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CHEMICAL DEVELOPMENT DIVISION
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AECD-3963

RECOVERY FROM SALVAGE RESIDUE

BY

FLUORINATION IN VERTICAL REACTORS

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Oak Ridge, Tennessee
September 6, 1946

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INTRODUCTION

The reclamation of the appreciable amounts of uranium which remain in the Beta salvage residue after standard salvage treatment has been an increasingly serious problem, due to the backlogging of this material at a considerable and growing rate.

Among the promising solutions to the problem was a small scale experiment on hydrofluorination of the residue to remove large quantities of interfering silicates, followed by a fluorination treatment to remove uranium. It was desired to investigate this method in a pilot plant to determine the practicability of applying it on a scale large enough to process the daily production of salvage residue in addition to a reasonable portion of the backlog, roughly 750 pounds per day.

A successful conclusion to the investigation would require the development of a process which would satisfy the following conditions:

- (a) It would be inexpensive enough, including amortization of the original cost, to make the uranium recovery profitable.
- (b) It would recover substantially all of the uranium from the residue--that is, prove a final salvage step.
- (c) It would be adaptable to production scale conditions of safety, ease of operation, large volume output, and low maintenance. In the latter categories a great many smaller problems arose under operating conditions.

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PREVIOUS WORK

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Laboratory Phase

Much laboratory work has been done on the treatment of heterogeneous solids by elemental fluorine for the removal of uranium as the volatile hexafluoride. Indeed, the method is the basis of one standard laboratory analysis for uranium.

Due to the complex nature of the general salvage residue and its consequent resistance to the usual chemical separation processes, Dr. Fred Smith, in the summer of 1944, investigated the application of a fluorination step to the residue.⁽¹⁾ It was found that a good separation could be effected of uranium from copper, nickel, and iron, which formed nonvolatile fluorides. The volatile uranium hexafluoride was easily condensed in a series of traps cooled by dry ice and trichlorethylene and by liquid oxygen.

A large amount of silica is present in the salvage residue, however, and this was found not only to cause severe clogging of the traps with silicon tetrafluoride but also to interfere with the subsequent chemical recovery of uranium from the trap wash. Hence, a pre-treatment with gaseous hydrogen fluoride was added, which removed the bulk of the silica and partially fluorinated the other materials present, thus conserving the more costly fluorine in the second step. Since only the nonvolatile uranium tetrafluoride is formed in hydrofluorination, it was not necessary to use traps in conjunction with this step.

Smith got optimum results hydrofluorinating at 500 to 600°C., and fluorinating at 450 to 500°C. He reported at length on a laboratory-scale chemical separation of uranium from the trap wash.

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Later, A. Milch investigated the hydrofluorination of various metals and oxides which appear in the salvage residue, further to delineate the optimum conditions and the results to be expected from the treatment.⁽²⁾ He found that the elements Si, Ta, Ti, W, and Mo could be substantially removed from the residue by HF at 650°C. Milch also stated⁽³⁾ that in fluorination of the residue it was necessary to operate at 650°C. or higher to break down a postulated manganese-uranium compound which resisted fluorination at 550°C. In a series of runs on various residues and pure compounds of uranium, he got widely varying recoveries, concluding that difficulties in condensing the uranium hexafluorides in the trap system used prohibited his recovery of more than 98%.

Initial Pilot Plant Phase

The first pilot plant work on the hydrofluorination-fluorination of salvage residue was reported on by V. P. Calkins and G. H. Clewett in July 1945.⁽⁴⁾ Their work, initially with 800 gram batches and eventually on a larger scale using 10 to 12 pounds of charge, was carried out in large, shallow trays inside nickel and monel reactors. The charge was spread in layers only 1/8 inch deep, since it was found that the reaction penetrated only to this depth during the fixed 9-hour HF run and 9-hour F₂ run. This limitation naturally severely restricted the amount of residue which could be processed by a single unit, eventually causing the abandonment of tray fluorination as a practical method for large scale recovery from the salvage residue.

It was found in these experiments that one treatment of the charge, at nine hours for each step, was not sufficient to effect removal of the bulk of the uranium; hence, in most cases three or four fluorinations of each batch were made.

In the development of a trap system for the process, it was found that copper was the best material of construction of those tried, corroding least and, when eventually dissolved in the trap wash, causing least difficulty in the final separation. Three traps cooled by a dry ice--trichloroethylene mixture and one cooled by liquid oxygen were found sufficient to condense all of the UF_6 . These copper traps were cylinders about four inches in diameter, set in dewar flasks filled with the coolant.

Calkins and Clewett discussed various methods of removing the remainder of the uranium from the fluorinated residue, including water and acid leaches, fluorination at $800^{\circ}C.$, and chlorination. They concluded that the latter was the most promising and that it might be preferable as a replacement of the entire fluorination step.

PRESENT WORK

The following pages report the investigation of $HF-F_2$ treatment of general salvage residue, pelletized and charged to vertical reactors in deep beds, in two pilot plant stages.

First, a study is described of the method using equipment designed to treat kilogram batches of residue. Twenty-two HF runs and 10 F_2 runs were made on this small scale, with results falling far short of those predicted by preliminary work but encouraging to further work.

The second section of this paper describes a 23 run investigation in virtually production scale equipment, handling 50 pounds per batch, and the disadvantages which finally resulted in abandonment of the program.

ONE KILOGRAM REACTOR

Introduction

Despite the measure of success achieved in hydrofluorination-fluorination of salvage residue on a pilot plant scale by Clowett and Calkins, after completion of their work the program was dropped in favor of other methods. Chief of the disadvantages in the method was the relatively small volume of charge which could be processed with a reasonable amount of equipment, because of the unfortunate necessity of charging the residue to the reactor in very thin layers.

The present experiment was conceived after G. S. Parsons had success in gaseous chlorination of various uranium oxides in large volume by pelletizing the charge and carrying out the reaction at high temperature in a vertical reactor.⁽⁵⁾ Investigation showed that the salvage residue could be successfully pelletized after being ball-milled and mixed with 10 to 20% water to act as a binder. It was decided to construct a vertical reactor and auxiliary equipment to hydrofluorinate and fluorinate kilogram batches of pelletized residue.

Discussion and Conclusions

A thorough investigation of the optimum conditions of reaction was not attempted in this series of runs in the one kilogram reactor. After it had been demonstrated that the hydrofluorination-fluorination of pelletized salvage residue in a vertical reactor was practical, it was decided to go to a unit of approximately production scale. Only enough further runs were made in the small reactor to determine the best reactor and trap design, construction materials, and rough operating procedure for planning of the larger unit.

Hydrofluorination.--It had been shown in preliminary laboratory work that fluorination of the salvage residue was a complicated and almost vain process unless the bulk of the silica present had been removed by a pre-hydrofluorination. Selective trapping of SiF_4 and UF_6 was not practical, and separation of the UF_6 from a 1:100 mixture with SiF_4 by chemical means would offer as difficult a problem as did treatment of the original residue. Therefore, when it was shown in the kilogram reactor that the pelletized material could be successfully treated with HF, interest was greatly stimulated in the whole process, since the fluorination reaction had been judged the more likely of the two to be efficient.

The pellets, after removal of their high moisture content during the initial drying phase, apparently were quite porous. Since the material had been finely ground before pelletization, it presented a very large surface to the gaseous reagents, as testified by the rapid reaction both with HF and F_2 . Random charging of the pellets prevented formation of channels for the gases initially, and although there was usually a large decrease in the bulk of the charge and some sintering during the reaction, the pellets retained their identity well enough to continue good gas dispersion. Hence, as was shown by temperature variations, the primary reaction zone did not include the whole charge immediately, but appeared at first at the bottom and moved slowly up the reactor.

The average silica content of twenty hydrofluorinated residues in this small unit was 1.92%, reduced from an average initial content of about 33%. These were grouped as shown in table 1. The preponderance of results below 0.5% silica gave hope that reaction conditions could be found

which would allow complete silica removal for every residue. No correlation could be drawn between silica analysis and temperature, reaction time, or HF flow rates for these results.

Table 1

Silica Analyses of HF Residues - Kg. Reactor

<u>Range of Analyses - % SiO₂</u>	<u>Number of Runs</u>
0.00	2
0.00-0.25	4
0.25-0.50	6
0.50-1.00	1
1.00-2.00	3
2.00-10.00	4

Average: 1.92%

Total: 20 runs

In comparison to the fluorination process, hydrofluorination seemed susceptible to large scale operation. The reaction required little attention beyond an occasional raising of the furnace temperature to maintain that of the reactor at the desired level. Since the gaseous products were valueless, no trap system was necessary and the unwanted fumes were very simply disposed of by dissolution in the water aspirator. Corrosion was very limited in these HF runs, the major problems arising during the use of fluorine.

Since it was assured that satisfactory silica removal could be attained, the major problems to be solved in further work were to develop tests to determine the extent of reaction, and to determine optimum operating conditions. No difficulty was anticipated in applying hydrofluorination to a large scale vertical unit.

Fluorination.--Because of numerous equipment failures during fluorination which precluded the completion of many of the runs, analytical

results for evaluation of the process were scanty in the first investigation. Three residues only were suitable for analysis, the uranium contents being reported as 0.011%, 0.01%, and 0.06%. Weight loss data were not available either because of contamination of the residue by corroded reactor parts, but assuming a figure of 50% weight loss and an original analysis of 0.25% uranium in the charge, the reaction efficiencies based on the analyses above would be about 98%, 98%, and 88%.

On the other hand, in five other runs the reaction efficiencies based on chemical analysis of the uranium found in the cold trap washes were 3.5%, 26.3%, 30.5%, 62.8%, and 70.3%. These results could not be correlated with reaction time, temperature, or F_2 rate, and much doubt was cast on the accuracy of analysis of the trap washes by the failure of the laboratory to get reproducible results. However, the wide variation illustrated clearly that analysis and control of the reaction variables were essential to the successful application of fluorination of the residue to a large scale recovery program.

The investigation of equipment for the process provided much more satisfactory results. It was apparent from study of the various grate failures that in so far as was possible all reactor parts which were in contact with fluorine at elevated temperatures should be fabricated of nickel, which had shown little or no corrosion. Where substitution of some other metal was necessary, monel was to be preferred over steel or copper. At room temperature or lower, however, copper proved to be relatively inert to fluorine and a safe and convenient material for lines and traps.

The reactor design proved satisfactory and was modified only slightly in planning for the larger unit. To obtain more efficient dif-

fusion of the entering gas, a third bottom grate was proposed and it was decided for extra protection from corrosion to encase the reactor thermocouple well in a sheath which would also support the grates for insertion and removal.

The double coil cold trap was used as a basis for design of the first traps in the larger unit. It was more easily fabricated than the tube nest trap and appeared to have a higher washing efficiency since the spray nozzle could be placed to avoid all "blind" spots. The cold finger trap design was used for the new liquid oxygen trap. In both cases, a standard jacket was adopted rather than the outside copper coil welded to the trap body.

