentrated caustic solutions. The fluoride removal efficiency could then be determined by monitoring the fluoride concentration in the spent caustic solution. These measures should provide more reliable data, and enable the prediction of scrubber performance over a wider range of operating variables.

Although the 5-inch scrubber will remove 90 percent of the inlet fluorine under the stated conditions, two very toxic reaction products, nitroxy fluoride and oxygen difluoride, are produced within the scrubber. High concentrations of OF_2 (maximum concentration = 5.7 mole percent) were encountered only at the start of each experiment. Therefore, it is hypothesized that this gas was produced by the reaction of fluorine with solid deposits of potassium hydroxide. Such deposits were produced by the evaporation of small amounts of caustic left in the scrubber after each previous experiment.

The oxygen difluoride concentrations dropped appreciably after the scrubber was in operation about 10 minutes, but the nitroxy fluoride

was more ubiquitous. Almost every sample of outlet gases showed traces of this toxic, explosive gas; the average concentration detected was 0.4 mole percent. Within the range of NO_3F concentrations encountered, there should be no explosion hazard. The presence of this toxic gas in the scrubber effluent reduces the effectiveness of the scrubber somewhat, but does not preclude the use of the scrubber as a pollution control device. However, further work should be performed to pinpoint the source of the NO_3F within the scrubber system, and qualified environmental scientists and industrial hygienists should be consulted to substantiate that the scrubber effluents are relatively harmless compared to the inlet fluorine flow.

Note that fluorine experiments should not be conducted without a complete commitment to safety and a thorough knowledge of the toxic, corrosive, and explosive properties of fluorine. Fluorine is extremely corrosive to pulmonary and epidermal tissues and can react explosively with many common materials.

COMPARISON OF THE CAUSTIC SCRUBBER AND FLUIDIZED BED PROCESSES

In an attempt to quantitatively compare the scrubber with the fluidized bed, preliminary designs and conceptual cost estimates were prepared for both systems. In the following narrative the two process designs are described briefly, and the relative merits of each system are discussed.

If the caustic scrubber were used as an industrial fluorine disposal device, a caustic regeneration system would have to be used. As described in Section II B, this system would consist of apparatus for adding slaked lime, filters or centrifuges for removing the calcium fluoride that would be formed, and sludge lagoons for retaining the calcium fluoride sludge. A pH - adjustment station also would be required at the outfall of the lagoons to avoid violating water quality standards.

Nuclear safety systems also would be required to assure that a nuclear criticality could not occur. One such system would consist of redundant ionization detectors to monitor the scrubber inlet gases; if the detectors sensed unusually high concentrations of uranium, the scrubber would be bypassed automatically, and the gases would be vented through special uranium-trapping systems to the atmosphere. The caustic regeneration system presents other nuclear safety problems, because the system is not geometrically safe and because uranium could conceivably precipitate and collect within the system. However, it seemed likely that any uranium entering the scrubber would precipitate immediately. Brief laboratory studies were performed by A. J. Saraceno of the GAT Process Technology Department to confirm this hypothesis; the results are shown in Table VIII.

Table VIII

EFFECT OF FLUORIDE CONCENTRATION ON URANIUM
SOLUBILITY IN A 5 WEIGHT PERCENT KOH SOLUTION*

<u>Fluoride Molarity</u>	<u>Dissolved Uranium, mg/l</u>
0.007	29
0.507	6.4
1.007	3.2

*These values were calculated from data presented in Reference 52.

Those results indicate that a filter installed between the scrubber and the caustic regeneration system would increase the inherent safety of that system. If a scrubber system were to be constructed, automatic, cartridge-type filters would be used for that purpose.

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The General Electric fluidized alumina bed³¹ discussed in Section II C did not provide a nuclearly safe geometry for high assay uranium. To properly evaluate the use of the fluidized bed at GAT, a new, annular, geometrically-safe design was prepared by R. L. O'Doherty⁵³ of ~~the~~ GAT Plant Engineering. The total design incorporated fluidized transport of the alumina feed and the aluminum fluoride waste stream. It also included a much more sophisticated control system than the General Electric design, and redundant ionization chambers were provided for as described above. Provision was made to permanently store the soluble aluminum fluoride wastes in an underground storage vault.

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Similar cost estimates were prepared for the caustic scrubber system. When both capital and operating costs were compared, it was discovered that the costs essentially were equal within the accuracy of the estimates ($\pm 35\%$). Therefore, a final process selection would have to be based upon more accurate cost estimates or intangible factors such as efficiency, safety, and ease of operation.

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In general, this author agrees with the comparison of Lambert and Dotson shown in Table IV. However, there are some disagreements. If a filter

were installed between the scrubber and the regeneration system, the author believes that the "confinement of radioactivity" and "nuclear safety" aspects of the two systems would be essentially equal. Lambert and Dotson favored the scrubber in both categories.

Lacking better cost estimates, it would appear that the fluidized bed would be the better process for the GAT Oxide Conversion Facility because of its higher fluorine removal efficiency (99% for the bed vs. 90% for the scrubber) and the lack of toxic by-products such as OF_2 and NO_3F . There also may be another advantage to the fluidized bed. Both the scrubber and the bed designs provide for long-term storage of the solid wastes. Such storage is necessary because there is no viable market for waste calcium fluoride and because the wastes from both processes would be contaminated with traces of uranium. However, the Energy Research and Development Administration plans to request a change in the present Nuclear Regulatory Commission limits on radioactivity in recycled metals, to allow the sale of small amounts of lightly contaminated scrap. If the limits were changed, it might be possible to sell the waste aluminum fluoride to aluminum companies as a feed stock or to steel mills for use as flux. If such wastes were salable, it would give the alumina bed a clear advantage over the caustic scrubber.

APPENDICES

- A. Experimental Results
- B. Analyses of Results
- C. An Introduction to Nuclear Safety
- D. References

APPENDIX A: EXPERIMENTAL RESULTS

Table A-1. Scrubber Efficiency Results

<u>Date</u>	<u>Total Caustic Flow (gpm)</u>	<u>Inlet Fluorine Flow (scfm)</u>	<u>Inlet Nitrogen Flow (scfm)</u>	<u>Time</u>	<u>Fluorine Concentration in Outlet Gases (mole %)</u>	<u>Fluorine Removal Efficiency (%)</u>
7/20/72	3	3	3	13:02 (5)*	4.7	92.8
				13:07	0.2	99.7
				13:12	5.1	92.2
				13:17	8.2	87.2
7/21/72	3	3	3	10:10 (4)	12.5	80.0
				10:17	6.4	90.1
				10:21	6.6	89.8
				10:27	4.2	93.6
7/24/72	3	1	1	10:00 (4)	1.5	97.7
				10:06	1.9	97.2
				10:13	2.2	96.7
7/25/72	3	1	1	13:05 (3)	7.1	89.0
				13:11	4.5	93.1
				13:20	1.8	97.2
8/07/72	3	3	3	10:00 (6)	2.9	95.6
				10:05	5.7	91.2
				10:12	3.6	94.5
8/08/72	3	3	3	9:50 (10)	8.4	86.8
8/09/72	3	3	3	9:55 (14)	5.5	91.5
8/10/72	3	3	3	10:41 (12)	2.5	96.2
8/14/72	3	3	3	13:05 (5)	9.7	84.7
				13:15	6.3	90.2
9/06/72	3	3	3	13:40 (6)	5.9	90.9
				13:44	6.6.	89.8
				13:52	7.1	89.0
				13:58	7.4	88.5
9/08/72	3	3	3	10:15 (5)	12.2	80.5
				10:19	11.0	82.5
				10:26	8.4	86.8
9/11/72	3	4	0	13:12 (?)	11.1	94.1
				13:19	3.7	98.1