Equipment

Reactor Assembly.--The reactor was fabricated from a piece of four-inch standard monel pipe with a 1/4 inch wall, 20 inches high, to which was welded a 1/4 inch monel flange on either end. This showed no signs of failure throughout the experiment, in a series of twenty-four HF runs and twelve F₂ runs at temperatures from 500 to 750°C.

The reactor head, of 1/4 inch monel plate, supported a 1/4 inch monel pipe thermocouple well and a 1-1/4 inch copper pipe exit arm. Both the well and the exit pipe had to be replaced because of corrosion several times during the series. A copper thermocouple well proved to offer no advantage over one of monel, both lasting five or six runs.

The chief corrosion problem, however, proved to be that of the metal grates supporting the charge. These were two in number, the first of 1/16 inch monel placed one inch above the reactor bottom for a preliminary

gas diffuser and the second, made at various times of the metals listed below, three inches above this. The top grate, which directly supported the charge, was the chief source of trouble, being in the reaction zone. The following top grates were used in the order and with the results noted.

a. Monel. One-sixteenth inch perforated plate stood up well under HF but suffered corrosion resulting in 1/4 to 1/2 inch diameter holes during F₂ runs. However, only slight corrosion was evident in monel grates of 1/8 inch or 1/4 inch thick.

b. Stainless Steel. (This was substituted by mistake for monel.) On completion of the F₂ run, this grate was found to be entirely consumed except for a thin outside ring next to the reactor wall.

c. Copper. With HF this grate showed no corrosion, but immediately upon introduction of fluorine in two runs, it ignited, melted, and dripped down to ignite the monel lower grate and gas inlet pipe. Although copper ignited almost spontaneously here, as noted above, copper thermocouple wells in the center of the charge were serviceable for five runs or more.

d. Steel. This grate disintegrated in fluorine in a manner similar to that of stainless steel, although to a lesser degree.

e. Nickel. In one-eighth inch grates, the only thickness tried, this metal showed no noticeable corrosion in either HF or F₂. It was deemed satisfactory for further use with these gases.

The reactor was heated in a cylindrical, 115 V, 1.7 KW, Hevi-duty furnace, Model M-5014, which had a temperature range of 1010°C. An insulating bonnet packed with magnesia was placed over the reactor and furnace top, allowing an upper limit of about 800°C to be reached.

Both reactor and furnace temperatures were indicated on a Wheel-co pyrometer using iron-constantan thermocouples.

Trap System.--The second major equipment problem lay in design of cold traps suitable for small scale production operation. Efficient traps had been fabricated during work on the tray reactors but these required laborious hand washing and were poorly adapted to large scale recoveries. Hence, after two fluorine runs using this type three other traps were designed and tested which were water washed with built-in spray nozzles. These were all efficiently insulated by the Steam and Cooling Department.

a. Tube Nest Trap. This trap consisted of a bundle of parallel, vertical copper tubes through which the reaction gases flowed, and around which, in counter-current flow, passed trichlorethylene precooled by dry ice. This coolant was used also in subsequently designed traps. Following the tube nest trap was one of the original design, cooled in liquid oxygen. Assuming that the latter condensed all of the UF_6 entering it, the tube nest trapped 61% of the product in a single run in which it was used. This is an unfavorable contrast to an average of about 90% found in the first trap by Clewett and Calkins, but the internal spray washing proved fairly satisfactory.

b. Double Coil Trap. A four inch diameter copper cylinder containing an inner coil was surrounded by tightly coiled tubing welded to the main body for efficient heat transference. The coolant was pumped through both coils while the reaction gases flowed through the cylinder. In three fluorine runs this trap gave efficiencies of 73%, 93%, and 73%, based again on the total weight of UF_6 condensed in the entire trap system. The spray nozzle appeared to wash down all the material collected in the trap.

c. Cold Finger Trap. This trap differed from that described immediately above only in that a cold finger replaced the central coil, four fins being attached to the finger and extending nearly to the trap wall. Data available for one run with this trap gave an efficiency of 76%, not significantly different from that of the double coil trap.

Refrigeration.--Initially a small centrifical pump was used to circulate trichlorethylene over a bed of crushed dry ice and thence through the cold trap coils. A great deal of gas was dissolved in the trichlorethylene passing over the bed, however, and some of this was evolved in the pump and in the trap as heat was picked up by the coolant, causing gas binding and stopping circulation. To correct this the circulatory system was modified to exclude contact with dry ice, the coolant being pumped through copper coils immersed in a static bath of trichlorethylene and dry ice. After this change, the performance of the pump was much improved.

Auxiliary Equipment.--Since it has been determined that no uranium compounds were volatilized during hydrofluorination, the reaction gases were drawn directly from the reactor tail pipe into a water aspirator where excess HF was dissolved, as well as volatilized SiF_4 . A two inch exit line was used to preclude plug-ups from condensed SiF_4 but this difficulty nevertheless occurred several times. The aspirator was made first from black iron pipe and fittings, these later being changed to Saron because of corrosion.

The excess gases from the fluorination, after passing through the closed trap system, entered a fluorine scrubber. This consisted of a 5 foot length of standard eight inch black pipe closed at the top, in the center of which were placed eight spray nozzles with adjacent pairs

pointing alternately up and down. The gases were drawn into the scrubber at the top by a slight aspirating effect and passed through the sprays and out at the bottom. It was judged that the unit was highly efficient for this application since no odor of fluorine was ever detected in its vicinity.

Although no satisfactory flow meter was available for either of the reaction gases, the essential close control of the fluorine rate was obtained by the use of a worm gear attachment with a 40:1 reduction ratio on the gas control valve. A quarter inch monel needle valve was used, usually being opened only one-eighth to one-quarter of a turn with a fluorine tank pressure of 20 to 30 psig.

The fluorine was obtained from the K-25 area in 400 gallon aluminum tanks, initially at about 30 psig, but later at pressures as low as 8 or 9 psig because of changed safety regulations with regard to filling of the tanks. Standard 3/8 inch copper tubing, used between the F₂ tank and the reactor, showed little corrosion, but it was changed occasionally as a safety precaution.

The hydrogen fluoride was received in liquid form in standard cylinders containing 70 to 80 pounds of reagent. Since the liquid has a low vapor pressure at room temperature (b.p., 19°C.), while in use the cylinders were warmed by electrically heated sheet copper jackets to assure a good flow of gas.

During the first few HF runs a decided cooling effect was noticed from the expansion of the gas from the inlet line into the reactor. To combat this and the possibility of condensation of the gas in the copper tubing a powerstat controlled electric heater was placed around the reactor inlet line and maintained at 200 to 300°C., eliminating the difficulty.

It was also found necessary to use an auxiliary electric heater on the reactor exit arm to prevent the deposition of SiF_4 during hydrofluorination, and of UF_6 and other chlorides during fluorination. With this heater the arm could be maintained at about 400°C .

Procedure

The charge material, originally containing 1000 recycle and later 1300 recycle uranium, was Beta salvage residue which had been ball-milled to a fine powder and homogenized. With the addition of 10 to 20% water, this was formed by a power pelletizer into lozenges about $3/8$ inch in diameter and $1/4$ inch high. In all, 26.7 kilograms of these pellets were hydrofluorinated, fluorinated, or both in this series of runs.

Hydrofluorination.--The reactor was charged with 500 to 2000 grams of pellets and lined up with the HF tail pipe. Since escape of reaction gases would not entail loss of uranium, a small air gap could be left to allow examination of the gases for excess HF. The aspirator had a large enough volume so that air would continually be drawn in at the air gap unless the tail pipe were blocked, and no HF could escape. During testing of the exit gases, the escaped HF was drawn into a large hood immediately above the apparatus.

During the initial heating up period the reactor was swept with nitrogen to aid in the removal of water vapor from the charge. The evolution of steam was usually overlapped and followed by that of copious NO_2 fumes, which in turn were followed by SO_3 . When the temperature had reached about 300°C . HF was admitted to the reactor at a rate sufficient to give an excess over the reaction requirement, as shown by the exit gases forming white fumes on contact with the moist air of the room.

During these runs, when no test had been devised for qualitative evaluation for the reaction progress, its duration was rather arbitrarily determined by the temperature record. Initially the furnace was raised as quickly as possible to about 600°C., the reactor temperature following rapidly or slightly preceding that of the furnace. After two to five hours, which period showed a certain but by no means absolute correlation with the amount of charge, the reactor temperature started to fall off and the furnace was again raised to compensate for the drop. Then the reaction temperature was usually held constant for an additional half hour and the hydrofluorination terminated.

On completion of the run, the reactor was purged with nitrogen until HF was absent from the exit gases. It was cooled and opened, the charge weighed, and a sample taken for silica analysis.

A series of 22 HF runs was made in this manner, the reaction being carried out at an approximately constant high temperature for an individually variable run time. Very little mechanical difficulty was occasioned with hydrofluorination, since a trap system was unnecessary and this gas had little corrosive action on the materials of construction used.

Fluorination.--The previously hydrofluorinated pellets were usually sintered to some degree and after weighing had to be broken up into lumps before being recharged for fluorination, to avoid excessive channeling of the gas through large interstices in the material. However, in the four final runs of the series the HF residue was not sampled and weighed, making it unnecessary to disturb the form of the residue in the reactor.

About a half hour before the fluorination was to be started, dry ice was charged to the trap cooling system and the trichlorethylene pump started. Care had to be taken in both steps, since copious foaming occurred

if the dry ice were not added cautiously, or if warm trichlorethylene were circulated rapidly through the cold bath in which much CO_2 was dissolved.

After a preliminary drying and purging period, during which the temperature of the reactor was raised to 200°C ., the F_2 valve was very cautiously cracked to admit a trace of gas. It was evident that the reaction was initially violent and highly exothermic, the temperature rising rapidly to 600 or 700°C . By careful control of the fluorine the reactor could be held in this range for one and one-half to two hours, after which the temperature started to drop and it was necessary gradually to raise the furnace temperature to maintain that of the reactor. The complete fluorine run usually took about five hours, except in those cases where ignition of the grate and lower reactive parts cut short the reaction. This occurred in two cases out of twelve; the resultant search for a satisfactory grate material kept the number of fluorine runs down to about half the number of HF runs, in which the trouble did not arise.

On completion of the fluorine run, the system was purged for at least an hour before it was dismantled and the scrubber turned off. The reactor was cooled and opened, and the residue weighed and sampled. During this time all of the traps were kept cold so that no UF_6 would volatilize and be lost before water could be added. In the case of the trichlorethylene traps, between three and four liters of water was sprayed through a fixed nozzle as a wash. The liquid oxygen cold finger traps were washed, after attachment to the washing vessel, with a volume of one to two liters of water. All trap washings were weighed and sampled and eventually sent back to Salvage.

FIFTY POUND REACTOR

Although the preliminary work on hydrofluorination-fluorination of pelletized salvage residue in a small vertical reactor had not been comprehensive enough to do more than show promise for the program, the pressing nature of the problem made immediate transition to larger equipment necessary.