<u>Date</u>	<u>Total Caustic Flow (gpm)</u>	<u>Inlet Fluorine Flow (scfm)</u>	<u>Inlet Nitrogen Flow (scfm)</u>	<u>Time</u>	<u>Fluorine Concentration in Outlet Gases (mole %)</u>	<u>Fluorine Removal Efficiency (%)</u>
9/12/72	3	3	0	13:03 (3)	3.2	98.4
				13:06	6.4	96.7
				13:09	9.3	95.1
				13:13	14.1	92.4
9/13/72	3	2	0	13:19 (?)	0.76	99.6
				13:22	2.1	98.9
				13:29	5.8	97.0
				13:38	6.1	96.8
9/15/72	2.25	3	3	13:06 (5)	8.5	86.7
				13:09	5.1	92.2
				13:13	7.9	87.7
				13:21	8.3	87.0
9/18/72	1.5	3	3	13:09 (5)	7.8	87.8
				13:12	9.4	85.2
				13:15	4.4	93.2
				13:23	4.2	93.6
9/19/72	3	2	2	13:05 (5)	6.02	90.7
				13:08	8.26	87.1
				13:12	5.26	91.9
				13:20	5.75	91.1
9/20/72	2.25	3	0	13:03 (3)	5.2	97.3
				13:06	9.2	95.2
				13:11	10.8	94.3
				13:19	3.7	98.1
9/22/72	1.50	3	0	13:09 (5)	7.4	96.2
				13:12	8.9	95.3
				13:17	17.5	90.4
				13:25	12.97	93.1
9/25/72	1.88	3	0	13:16 (5)	8.5	95.6
				13:19	10.5	94.5
				13:23	13.1	92.1
				13:31	19.4	89.3
9/26/72	1.88	3	0	10:25 (6)	10.7	94.4
				10:27	10.9	94.2
				10:31	24.9	85.8
				10:38	20.7	88.5
9/26/72	1.5	3	0	13:27 (6)	37.6	76.9
				13:29	17.3	90.5
				13:34	10.9	94.2
				13:41	18.5	89.8

*The values in parentheses refer to the time elapsed in minutes since the fluorine flow was initiated.

Table A-2. Results of Infrared Analyses

<u>Date</u>	<u>Time/Location</u>	<u>OF₂</u> (mole %)	<u>NO₃F</u> (mole %)	<u>CF₄</u> (mole %)
7/20/72	13:01/O*	<0.02 ND**	---***	---
	13:02/D	<0.07 ND	---	---
	13:07/O	<0.01 ND	---	---
	13:08/D	<0.06 ND	---	---
	13:13/O	<0.01 ND	---	---
	13:14/D	<0.06 ND	---	---
	13:16/O	<0.01 ND	---	---
	13:18/D	<0.08 ND	---	---
7/21/72	10:09/O	2.9	---	---
	10:12/D	<0.01 ND	---	---
	10:17/O	<0.02 ND	---	---
	10:18/D	<0.03 ND	---	---
	10:20/O	<0.04 ND	---	---
	10:21/D	<0.01 ND	---	---
	10:28/O	<0.02 ND	---	---
	10:29/D	<0.07 ND	---	---
7/24/72	10:02/O	<0.01 ND	---	---
	10:03/D	<0.08 ND	---	---
	10:05/O	<0.5****	---	---
	10:07/D	<0.05 ND	---	---
	10:13/O	<0.3****	---	---
	10:14	<0.05 ND	---	---
7/25/72	13:06/O	<0.11 ND	---	---
	13:07/D	<0.11 ND	---	---
	13:12/O	<0.11 ND	---	---
	13:13/D	<0.12 ND	---	---
	13:19/O	<0.11 ND	---	---
	13:21/D	<0.07 ND	---	---
8/07/72	9:58/O	0.4	---	---
	10:01/D	<0.1 ND	---	---
	10:06/O	<0.15 ND	---	---
	10:07/D	<0.02 ND	---	---
	10:13/O	<0.07 ND	---	---
	10:14/D	<0.03 ND	---	---
8/08/72	9:52/O	<0.07 ND	---	---
8/09/72	9:54/O	<0.05 ND	---	---
8/10/72	10:42/O	<0.03 ND	1.03	---

<u>Date</u>	<u>Time/Location</u>	<u>OF₂</u> (mole %)	<u>NO₃F</u> (mole %)	<u>CF₄</u> (mole %)
8/14/72	13:06/O	<0.02 ND	0.7	--
	13:07/D	<0.01 ND	<0.06 ND	--
	13:16/O	<0.01 ND	0.6	--
	13:17/D	<0.01 ND	<0.06 ND	--
9/11/72	13:12/O	<0.03	<0.03 ND	0.01
	13:19/O	0.10	<0.03 ND	0.01
9/12/72	13:04/O	0.04	<0.06	0.01
	13:07/O	0.07	<0.06	0.06
	13:10/O	0.07	<0.03 ND	0.08
	13:14/O	0.07	<0.1****	0.08
	13:18/D	<0.01 ND	<0.03 ND	ND
9/13/72	13:19/O	<0.01 ND	0.3	0.02
	13:22/O	<0.01 ND	0.3	0.02
	13:29/O	<0.02 ND	1.3	0.02
	13:34/D	<0.01 ND	<0.01 ND	ND
	13:38/O	<0.01 ND	0.5	0.01
9/15/72	13:07/O	4.5	<0.01 ND	0.02
	13:10/O	<0.03 ND	0.6	0.01
	13:14/O	<0.02 ND	0.5	0.01
	13:19/D	<0.01 ND	<0.02 ND	ND
	13:22/O	<0.03 ND	0.6	0.01
9/18/72	13:09/O	3.6	<0.4	0.1
	13:12/O	SAMPLE LOST		
	13:15/O	<0.01 ND	1.2	0.1
	13:20/D	<0.01 ND	<0.01 ND	0.001
	13:23/O	<0.01 ND	1.3	0.08
9/19/72	13:05/O	5.6	<0.07	0.1
	13:08/O	5.7	<0.01 ND	0.1
	13:12/O	<0.01 ND	0.6	0.08
	13:16/D	<0.01 ND	<0.01 ND	ND
	13:20/O	<0.01 ND	0.5	0.07
9/20/72	13:03/O	0.2	0.2	0.01
	13:06/O	0.05	0.2	0.007
	13:11/O	0.02	0.2	0.006
	13:15/D	<0.01 ND	<0.01 ND	0.002
	13:19/O	<0.02 ND	0.2	0.005
9/22/72	13:09/O	<0.02 ND	0.1	0.005
	13:12/O	<0.02 ND	0.1	0.007
	13:17/O	<0.02 ND	0.1	0.008
	13:20/D	<0.01 ND	<0.01 ND	0.001
	13:25/O	<0.02 ND	0.1	0.008

<u>Date</u>	<u>Time/Location</u>	<u>OF₂</u> <u>(mole %)</u>	<u>NO₃F</u> <u>(mole %)</u>	<u>CF₄</u> <u>(mole %)</u>
9/25/72	13:16/O	0.1	0.1	0.001
	13:19/O	0.02	0.3	0.02
	13:23/O	<0.02 ND	0.1	0.02
	13:27/D	<0.01 ND	<0.01 ND	0.001
	13:31/O	0.1	0.1	0.02

*The "O" symbol refers to a sample of the outlet gases from the scrubber; "D" refers to a gas sample from the leveling drum.

**"ND" means "not detected." An entry such as "<0.01 ND" means that the gas in question was not detected and that the limit of detection was 0.01 mole %. An entry such as "<0.03" means the gas was detected, but at a low concentration very near the limit of detection.

***The sample was not analyzed for the indicated species.

****This sample indicated possible interference at the requisite wavelength from an unknown molecular species; the result is questionable.

APPENDIX B: ANALYSIS OF RESULTS

B-1. Derivation of Fluorine Removal Efficiency (Dry Basis)

The equation to be derived, called Equation 1 in the narrative, was used to calculate the scrubber efficiencies presented in Table V and in Appendix A. In this derivation it is assumed that fluorine, not hydrogen fluoride, is present in the outlet gases, and the presence of water vapor is ignored.

Let F = inlet flow of fluorine to the scrubber (scfm),
 N = inlet flow of nitrogen to the scrubber (scfm),
 M = the mole fraction of fluorine measured in the outlet gases, and
 X = the fraction of fluorine removed by the scrubber.

The proportions of the gases in a sample of outlet gases is

fluorine = $(1-X)F$,
 nitrogen = N ,
 oxygen = $XF/2$, and
 water = zero.

Therefore, the mole fraction of fluorine in the outlet gases is

$$M = \frac{(1-X)F}{N + \frac{(1-X)F + XF}{2}}$$

Then, $X = \frac{F-M(N+F)}{F(1-\frac{M}{2})}$, and

$$\text{Fluorine Removal Efficiency (\%)} = 100 \left[\frac{F-M(N+F)}{F(1-\frac{M}{2})} \right]$$

B-2 Derivation of Fluorine Removal Efficiency (Wet Basis)

The following derivation will be made assuming the presence of water vapor in the outlet gases. The expressions that are derived were used to produce Figure 5 in the narrative.

Use the definitions in the previous derivations; in addition,

Let

W = mole fraction of water vapor in outlet gases.