It was decided to construct apparatus which could take a charge of fifty pounds of pelletized residue, with the prospect of doubling the unit capacity later should the second stage prove satisfactory.

Discussion and Conclusions

This experiment, although a pilot plant because it was primarily concerned with discovery and solution of problems inherent to the process of fluorination of pelletized general salvage residue, can be considered essentially a production operation. It is probable that if the process were put into production the size of the units would not be changed but that increased capacity would be obtained by multiplicity of fifty pound units; even if the individual size were doubled, few operating conditions would change except reagent flow. Hence, it can be safely said that production operation could be expected to have substantially the degree of success that was obtained in the pilot plant.

A detailed presentation of data from the twenty-three runs would be of little value. Unfortunately, a concrete, quantitative evaluation of the process was not obtained for several reasons, but a general indication of its limitations and successes can be presented.

Due probably to the very complex nature of the original residue and the reaction products, the sample analyses were usually widely variable and

undependable. Analyses of duplicate samples sent to different laboratories commonly showed variation by factors of 2 or 3 and in some instances, by factors as high as 20 to 25. Duplicate trap wash samples sent to the same laboratory rarely agreed within 50%, although no variations as high as those mentioned above were obtained. Since charge, final residue, and trap wash all appeared difficult of analysis, it is not surprising that individual material balances were poor and that little correlation of results with operating variables could be found.

It would of course be unfair and untrue to ascribe all errors in data and difficulty in their correlation to sample analysis. Sampling of the original charge could be done only by selection of a few pellets, which might or might not have been representative. The trap wash solutions occasionally contained some solid material, making accurate sampling difficult. There is also some reason to think that trap washing may not have been 100% efficient, especially in the first few runs when the procedure had not become standardized. Finally, as stated above, a large number of different batches were used in the runs and since each had an individual composition, each could be expected to react differently to the treatment.

Hydrofluorination.--Although no correlation could be found between silica removal in the hydrofluorination step and temperature or reaction time (no data being available on gas rate), examination of the HF residue analyses for silica shows that the method was in general very successful. Analysis of residues from ten of the first twelve runs averaged 0.81% SiO_2 , half of them being less than 0.1% and the highest value being 2.9%. Subsequent to Run 12, samples of this residue were not taken since the previous three runs had been reported as less than 0.02% SiO_2 and it was decided that operating

technique had been developed to the point of assuring dependably complete silica removal.

Silica had proved the chief problem in the previous salvaging of uranium from these residues by leaching. A reduction of their silica content from an average of about 30% to less than 1% and possibly less than 0.1%, therefore, would materially aid in subsequent uranium recovery by other methods as well as by fluorination.

It has already been stated that a pre-hydrofluorination was found essential in laboratory development of the fluorination process. This was clearly proved in two runs of this series when silica, left evidently by an incomplete HF reaction, completely plugged up the exit line at the final trap during fluorination. By the time the plug-up was discovered the entire system was under considerable fluorine pressure and a two-hour shut down was necessary to vent the system and free the tail pipe. Subsequently, a trap pressure gage and emergency vent line were installed but the plug-ups were not repeated.

It is thought that hydrofluorination would be a valuable preliminary step in many of the salvage methods now under consideration, after the development of a suitable HF flow meter and some refinement of the tests of reaction progress. The process greatly simplifies the nature of the residue, and hence the problem of recovering its uranium, by removing the bulk of the silica and a few other minor constituents. In addition it requires very little equipment or attention from the operators. With the use of pelletized material in a vertical reactor the operation can be done in bulk consistent with production requirements.

Before this process could be put into production, however, further work would have to be done on the problems mentioned above and others. First, it is not yet clear which reaction variables control the reaction time, and optimum operating conditions have not been satisfactorily determined*. Second, the problem of corrosion by HF was not completely investigated. It seems probable that materials of construction, reactor design, and modifications of reaction conditions could be found which would permit operation at 700 to 800° C. rather than the 575° C. maximum observed in most of the present work. This higher temperature should allow a much shorter time cycle and perhaps give more uniform results.

Fluorination.--a. Reaction Data. The attempt to correlate results of the various fluorination runs with variables of reaction was not based on chemical analysis but on an alpha count "efficiency". This factor was a ratio of the (gram) (counts per minute) of the residue to that of the charge, and although it was not entirely accurate because no absorption correction could be applied to the count analyses, it was considered a better measure of the reaction than a material balance based on chemical analysis.

Correlations were in every case negative, probably because of the multiplicity of variables involved. Numerous plots, which will not be reproduced herein, were made of the count efficiency versus the following variables and combinations of them: percent weight loss; run time; average fluorine rate; average reactor temperature; and total volume of fluorine. Considered as a whole, the twenty-three runs showed "shotgun" distribution when the variables were plotted; when runs using charge from one original salvage residue batch were grouped, in some instances vague trends could be recognized, but these were not clear enough to warrant definite conclusions.

*Recent experiments⁷ have indicated that a large increase in gas flow will materially shorten the hydrofluorination time from that found necessary in these runs. Such an increase in gas rate was prohibited in the experiments reported on here by limitations of the equipment.

Table 2, below, presents average, high, and low values of the data used in some of these attempted correlations, and those for Run 23, which was of special interest.

Table 2

Representative Fluorination Data - Large Reactor

	Chg. Wt. lbs.	Av. Reactor Temp. °C.	F ₂ Run Time Hrs.	Av. F ₂ Flow Rate Ft ³ /hr.	Total F ₂ Ft ³	Wt. Loss of Charge %	Count "Efficiency" %	U in Traps % of U in Chg. (chem)	Run Mat'l Bal. (chem) %
Av.	44.0	475	26.6	5.0	128.5	48.7	78.2	48.9	70.7
High	53.5	575	31.7	5.8	172.1	61.6	99.6	144.8*	150.0*
Low	21.0	382	8.3*	3.5	36.3	-10.7*	23.1	1.9*	22.5
Run 23	25.0	422	24.0	5.4	129.6	10.0	99.6	62.2	69.3

*Isolated datum - few or no others comparable

It will be noted that relative to the average, Run 23 was given almost double the normal fluorination per pound of charge. This was reflected, as expected, in a much more complete reaction than usual even though the average temperature was well below normal. Since the flow rate was in most cases limited by the temperature rise an increase entailed, greater fluorination dictated a longer run time. However, as reference to the cost breakdown, page 42, will show the fluorination was exceedingly expensive to operate, and a longer period would be economically unfeasible.

It is also of interest that Run 23 showed a much smaller weight loss than the average, supporting the contention that fluorination was usually incomplete and that during the "extra" period much of the material which had resisted initial reaction was raised to a higher valence state and gained additional fluoride ions.

In spite of the fact that individual material balances based on chemical analyses were erratic and in general quite low, an over-all balance taken at the completion of the series showed good accountability. In table 3, below, Lab. I refers to the laboratory to which all charge, residue, and trap wash samples were sent in the course of the experiment; Lab. II was sent occasional check samples and in general showed much better reproducibility of results.

Table 3

Over-all Material Balances - Large Reactor

	<u>Lab. II</u> <u>Final Anal.</u>	<u>Lab. I</u> <u>Final Anal.</u>	<u>Lab. I</u> <u>Individ. Anal.</u>
U in Charge, gm.			1008.13
U in F ₂ Residue, gm.			<u>318.63</u>
Debit to Trap Wash, gm.			689.50
U in Final Batched Trap Wash, gm.	489.8	532.0	338.6
U extracted from Trap Wash to date, gm. (Lab. I)	<u>139.9</u>	<u>139.9</u>	<u>139.9</u>
Credit to Trap Wash, gm.	629.7	672.9	478.5
Material Balance, % (based on 689.5 gm.in)	91.5	97.5	69.5

A more accurate accounting of the uranium in the trap wash will be made after all of the batch has been subjected to carbitol extraction, since analysis of the extraction solution is considerably easier than that of the complex trap wash solution. The uncertainty in the analyses of the solid samples, however, will probably prevent a close approach to a perfect uranium balance.

Consideration of the data in table 4, below, will show that the cold trap system used in the experiment was inadequate and would require modification before being applied to a production operation. It was hoped and expected that 90% or more of the UF_6 would be condensed in the first trap and that all but a trace of the remainder would be condensed in the second, but results fell far short of this.

The change after Run 17 from two large trichlorethylene traps and three smaller liquid nitrogen traps to four of the former and one of the latter severely taxed the capacity of the cooling system. Since this change was not accompanied by installation of a larger trichlorethylene pump to compensate for the increased volume of the system, it was inevitable that the individual trap efficiencies should decline. In calculating the trap efficiencies it is necessarily assumed that the final liquid nitrogen trap condensed all entering UF_6 . Although a first glance at the data of Runs 18 to 23 makes this assumption doubtful, its probable validity is apparent if one considers that the average temperature of this trap was 35° to 40° C. lower than those of the preceding trichlorethylene traps.

Table 4

Comparative Average Cold Trap Efficiencies - Large Reactor

	<u>Runs 1-17</u>					<u>Trap No.</u>	<u>Runs 18-23</u>				
	<u>I</u>	<u>II</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>I'</u>	<u>II'</u>	<u>III'</u>	<u>IV'</u>	<u>V'</u>	
% of Total UF_6 Condensed by Entire System	64.9	25.7	6.0	1.8	1.1	39.8	27.4	16.4	9.4	8.3	
Trap Efficiency-% Condensed of UF_6 Entering Trap	64.9	73.4	67.5	62.0	(100)	39.8	44.5	48.1	53.1	(100)	

Should the need arise, it would not be difficult to design a satisfactory cold trap system of one large trichlorethylene trap, followed for safety's sake by one or more liquid nitrogen traps. Using a cooling surface slightly greater than the combined areas in the present trap system, about 25 sq. ft., and a standard refrigeration unit capable of -75°C ., or, trap should be able to condense all but a trace of the entering UF_6 . A design similar to that of the trichlorethylene trap described herein is recommended, since the inside area is easily washed with properly placed water spraying nozzles.

b. Time Cycle. Considering the process as a whole the time cycle for best operation would probably be prohibitively long. In table 5 an estimate of the various periods is given for hydrofluorination and fluorination of 50 pounds of salvage residue in the present equipment with an operating force of two well trained men.

Table 5

Breakdown of HF-F_2 Time Cycle

Charging and preliminary heating of reactor	3 hours
Hydrofluorination time (estimated eventual av.)	20 "
Cooling and purging reactor	3 "
Cooling traps and assembling for F_2 run	
Fluorination time (estimated optimum)	40 "
Cooling and purging of reactor	4 "
Trap washing and thawing time	
Total Cycle	70 hours

The above accounting does not include maintenance time, although in almost every experimental run equipment repair and improvement was a large

factor. Such operations as trap pressure testing and sample preparation are not included since they could be completed by the two men during the reaction periods. It is doubtful that use of additional personnel would shorten the cycle by more than an hour; on the other hand, except during the reaction periods two men are definitely required to perform the necessary operations. It should be borne in mind that safety requirements call for at least two persons in a room at all times where the use of fluorine is involved.

c. Disadvantages of Fluorination.--Whereas it appears that hydrofluorination of the general salvage residue was efficient in its primary purpose of removal of silica and it could be recommended that it be applied to further reclamation efforts, the disadvantages in the fluorination step were deemed to outweigh the advantages.