For clarification, note that the composition (i.e. molar flow rates) of the outlet gases before the reaction between fluorine and water is:

Outlet gases (scfm) = $\left[(1-x)F + N + \frac{XF}{2} \right] [1 + W]$, and

the molar flow rate of each gas (i.e. the relative proportions of the gases in the sample bulb) before reaction is:

fluorine = $(1-x)F$,

nitrogen = N ,

oxygen = $\frac{XF}{2}$, and

water = $W \left((1-x)F + N + \frac{XF}{2} \right)$.

Then, the fluorine and water in the sample bulb react forming hydrogen fluoride and oxygen.

Two equations will now be derived. One equation for the situation where the moles of fluorine exceed the moles of water; the other equation, where water vapor is in excess. In all of the equations, it is assumed that the reaction goes to completion.

a. Moles fluorine > moles water

After reaction the proportions of gases in the sample bulb may be expressed as:

$$\text{fluorine} = \left\{ (1-X)F - \left[(1-X)F + N + \frac{XF}{2} \right] W \right\},$$

$$\text{hydrogen fluoride} = 2W \left[(1-X)F + N + \frac{XF}{2} \right],$$

$$\text{nitrogen} = N,$$

$$\text{oxygen} = \frac{XF}{2} + \frac{W}{2} \left[(1-X)F + N + \frac{XF}{2} \right], \text{ and}$$

$$\text{water} = \text{zero}.$$

Therefore, as measured by the laboratory,

$$M = \frac{(1-X)F}{\left\{ (1-X)F - \left[(1-X)F + N + \frac{XF}{2} \right] W \right\} + 2W \left[(1-X)F + N + \frac{XF}{2} \right] + N + \frac{XF}{2} + \frac{W}{2} \left[(1-X)F + N + \frac{XF}{2} \right]}$$

$$= \frac{(1-X)F}{\left(1 + \frac{3W}{2}\right) \left[(1-X)F + N + \frac{XF}{2} \right]}, \text{ and}$$

$$\text{fluorine removal efficiency (\%)} = 100 \times$$

$$= 100 \left[\frac{F - M \left(1 + \frac{3W}{2}\right) (N+F)}{F \left(1 - \frac{M \left(1 + \frac{3W}{2}\right)}{2}\right)} \right].$$

b. Moles water > moles fluorine

After reaction the proportions of gases in the sample bulb may be expressed as:

fluorine = zero,

nitrogen = N,

$$\text{water} = W \left[(1-X)F + N + \frac{XF}{2} \right] - (1-X)F,$$

$$\text{oxygen} = \frac{XF}{2} + \frac{(1-X)F}{2}, \text{ and}$$

$$\text{hydrogen fluoride} = 2F(1-X).$$

Then, as measured by the laboratory,

$$M = \frac{(1-X)F}{N + \left\{ W \left[(1-X)F + N + \frac{XF}{2} \right] - (1-X)F \right\} + \frac{XF}{2} + \frac{(1-X)F}{2} + 2(1-X)F}$$

$$= \frac{(1-X)F}{(1+W) \left[(1-X)F + N + \frac{XF}{2} \right] + \frac{(1-X)F}{2}};$$

fluorine removal efficiency (%) = 100X

$$= 100 \left[\frac{M(1+W)(F+N) - F(1 - \frac{M}{2})}{\frac{MF}{2}(1+W) - F(1 - \frac{M}{2})} \right].$$

B-3. Derivation of Fluorine Removal Efficiency (with Condensation)

The following derivation will be made assuming that a very high concentration of water vapor is present in the gas sample, a much higher concentration than assumed in derivation B-2. The water vapor would condense before the pressure of the sample was measured, and the condensation would appreciably reduce the vapor pressure of hydrogen fluoride in the sample bulb. In fact, it will be assumed that the vapor pressure of both water and hydrogen fluoride is negligible. This situation also could arise if traces of caustic solution were entrained and carried over into the sample bulb. The equation derived was used to produce Figure 6 in the narrative, it represents the maximum bias (compared to the "dry basis" derivation) that could result.

The proportions of the gases in the sample bulb may be expressed as:

fluorine = zero,
hydrogen fluoride $\approx$ zero,
nitrogen = N,
water $\approx$ zero, and
oxygen = F/2.

Then, as measured by the laboratory,

$$M = \frac{(1-X)F}{N + F/2} .$$

Note that M is the mole fraction of fluoride measured by the laboratory, when essentially all of the fluoride is contained in the liquid in the sample bulb. The laboratory would measure the pressure of the gases in the sample bulb to determine the total moles of material in the bulb. However, they would ignore the liquid in the

bottom of the bulb. Therefore, they would measure all of the fluoride in the bulb when they titrated, but only a portion of the total moles in the bulb would be measured (i.e., The fluoride in the liquid phase would be missed.).

Under the stated conditions (i.e., condensation of water and hydrogen fluoride with negligible vapor pressure), the actual fluoride removal efficiency would be equal to

$$\text{Fluorine Removal Efficiency (\%)} = 100 \left[1 - M \left(\frac{1}{2} + \frac{N}{F} \right) \right] .$$

However, the efficiency values in the tables were calculated assuming no water vapor and no condensation (i.e., "dry basis"). On a dry basis the efficiency would be equal to

$$100 \left[\frac{F - M(N + F)}{F \left(1 - \frac{M}{2} \right)} \right] .$$

Therefore, the maximum percentage error, assuming that condensation occurred, would be

$$\% \text{ Error} = 100 \left\{ 1 - \frac{\left[\frac{F - M(N + F)}{F \left(1 - \frac{M}{2} \right)} \right]}{\left[1 - M \left(\frac{1}{2} + \frac{N}{F} \right) \right]} \right\} .$$

This is the quantity plotted in Figure 6.

B-4. Data for Analysis of Variance Calculations (Table VII)

The following data are listed within groups in the order that they appear in Appendix A. All of these fluorine removal efficiencies were calculated from runs where the fluorine flow was 3 scfm.

	<u>Nitrogen flow = 3 scfm</u>			<u>Nitrogen flow = 0</u>		
	<u>3 gal/min.</u>	<u>2.25 gal/min.</u>	<u>1.5 gal/min.</u>	<u>3 gal/min.</u>	<u>2.25 gal/min.</u>	<u>1.5 gal/min.</u>
	92.8	86.7	87.8	98.4	97.3	76.9
	99.7	92.2	85.2	96.7	95.2	90.5
	92.2	87.7	93.2	95.1	94.3	94.2
	87.2	87.0	93.6	92.4	98.1	89.8
	80.0					96.2
	90.1					95.3
	89.8					90.4
	93.6					93.1
	86.8					
	91.5					
	96.2					
	84.7					
	90.2					
	90.9					
	89.8					
	89.0					
	88.5					
	80.5					
	82.5					
	86.8					
	95.6					
	91.2					
	<u>94.5</u>					
k	23	4	4	4	4	8
ΣX	2064.1	353.6	359.8	382.6	384.9	726.4
ΣX^2	185,758.57	31,278.02	32,415.08	36,615.22	37,046.43	66,217.84
$\bar{X}$	89.74	88.40	89.95	95.65	96.23	90.80
σ	4.86	2.57	4.13	2.55	1.77	6.10

Effect of OF_2 and NO_3F on the Effectiveness
of the Caustic Scrubber

Because both OF_2 and NO_3F are quite toxic, the following relationship is derived to compare the "relative toxicities" of the inlet and outlet scrubber gases to the environment. We will define the "toxicity" to be directly proportional to the molar flow rates (scfm) of the halogen compounds, and inversely proportional to the threshold limit values (TLV's) for the respective gases. The use of such comparisons is not recommended,³⁹ but there is no other readily available method to use for such calculations.

The following conditions are assumed:

1. Inlet fluorine flow = 3 scfm,
2. Inlet nitrogen flow = 3 scfm,
3. Fluorine removal efficiency = 90%,
4. Outlet NO_3F concentration = 0.4 mole percent, and
5. Outlet OF_2 concentration = 0.05 mole percent.

The major reaction within the scrubber produces one-half mole of oxygen for each mole of fluorine consumed. Therefore, the major components of the outlet gases will consist of 3 scfm N_2 , 0.3 scfm F_2 , and 1.35 scfm O_2 . Therefore, the total outlet gas flow will be about 4.65 scfm.