Among the former the following points can be listed:

1. Cost. Initial cost of the equipment and the installation that is required for safety and the cost of operation were high in comparison to those of other proposed processes. Such items as a refrigeration unit, transite-lined rooms, and proper cold traps were not standard equipment and required large initial outlay. Superior operating personnel, expensive reagents, and extensive equipment replacement kept running expense high.
2. Reaction Efficiency. Results from any standardized procedure were quite irregular due to the heterogeneous nature of the charge material and the difficulty in analysis. The time cycle for removal of any substantial portion of the uranium present was very long when the size of the charge, fifty pounds, was considered. A leaching process, for instance, could handle 750 pounds of residue (the safe limit of uranium) in less than the fluorination time for 50 pounds, although probably with less satisfactory results.

3. Safety. Not only is fluorine highly dangerous to operating personnel if allowed to escape carelessly, but its corrosive nature provides danger of sudden leaks from apparently sound equipment. Its extremely reactive nature increases the hazard of fire, since most organic materials spontaneously ignite in contact with a stream of the gas, and almost all inorganics will burn in it as the temperature rises.

A study was made in conjunction with this work of the effect of fluorine leaking from a line under 30 psi on many materials of construction and of safety clothing. The results of the investigation, supporting the above statements, have been reported elsewhere.

In this experiment, although small fluorine leaks were not infrequent, no real difficulty was occasioned from the use of the gas since proper safety precautions were taken, and the operating personnel were capable of coping with the emergencies as they arose. In plant operation, much closer supervision than is usual would be necessary to avoid serious trouble.

d. Advantages of Fluorination.--It was demonstrated that the primary purpose of the experiment, substantially complete removal of uranium from salvage residue by fluorination, was attainable. With a sufficiently long reaction period it should be possible to recover 98 to 99% of the uranium from any salvage batch.

The uranium volatilized by the reaction was put in an easily recoverable form. First, the spray system in the traps made washing convenient and efficient. Second, the trap wash was amenable to a standard carbitol extraction, equipment for which is currently operating in the plant. The solution from this extraction did not offer the same analytical difficulty as did the trap wash, and so provided a convenient point for accurate material accounting.

e. Future Work.--Should it be desired to investigate fluorination of salvage residue further, a carefully planned program of variable control should be made, with special emphasis on reaction time. Successful application of any conclusions drawn from this study would require the development of a test for the extent of fluorination at any time during the run. The most promising fields of investigation on this problem are exit gas analysis and comparison of gas rates into the reactor and out of the traps.

Further work on corrosion resistant materials of construction would be profitable with regard to increasing safety and reducing replacement of the equipment.

It is suggested that batches of charge sufficiently large for at least ten runs be homogenized so that the results obtained from the variable studies may be strictly comparable. Since the residues do vary in proportions of most constituents, however, more than one such homogenized batch should be studied.

Finally, in order that the investigation might produce any reliable results, analytical methods for both solids and solutions should be improved.

Equipment

Reactor Assembly.-- In view of the excellent corrosion resistance which nickel grates had shown in the one kilogram reactor, it was decided to construct all possible parts of this metal in the larger unit. The reactor design was changed little, its dimensions being 9-1/2 inches in diameter, by 30 inches in height, with a 1/4 inch wall. In spite of the previous good results, however, failure of the nickel reactor was the major source of difficulty in the large scale operation. Failure usually occurred in the form of circumferential cracks about the middle of the reactor, with occasional

radiating longitudinal cracks. It appeared to be a combination of chemical corrosion and thermal shock, the former being due primarily to sulfates in the charge. A more detailed discussion of this problem may be found in the Appendix, page 44.

Initially the reactor head had one central well in which three thermocouples were inserted at various levels. This well was protected from direct contact with the charge and flowing gases by a sheath which also served to support the grates for insertion and removal. Probably because of the extra protection, the well stood up satisfactorily in the twenty-three runs, in contrast to regular failures in the small reactor.

In order to get a more complete idea of temperature variation in the reacting mass, a modified head was used in the last 14 runs. Five additional wells of one-fourth inch standard monel pipe were added, placed at various levels and various distances from the center of the reactor. Surprisingly, there was no failure of any of these in spite of the construction material and its direct contact with the charge.

The grates were of one-fourth inch and one-eighth inch nickel plate and showed little evidence of corrosion at the end of the series.

A cylindrical, 10-1/2 inch opening Hevi-duty furnace (110 V, 10 KW, 1010° C. working temperature) was obtained from Building 9210 and installed on channel iron tracks set in the concrete floor. The reactor was lifted into and out of the furnace with the aid of a one-fourth ton Wright chain hoist suspended from an overhead beam.

Trap System.--The cold trap system was permanently installed before the series was begun and changed only once during operations. Initially two trichloroethylene and three liquid oxygen traps were suspended on a

framework of 1-1/2 inch pipe. The former traps were of the type shown in figure 7-A, Appendix, jacketed and with a central cooling coil. Two of the liquid oxygen traps had trichlorethylene jackets with 2-1/2 inch cylindrical cold fingers for the oxygen, while the third had a 4 inch spherical cold finger. After Run 17, the system was modified by the substitution of two more trichlorethylene traps of the same design for two of the liquid oxygen traps. The spherical cold finger trap was retained since it consistently maintained a lower temperature than the other two and required less constant filling. It was decided, in making the changes, that no over-all reduction of trap efficiency could be occasioned and that a considerable saving in direct cost and labor would result from elimination of two liquid oxygen traps.

It was calculated that modification of the trap assembly increased the volume of the trichlorethylene jacket and coil system from 3.45 gallons to 5.18 gallons, and increased the total cooling surface from 18.5 sq. ft. to 25.7 sq. ft.

Shortly after the beginning of the series liquid nitrogen (b.p., -196° C.) was substituted for liquid oxygen (b.p., -183° C.) in the traps, when it had been determined that there was no danger of condensing fluorine (b.p., -187° C.) under the existing conditions.

Average gas temperatures in the traps over the whole series of runs were -17° C. for the first trap, -40° C. for the second, and -53° C. for the last. Occasionally the first trap warmed up as high as $+20^{\circ}$ C. and when circulation of the coolant was impeded by air binding, and at times too much liquid nitrogen lowered the last trap to -110 or 120° C. These temperatures were rare, however, and had small effect on the averages given.

The trichlorethylene was cooled in a copper coil immersed in a bath of crushed dry ice and trichlorethylene, and it was circulated by means

of a 5 gpm centrifugal pump. Several types of pump packing were tried, the least troublesome proving to be a graphite impregnated rope packing; even with that, however, progressively bad leakage necessitated its replacement every two or three weeks. The trap efficiencies were seriously impaired from time to time by air leakage into the system, causing air binding of the traps and stopping circulation in one or more of them. This was somewhat ameliorated by placing baffles in the circulating trichlorethylene reservoir to break up the vortex in the discharge pipe, and by occasionally diverting the entire output of the pump to the air-bound trap for a short time. The trouble was never satisfactorily eliminated, however.

Water, air, and steam lines were installed over the trap system, with rubber hose connections to the washing spray nozzles. Water was found satisfactory for washing, except that a three or four hour delay was required after the operation to allow the resulting ice to melt and the solution to be withdrawn. Occasionally, too, the initial drop of water entering the nozzle froze on contact and prevented washing altogether until it had been thawed.

It was postulated that steam, in giving up its heat of vaporization, would warm the traps enough to obviate the long thawing out period, in addition to producing a more concentrated wash solution and perhaps cleaning certain inside surfaces which the water spray might not reach. Consequently steam lines were installed and the method tried on several runs, but with no success. In every case the steam, or perhaps entrained water, froze on contact with the spray nozzle and prevented access of steam to the trap. Further washing was done with water, which did not freeze at the nozzles if the initial spurt had sufficient velocity, the steam being useful only as an aid in thawing out the main body of the traps later. After the traps were drained and rinsed, they

were dried by prolonged blowing with air to prevent the formation later of an insulating ice layer.

The trap wash, after sampling and weighing, was batched in a 250 gallon rubber-lined tank, from which 25 gallon portions were withdrawn for extraction.

Auxiliary Equipment

Temperature histories were kept during all runs of the gas in all of the traps and of the bath and return trichlorethylene stream. In the first twenty-one runs the copper-constantan thermocouples were read by means of a Leeds & Northrup potentiometer. Since this method was too laborious and lengthy to be consistent with production operations, a Wheelco pyrometer, calibrated to read from 0° to -120° C., was installed, the correct reading being obtained after subtraction of room temperature from that indicated. This apparatus proved quite satisfactory during the two runs in which it was used.

An aspirator of larger size but the same design as that used with the one kilogram apparatus was used during the hydrofluorination. In this case, black iron pipe and fittings were used without corrosion failure. The same fluorine scrubber was used as before, but with the addition of an aspirator to withdraw the reaction gases more rapidly.

Both the nitrogen and fluorine rates were measured by a thermal type flow meter, elsewhere described⁽⁶⁾, to the nearest tenth of a cubic foot per hour. The reactor and furnace temperatures were indicated by a Wheelco pyrometer, a Brown recorder being used to control the furnace temperature. Some difficulty was experienced with faulty connections of the thermocouples under the first temporary arrangement, but this was eliminated later with redesign of the reactor

head and insulating bonnet to allow, in effect, a permanent thermocouple installation.

Procedure

The charge material used in all runs in the fifty pound apparatus was 1300 recycle salvage residue, formed into pellets about one inch in diameter and one-half inch high. These were received in batches of from 25 to 250 pounds, composition of the various batches differing somewhat in all constituents. This variation dictated some non-uniformity in run procedure and probably accounted to a large extent for the inconsistencies in recovery data. A total of 1012 pounds of salvage residue was treated in the large unit, an average of forty-four pounds per run.

The procedure outlined below is somewhat generalized, some of the steps and conditions described not having been standard for all runs throughout the series. An attempt is made to present a procedure which would obtain for the process as later applied to plant operation.

Hydrofluorination.--About fifty pounds of these pellets were charged to the reactor, filling it to a level about two inches below the side exit arm. The head was bolted on with a copper-asbestos gasket, the reactor hoisted into the furnace, the insulating bonnet put in place, and the whole raised to the proper level to coincide with the HF tail line. An air gap of about one-fourth inch was left between the reactor arm and the tail pipe to permit testing of the exit gases. The furnace, various instruments, and the arm heater were turned on and nitrogen was admitted to the reactor at about ten cubic feet per hour to sweep out evolved gases.