The flowrates of the toxic outlet gases will be as follows:

Fluorine flowrate = 0.3 scfm,
 NO_3F flowrate = $0.004 \times 4.65 \text{ scfm} = 0.0186 \text{ scfm}$, and
 OF_2 flowrate = $0.0005 \times 4.65 \text{ scfm} = 0.002325 \text{ scfm}$.

The threshold limit values for the respective gases are presented in the following table:

<u>Compound</u>	<u>TLV³⁹ (ppm)</u>
F ₂	1
OF ₂	0.05
NO ₃ F	0.1 (assumed by author*)

The "relative toxicity" of the outlet gases compared to the inlet gases will be calculated as follows:

$$\begin{aligned}
 \text{"Relative Toxicity"} &= \frac{\frac{\text{F}_2 \text{ Outlet Flow}}{\text{TLV}(\text{F}_2)} + \frac{\text{OF}_2 \text{ Outlet Flow}}{\text{TLV}(\text{OF}_2)} + \frac{\text{NO}_3\text{F Outlet Flow}}{\text{TLV}(\text{NO}_3\text{F})}}{\frac{\text{F}_2 \text{ Inlet Flow}}{\text{TLV}(\text{F}_2)}} \\
 &= \frac{\frac{0.3 \text{ scfm}}{1 \text{ ppm}} + \frac{0.0186 \text{ scfm}}{0.05 \text{ ppm}} + \frac{0.902325}{0.1 \text{ ppm}}}{\frac{0.3 \text{ scfm}}{1 \text{ ppm}}} = 0.18
 \end{aligned}$$

The calculation leads one to assume, under the stated conditions, that the scrubber would reduce the toxicity of the inlet gases to the environment by about 80 percent. However, this is a very tentative result. For a proper evaluation of any pollutant mixture, environmental scientists and certified industrial hygienists should be consulted.

* The TLV for NO₃F is assumed to be twice that of OF₂, because OF₂ would be produced⁴⁶ by the effect of NO₃F on the water in the lungs. Assuming complete conversion to OF₂, each mole of NO₃F would produce one-half mole of OF₂.

APPENDIX C: AN INTRODUCTION TO NUCLEAR SAFETY

Nuclear safety precautions are taken to avoid an uncontrolled fission reaction; such a reaction is commonly called a criticality. A criticality will generate large amounts of heat and a potentially lethal neutron burst lasting about one second and containing about 10^{17} neutrons. The criticality also creates gamma radiation from slowly decaying fission products. Obviously it is an incident to be avoided.

The most important factors that influence the nuclear safety of a system are (1) the enrichment of the uranium, (2) the density and composition of the given material, (3) the available neutron moderators and reflectors, (4) the size and shape of the material, and (5) interactions with nearby nuclear materials. One sure way of providing the maximum safety in a given system is to provide an always-safe geometry in the design. Certain always-safe design parameters are presented in Table C-1. The values in that table apply only to individually-safe containers (i.e., It is assumed that there are no nuclear materials near enough to the containers to increase the internal neutron flux.). Also, the values in Table C-1 contain a safety factor; for a comparison with actual, experimental critical values, see Tables C-2 and C-3.

The tables cited were taken from internal GAT publications by J. L. Feurbacher, group leader of the GAT Nuclear Engineering Section. For a more detailed review of nuclear safety analysis, the publication by H. C. Patton⁵⁵ is recommended. The publication is available from both NTIS and the Los Alamos Scientific Laboratory Library.

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TABLE C-1
INDIVIDUALLY-SAFE PARAMETERS