As in the case of the one kilogram equipment the reactor was allowed to attain a temperature of about 300° C. before the HF was turned

on, in order that water might be driven off and nitrates and sulfates broken down. This took about two hours if the furnace was kept at 350 to 400° C. Temperatures of the reactor and furnace, and during fluorination, of the traps, were observed and recorded every half-hour during the reaction.

After the HF had been turned on to show an excess at the tail pipe, a rate estimated at 80 to 100 cubic feet per hour initially and 40 to 50 cubic feet per hour finally, the reaction and equipment required little or no attention for about eighteen hours, other than an occasional increase of the furnace temperature as the heat of reaction decreased and the cooling effect of the incoming HF became appreciable. A representative temperature curve for the reaction is shown in the Appendix, figure A-9.

After the rather arbitrary period had elapsed, two tests were begun to determine the completion of reaction.

Every half hour a cold copper plate was inserted in the exit gas stream to condense any moisture present in the reaction product. Although no quantitative evaluation of the reaction intensity could be made in this manner, after a little training the operators were able to follow its course and make rough predictions of the time necessary to complete the hydrofluorination. At this termination point the plate showed not even a trace of moisture, although at the beginning of the test condensation was enough to produce one or two drops of water a second. Absence of moisture indicated that the hydrofluorination of oxygen containing compounds--primarily silica and metal silicates, oxides, nitrates, and sulfates--had dropped off to a point where continued operation was impractical. This test, although not quantitative as it was carried out, was a valuable criterion of the extent of reaction, since the reaction time varied from 25 to 66 hours with

sundry batches, making a fixed procedure impractical.

In conjunction with the moisture test an exit gas sample was bubbled through water every two hours and the resulting solution tested for silica colorimetrically, a test based on the formation of the blue silico-molybdate complex. This test was considered semi-quantitative, since it was made by visual comparison to a series of standard solutions, but was found to be less satisfactory for the purpose than the moisture test, for three reasons. First, the amount of silica in the exit gases was so great during a large part of the run that a definite coating was formed on the walls of the sampling apparatus, making it almost impossible to clean it well enough between samples to avoid serious contamination. Second, the test value indicating a completion of the reaction ($\mu\text{g Si/cc}$ of sample) was entirely arbitrary, and did not take into consideration such variables as sampling efficiency, HF flow, and correlation between the extent of reaction and reaction rate, reflected in the amount of SiF_4 in the exit gases. Third, it was not determined that metal oxides were hydrofluorinated at the same or a faster rate than silica and the silicates, so that even with SiF_4 absent from the exit gases, the reaction might have been still incomplete. Comparison of the two tests threw little light on the latter point, since, probably because of the contamination mentioned above, there were runs in which each indicated completion before the other, as well as runs in which the two were in coincidence. In most cases, the reaction was continued until both tests were negative.

On termination, the reactor was swept with nitrogen and cooled. In the first 12 runs, the residue from this first test was sampled, but subsequently fluorination was begun without the opening of the reactor.

Fluorination.--about one and one half hours before the fluorination was begun it was necessary to start the cooling system in order that the traps would reach the required temperature before the reaction began. Dry ice was added cautiously to the trichloroethylene to avoid violent foaming and the trichloroethylene pump was turned on. The bath usually required about 30 minutes to reach an equilibrium temperature of -75 to -85° C., at which point it was loaded with about 40 pounds of dry ice in egg size lumps; thereafter, about 20 pounds an hour sufficed to maintain the temperature. Liquid oxygen or nitrogen was forced by air pressure into the cold finger traps from the 25-gallon cans about every 10 minutes, its presence in the fingers being indicated visually by ether vapor frozen in the vapor from the boiling coolant.

The furnace and reactor were lowered to fluorination position, the reactor bolted to the first trap, using a D-29 gasket, and the F_2 scrubber turned on. When the reactor temperature reached 200° C. by either cooling or heating, the furnace temperature was set at 200° C. and the fluorine cautiously turned on. As the gas rate was gradually raised to five or six cubic feet per hour, the reactor temperature climbed rapidly to about 500° C. and could be controlled for some hours by regulation of the fluorine rate. After the initial violence of the reaction had subsided, it was necessary to raise the furnace temperature gradually to maintain the reaction temperature at the desired level. The heat of reaction was sufficient, however, to hold the reactor temperature at least slightly above that of the furnace, since the apparatus was well insulated and the gas rate too low to produce an appreciable cooling effect from expansion into the reactor, as in the case of the HF. Figure A-10, Appendix, shows a representative temperature curve for fluorination.

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Unfortunately, as before no test other than temperature drop was available for measuring the extent of the fluorination, so after the first few runs the reaction was set at 30 hours for 30 pounds of original charge to eliminate one variable in the study.

On completion of the run the system again was swept with nitrogen to remove fluorine from the reactor and traps. A two hour period, which was probably much longer than was actually necessary to purge the system, was allowed as a safety precaution. While the reactor cooled, the trap system was blanked off at the reactor and scrubber ends so that the system should be closed to prevent the possible escape of vaporized UF_4 during the warming up of the traps attendant to washing. After the water line has been attached to the spray nozzle line, the system was pressure tight and it was safe to turn off the circulating cold trichloroethylene.

The admission of water to the trap, three gallons to each of the first two and one gallon to each of the others, was usually accompanied by formation of gases which raised the pressure very rapidly to 30 or 35 psig. Occasionally this rise was so large that the system had to be vented intermittently through an emergency line during the trap washing to avoid rupture of the traps. A check made by bubbling these vented gases through a weak ammonia solution showed that no detectable uranium was being lost. Although the cause of the pressure is not definitely known, it is postulated that fluorine compounds of carbon formed during the reaction were boiled off as the traps warmed from -60 or $-70^\circ C.$ to $0^\circ C.$, and that the inevitable traces of SiF_4 warming up contributed to the pressure.

Since the traps had been kept cold to the moment of washing, the water froze upon entering and required about four hours to melt. This period

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could be halved by playing steam constantly upon the exposed metal parts of the trap, but since time was not particularly important at this stage, it was usually not done. When the traps had thawed, the bottom valves were opened and the solution allowed to drain into the copper container attached to the traps with pipe unions. The traps were then rinsed with a little water, the wash containers removed, and the traps air dried through the spray nozzles. Later, with the first and last trap still blanked off and the drain valves closed the system was pressure tested for leaks developed during washing. If the pressure drops were less than one psi per minute at 30 psig, it was deemed satisfactory and the equipment was assembled for the next run.

The trap wash solutions were air agitated for 30 to 60 minutes and individually sampled, afterwards being batched with those of previous runs in a rubber lined tank. From this tank 25 gallon portions were withdrawn, saturated with 12.5 lbs. of $Al(NO_3)_3$ per gallon of solution, and sent to Building 973)-1 for orbital extraction in the spinner column.

The solid residue from the fluorination, after cooling, was weighed and put through a jaw crusher and a disc mill. The fine powder product was easily homogenized and sampled.

a. Both initial and operating costs would be higher than those for other processes under investigation.

b. The operational time cycle was very long, 70 hours for treatment of 50 pounds of residue being predicted.

c. The reaction efficiency was low or at least highly variable with different residue batches.

d. The use of fluorine constituted a great safety hazard to personnel and a difficult corrosion problem to equipment.

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Bibliography

1. Smith, F., CD-4101, (Jan. 16, 1945)
2. Milch, A., C-O.355.2, (Sept. 25, 1945)
3. Milch, A., C-O.355.1, (Sept. 25, 1945)
4. Calkins, V. P. and Clewett, G. H., C-5.355.1, (July 16, 1945)
5. Parsons, G. S., McCabe, C. L., Engle, G. F. and Larson, C. E., reported in CD-564 CELa, p. 8, (Apr., 1945)
6. Johnson, E. D., Ford, W. F., and Clewett, G. H., C-5.355.8 (June 24, 1945)
7. Blasewitz, A. and Clewett, G. H., reported in C-5.100.32, p. 1. (Aug. 11, 1945)
8. Clewett, G. H. and Henderson, G. C., C-5.355.9 (July 24, 1946)
9. House, H. F. and Susano, C. D., C-5.500.4 (Feb. 25, 1946)

APPENDIXComparative Cost Breakdown of Various Recovery Programs

Estimates were made by the Engineering Department of the costs of installing and operating three salvage recovery processes in Building 9762. These were based on a desired treatment of 750 pounds of general salvage residue per day. In the case of hydrofluorination-fluorination it was planned to use 12 hundred pound reactors for the first step and 10 for the second, with an estimated over-all time cycle of 70 hours. This process was compared in cost with low temperature chlorination using vapor phase $COCl_2$ and with high temperature chlorination using Cl_2 .

Table A-1

Over-all Cost Comparison

	<u>Low Temp. Chlor.</u>	<u>High Temp. Chlor.</u>	<u>HF-F₂</u>
Initial Equip. Cost	\$26,300	\$167,500	\$287,000
Daily Mat'ls Cost	150.00	256.00	667.00
Daily Labor Cost	146.00	362.00	492.00
Daily Leach Cost	<u>450.00</u>	<u>450.00</u>	--
Total	\$726.00	\$1048.00	\$1169.00
Cost per g. U Recovered	1.06	1.45	1.48

Table A-4
Breakdown of HF-F₂ Cost

Initial Cost

Purchase and installation of HF furnaces	\$207,000
P. and i. of 10 trap systems, 30 reactors, and necessary aux. equipment	94,000
P. and i. of piping, gas storage system and also, aux. equipment	\$1,500
Contingencies	15,000
P. and i. of refrigeration unit	34,000
Alterations to Building 9769	<u>4,000</u>
Total Initial Cost	\$287,000

Daily Operating Cost

A. Materials

HF	\$124.58
F ₂	300.00
S ₂	90.00
Al(SO ₄) ₃	\$1.18
Handling F ₂	90.00
Power	<u>\$1.48</u>

Total Mat'l's Cost **\$607.06**

B. Labor

\$492.00

Total Daily Cost **\$1109.00**

Recoverable U in 750 lb. of residue 775 g.

Operating cost per g. of U recovered \$1.48

Corrosion of Nickel Reactors

The primary equipment problem in the large-scale study was frequent failure of the nickel reactors, apparently in both stages of the operation. After one to five runs the wall of the reactor would exhibit one or more large circumferential cracks, some scaling, and deep intergranular corrosion.

Following is a schedule of reactor failures and the data available for their correlation. Since failure occurred only in a zone about the middle of the reactor body, the "new" reactors generally consisted of a new body cylinder to which had been welded the old flanges, side arm, and bottom.

Table A-3

Schedule of Reactor Failures

<u>Reactor Number</u>	<u>Number HF Runs</u>	<u>Number F₂ Runs</u>	<u>Average Highest Temp. HF - °C.</u>	<u>Average Highest Temp. F₂ - °C.</u>
1	2	2*	745	665
2	4*	3	695	650
3	1	2*	690	665
4	1*		670	
5	2	3*	630	640
6	4	4*	635	640
7	4*	5	525	600
8		4		565
9	3		520	

* Type run during which failure occurred



It was thought at one time that the failures might have been due mainly to thermal shock, aided to some extent by corrosion of the gaseous reagents. A dummy was made up of the same nickel used for the process reactors, therefore and subjected to heat tests. The dummy reactor was heated to a dull cherry red (about 800°C.) six times and cooled rapidly in a stream of air, but pressure tests at 30 psi after each cooling showed no leaks. The dummy was then subjected to twelve tests of the same type in which it was cooled abruptly with a water spray. In this case only one pin hole leak could be detected after the last run. Since there was no evidence of degeneration of the metal structure, it was necessarily concluded that thermal shock alone was not responsible for the failures.

Analyses of the original charge material to the reactor showed some sulfate contents ranging up to 30%. This information, an outline of the other reaction conditions and a sample of badly corroded nickel were sent to the laboratories of the International Nickel Company, source of the sheet nickel used. It was the opinion of this authority that the metal had been in no way imperfect originally and that failure had been due only to intergranular sulfide attack and embrittlement, rather than to HF or F₂. This corrosion could be due to sulfates, it was stated, if the temperature exceeded 700°F., or 360°C. It would, of course, be advanced by higher temperatures and by rapid temperature changes, conducive to cracking of the metal.

It will be noticed in table A-3 that as the maximum operating temperature was reduced after successive reactor failures, these failures became less frequent. In the last four runs the residue was hydrofluorinated and fluorinated in separate reactors but not enough runs were made

properly to indicate the corrosion resistance of the nickel under these conditions.

In a further study of corrosion of various metals under conditions obtaining in these reactions, five racks of 1/6 inch sheet metal samples were placed on top of the charge in one run. The metals studied were copper, nickel, silver, monel, 316 stainless steel, and Hastelloy C. Rack 2, subjected to the original ignition only, and Rack 3, inserted only during hydrofluorination, showed little or no attack on any sample. In Rack 1, left in the reactor throughout the entire run, the silver was entirely consumed, Hastelloy C and 316 stainless steel were converted to the fluorides in layers of scale, and monel, copper, and nickel, in that order, showed a descending degree of scaling around a core of sound metal. Rack 4, subjected to HF and F₂ only, was in almost the same condition as Rack 1, except that copper seemed to stand up better than nickel. Rack 5 was two samples of nickel subjected only to F₂ and showed almost no scaling or pitting. It was impossible to obtain weight loss data on any of these samples because of contamination by adjacent samples and by the charge.

It will be noted that the test results presented above are not consistent within themselves nor with other test data, especially with regard to nickel. However, it is thought that the substantial corrosion shown by the latter in Racks 1 and 4 was due to contamination by the adjacent metallic silver which rendered the nickel more vulnerable to fluorination. There is little doubt that it is the preferable metal of those tested for construction of high temperature fluorination equipment.

Salvage Residue Analysis

Shown in table A-4, below, is a fairly complete analysis⁽⁹⁾ for one batch of 1000-recycle salvage residue. This is not presented necessarily as a typical composition of these residues, but merely to illustrate their complexity. The average uranium content of the 1300-recycle residues processed in the large reactor, for instance, was 0.23%, while silicon averaged 29.7%.

Table A-4Analysis of a Salvage Residue

<u>Analysis Sought</u>	<u>Dried Residue</u> %	<u>Ignited Residue</u> %
Uranium, U	0.31	0.55
Silicon, Si	22.5	25.4
Aluminum, Al	6.71	6.14
Iron, Fe	6.65	8.05
Magnesium, Mg		0.13
Calcium, Ca	3.28	4.15
Sodium, Na		None
Titanium, Ti	0.55	0.62
Chromium, Cr	2.41	2.58
Nickel, Ni		0.56
Copper, Cu	2.36	2.51
Manganese, Mn		0.012
Tin, Sn	2.99	2.14
Lead, Pb		0.055
Silver, Ag	1.3	
Chloride, Cl	0.58	
Sulfate, SO ₄	3.38	
Nitrate, NO ₃	1.96	
Fluoride, F	0.13	
Hydrogen, H	0.45	
Carbon, C	6.3	
Water, H ₂ O	2.4	
Oxygen, O (By difference)	35.74	

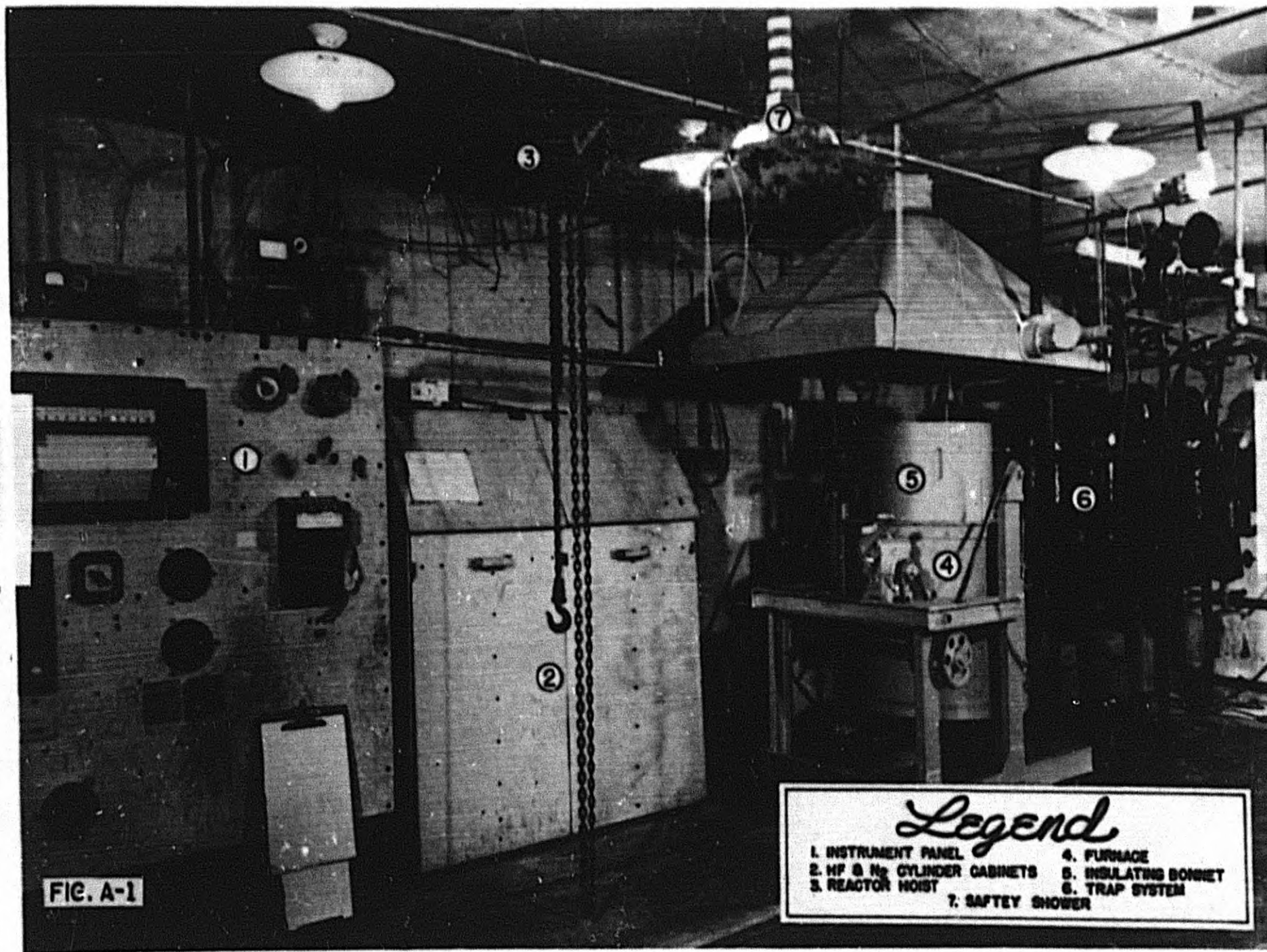
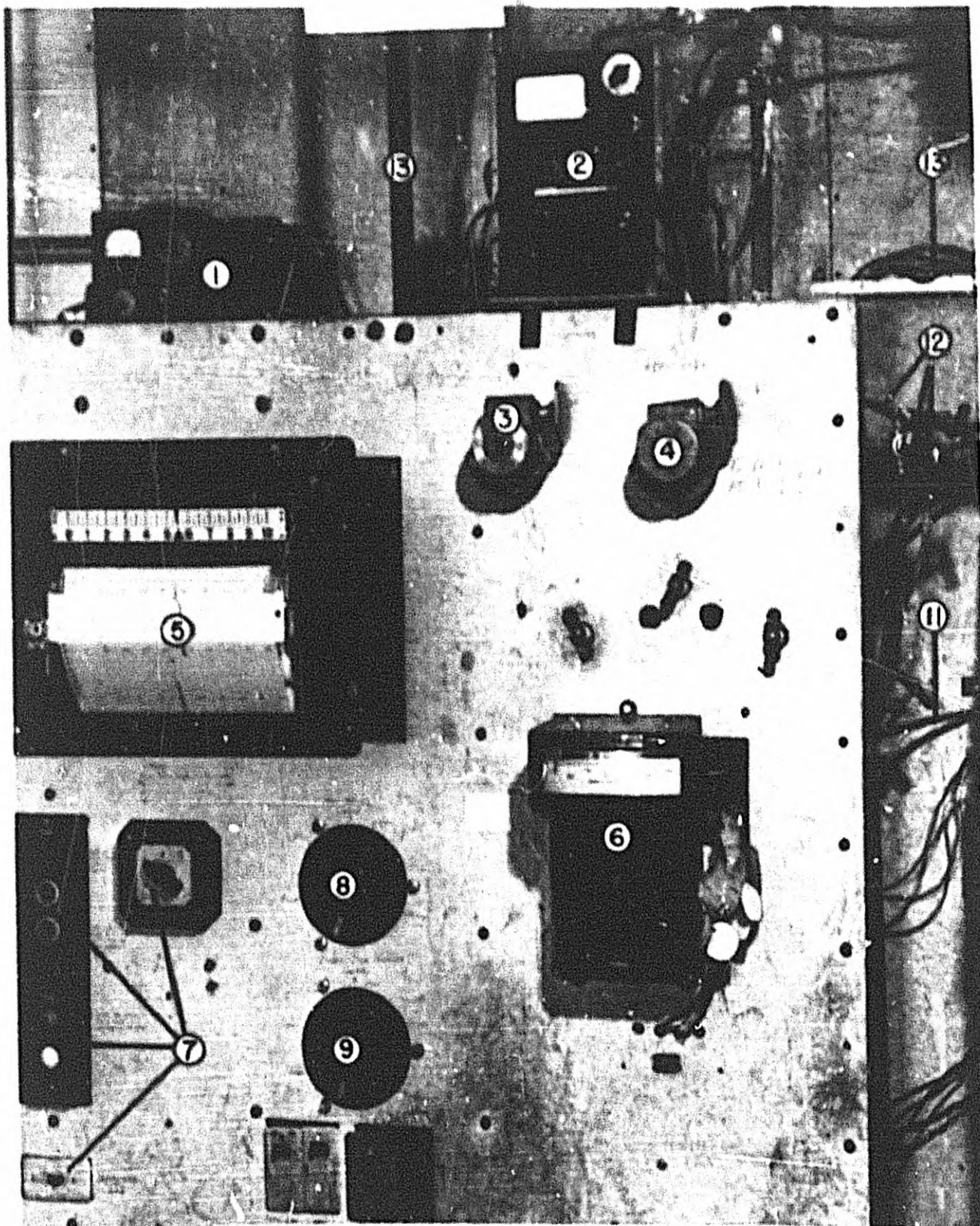