Assay (% U-235)	Pipe Diameter		Sphere Diameter		Volume		Slab*	Mass (Kg. U-235)
	(Inches)	(CM)	(Inches)	(CM)	Liters	Cubic Inches		
0.95	∞	∞	∞	∞	∞	∞	∞	∞
1.0	39.6	101	53.4	135	1300	79,600	24.0	55.6
1.25	24.0	61.0	33.0	83.8	308	18,800	13.5	13.2
1.5	20.0	50.8	27.9	70.9	186	11,300	11.0	5.81
1.75	17.6	44.7	24.5	62.2	126	7,700	9.6	3.43
2.0	16.0	40.6	22.3	53.6	95.1	5,800	8.7	2.40
2.5	14.0	35.6	19.6	49.8	64.6	3,940	7.1	1.50
3.0	12.8	32.5	17.9	45.5	49.2	3,000	6.5	1.13
3.5	11.8	30.0	16.7	42.4	40.0	2,440	6.0	1.00
4.0	11.2	28.4	15.8	40.1	33.8	2,060	5.5	0.900
5.0	10.25	26.0	14.6	37.1	27.0	1,650	5.0	0.800
6.0	9.6	24.4	13.4	34.0	20.5	1,250	4.5	0.740
8.0	8.7	22.1	12.3	31.2	16.0	976	3.9	0.650
10	8.2	20.8	11.8	30.0	14.0	854	3.6	0.600
12	7.8	19.8	11.3	28.7	12.5	763	3.4	0.560
15	7.4	18.8	10.9	27.7	11.0	671	3.1	0.520
20	6.9	17.5	10.3	26.2	9.5	580	2.7	0.480
30	6.3	16.0	9.6	24.4	7.7	470	2.2	0.440
40	6.0	15.2	9.2	23.4	6.7	409	2.0	0.410
50	5.7	14.5	8.9	22.6	6.0	366	1.9	0.390
75	5.2	13.2	8.3	21.1	5.0	305	1.6	0.360
93	5.0	12.7	8.24	20.9	4.8	293	1.5	0.350
100	5.0	12.7	8.24	20.9	4.8	293	1.5	0.350

*Steel container or half-reflected.

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TABLE C-2
EXPERIMENTAL MINIMUM CRITICAL CYLINDER DIAMETERS

Assay (wt. % U ²³⁵)	Container	Moderation* (H/U ²³⁵)	Reflector	Critical Diameter		Maximum Non-Critical Diameter	
				(cm.)	(in.)	(cm.)	(in.)
~90	Aluminum	52.9	Water	15.2	6.0	14.0	5.5
~90	Aluminum	44.3	Air	22.3	8.76	20.3	8.0
~90	S. Steel	44.3	Water	15.2	6.0	-	-
~90	S. Steel†	62.7	Water	20.3	8.0	17.8	7.0
~90	S. Steel	74.6	Air	22.9	9.0	20.3	8.5‡
4.9	Aluminum	530§	Water	38.1	15.0	-	-
4.9	S. Steel	530§	Water	38.1	15.0	30.5	12.0
2.0	None	294	Paraffin	50.8	20.0	-	-

*Moderation for shortest critical length measured; probably near optimum moderation except as noted.

†0.02-inch cadmium shield (~0.44 g./cm.²).

‡Solution height 90 inch, H/U²³⁵ ratio 44.3.

§Optimum moderation probably much lower.

TABLE C-3
EXPERIMENTAL MINIMUM CRITICAL VOLUMES

Assay (wt. % U^{235})	Container	Moderation* (H/ U^{235})	Reflector	Diameter (cm.) (in.)		Height (cm.) (in.)		Min. Volume (liters)	Corresponding Sphere Diameter (cm.) (in.)	
~90	Aluminum	52.9	Water	20.3	8.0 [†]	19.5	7.7	6.32	22.9	9.02
~90	Aluminum	47.4	Water	23.0	9.07 [‡]	-	-	6.32 [§]	22.9	9.02
~90	Aluminum	52.9	Air	25.4	10.0 [†]	34.0	13.4	17.22	32.0	12.6
~90	S. Steel	58.8	Water	20.3	8.0 [†]	20.8	8.2	6.74	23.4	9.2
~90	S. Steel ^ψ	31.6	Water	25.4	10.0 [†]	21.1	8.3	10.69	27.3	10.8
~90	S. Steel	62.7	Air	25.4	10.0 [†]	31.7	12.5	16.05	31.3	12.3
4.9	Aluminum	530 [¶]	Water	38.1	15.0 [†]	44.7	17.6	51.0	45.8	18.0
4.9	S. Steel	530 [¶]	Air	50.8	20.0 [†]	38.6	15.2	78.2	53.0	20.9
2.0	None	404	Paraffin	58.4	23.0	55.4	21.8	146.3	65.4	25.7

*Moderation for minimum critical volumes measured; probably near optimum moderation except as noted.

[†]Diameter of cylinder.

[‡]Diameter of sphere.

[§]The critical volume lacked 80 cc. of filling the spherical reactor..

^ψ0.02-inch cadmium shield (~0.44 g./cm.²)

[¶]Optimum moderation probably lower.

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