FIG. A-1

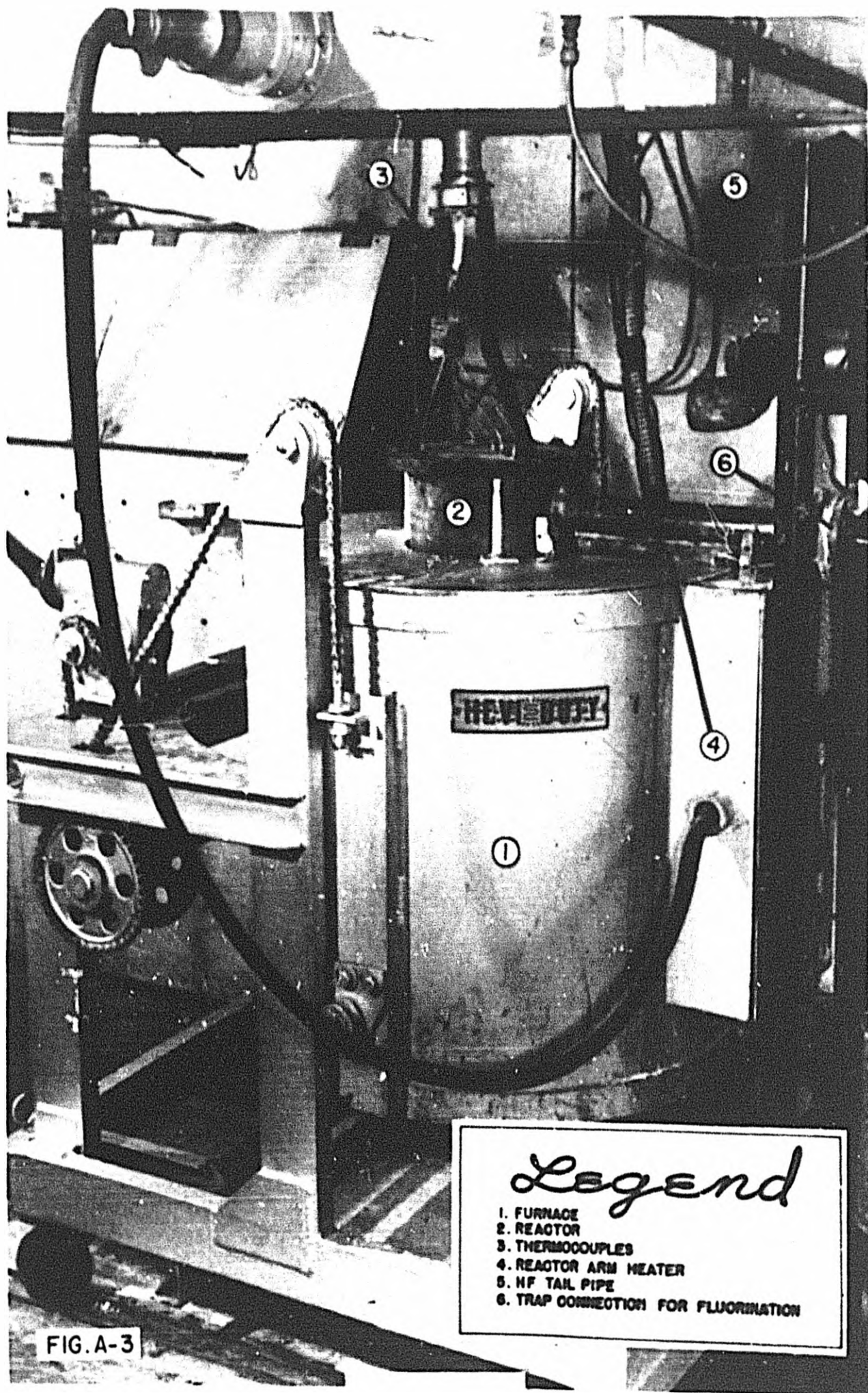
Legend

- | | |
|--|----------------------|
| 1. INSTRUMENT PANEL | 4. FURNACE |
| 2. HF & N ₂ CYLINDER CABINETS | 5. INSULATING BONNET |
| 3. REACTOR HOIST | 6. TRAP SYSTEM |
| | 7. SAFETY SHOWER |



- Legend*
- | | |
|-----------------------------------|----------------------------------|
| 1. N ₂ FLOW METER | 7. BROWN POTENTIOMETER CONTROLS |
| 2. F ₂ FLOW METER | 8. ARM HEATER POWERSTAT |
| 3. N ₂ WORM GEAR VALVE | 9. INLET LINE HEATER POWERSTAT |
| 4. F ₂ WORM GEAR VALVE | 10. HF CYLINDER HEATER POWERSTAT |
| 5. FURNACE TEMPERATURE RECORDER | 11. HF LINE |
| 6. REACTOR TEMPERATURE INDICATOR | 12. N ₂ LINES |
| | 13. THERMOCOUPLES |

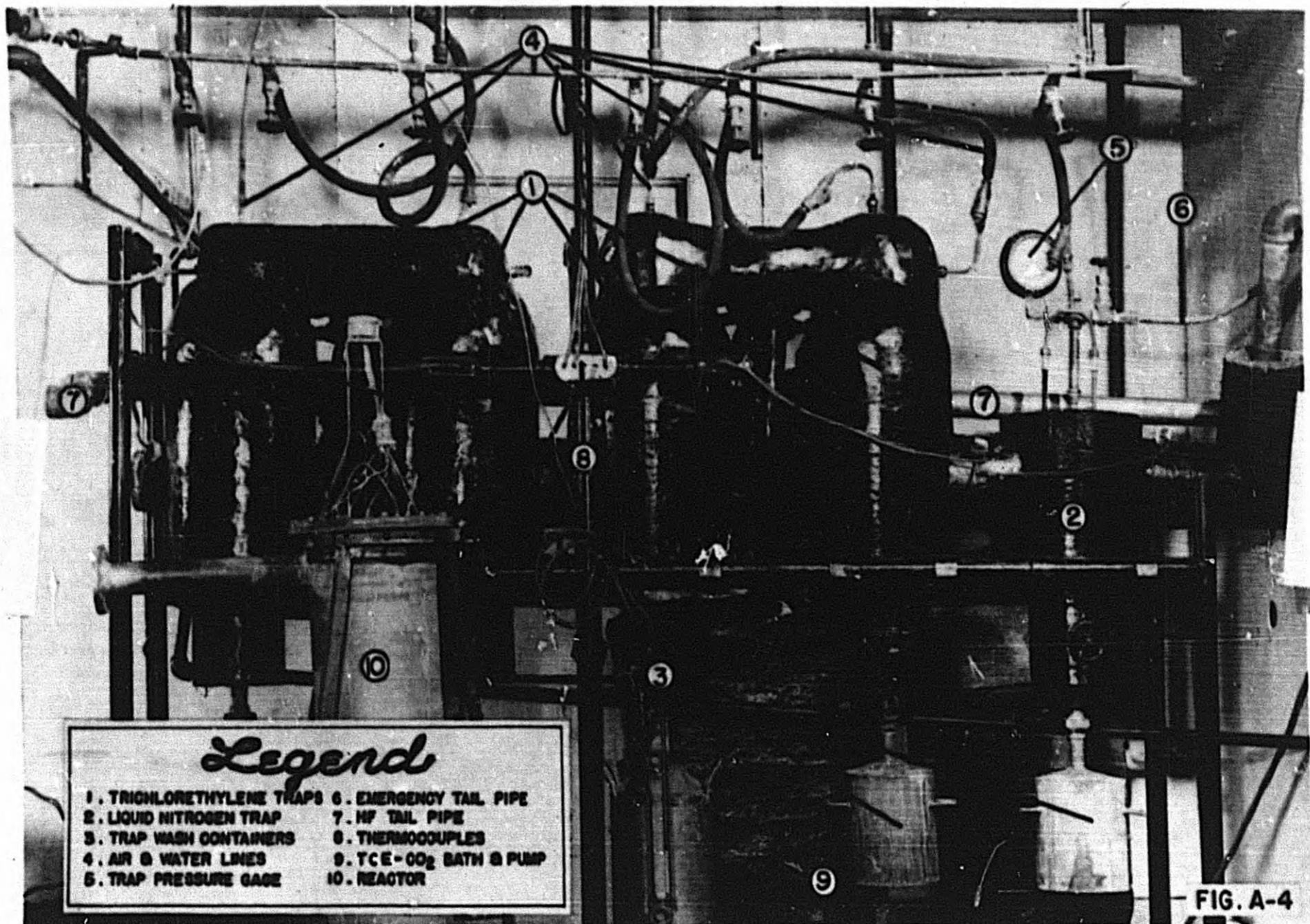
FIG. A-2



Legend

1. FURNACE
2. REACTOR
3. THERMOCOUPLES
4. REACTOR ARM HEATER
5. HF TAIL PIPE
6. TRAP CONNECTION FOR FLUORINATION

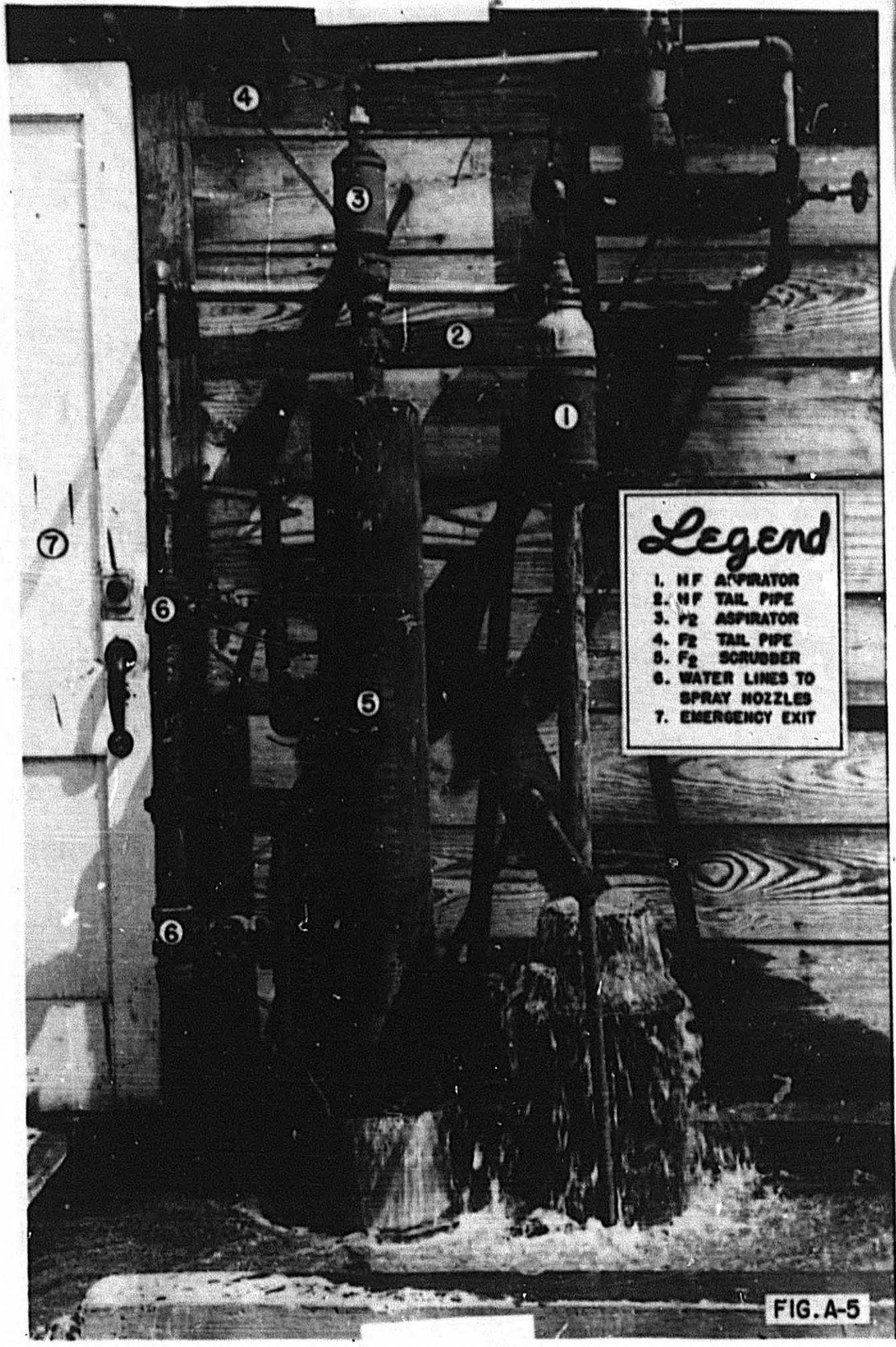
FIG. A-3



Legend

1. TRICHLOROETHYLENE TRAPS	6. EMERGENCY TAIL PIPE
2. LIQUID NITROGEN TRAP	7. HF TAIL PIPE
3. TRAP WASH CONTAINERS	8. THERMOCOUPLES
4. AIR & WATER LINES	9. TCE- CO_2 BATH & PUMP
5. TRAP PRESSURE GAGE	10. REACTOR

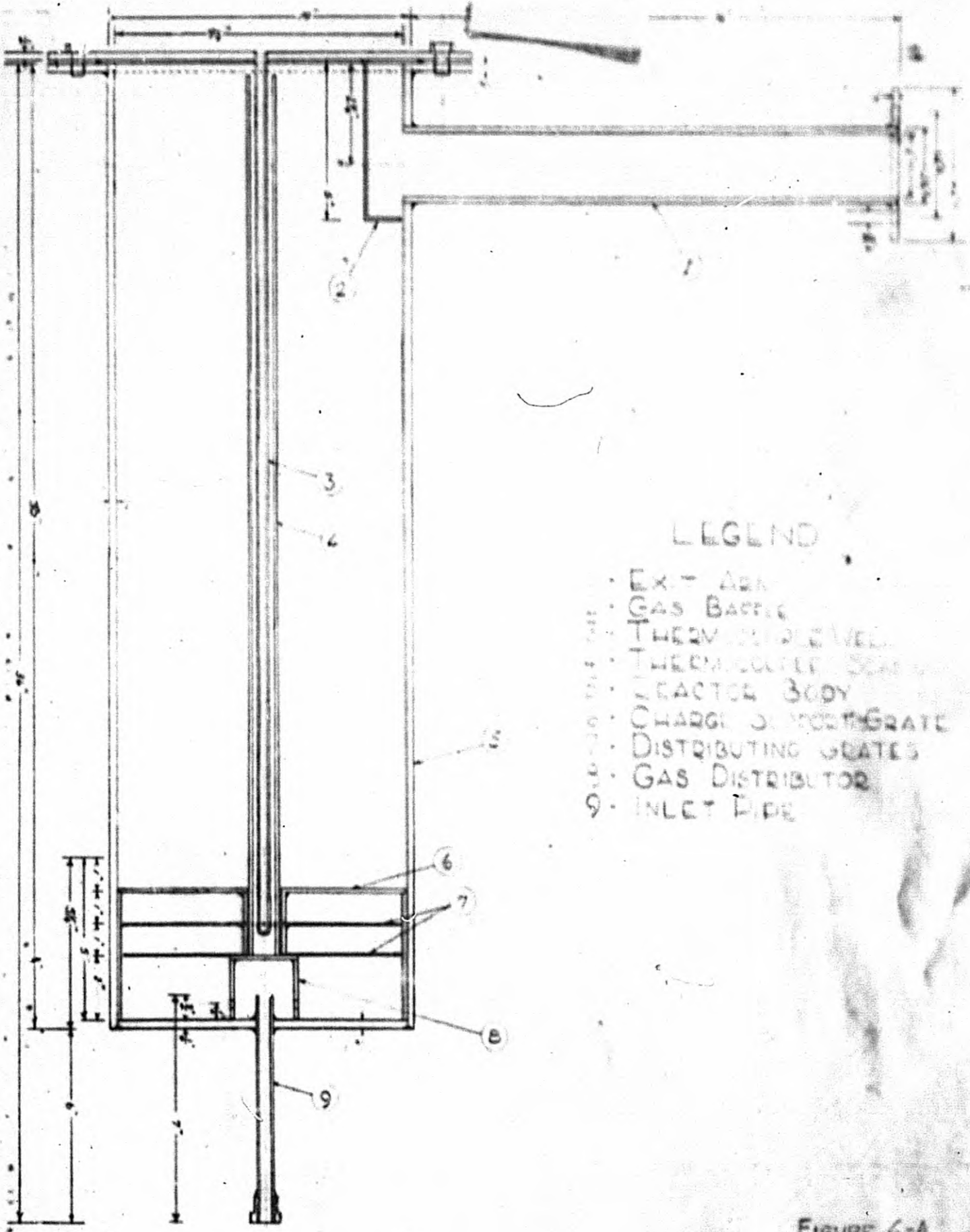
FIG. A-4



Legend

- 1. HF ASPIRATOR
- 2. HF TAIL PIPE
- 3. P2 ASPIRATOR
- 4. F2 TAIL PIPE
- 5. F2 SCRUBBER
- 6. WATER LINES TO SPRAY NOZZLES
- 7. EMERGENCY EXIT

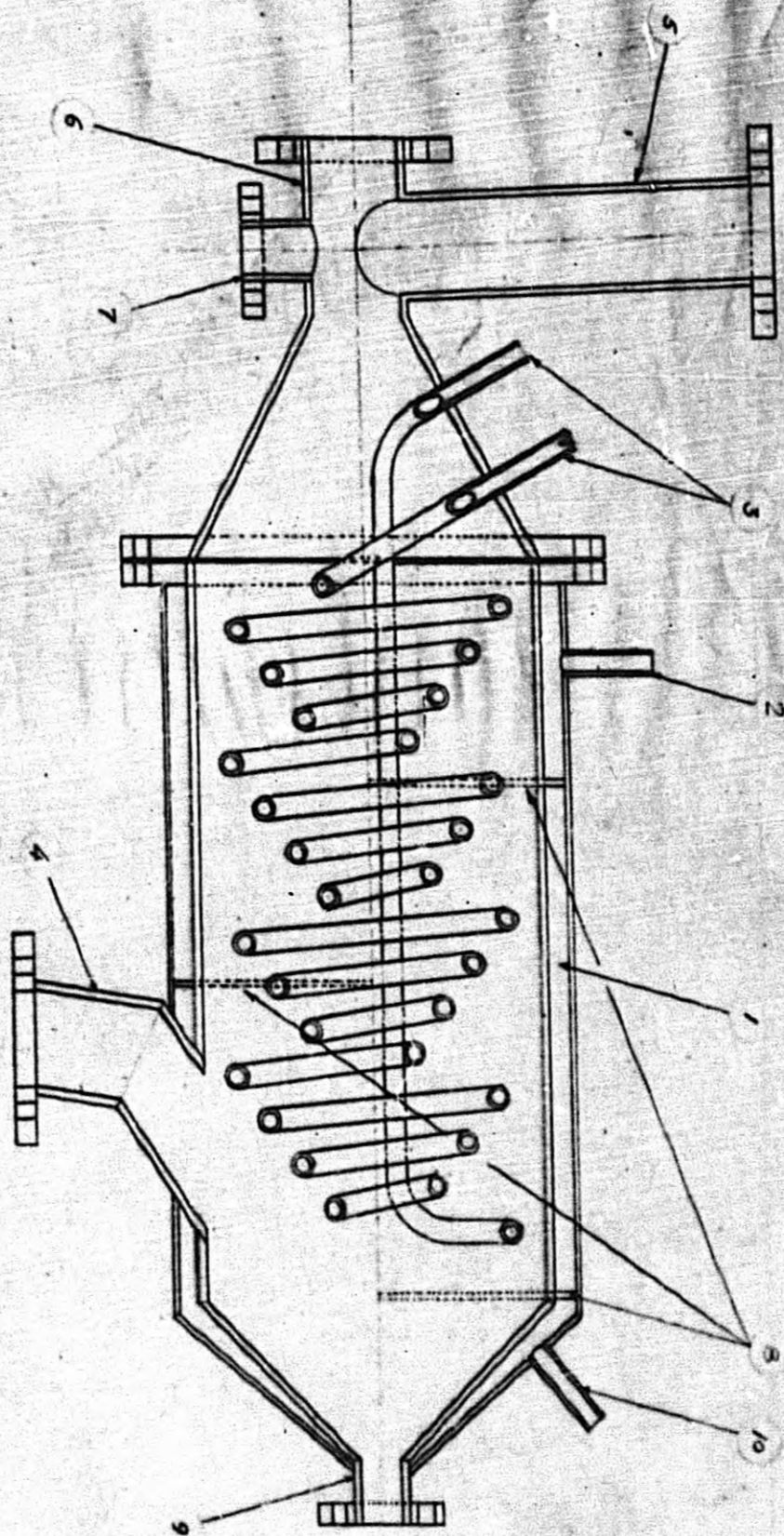
FIG. A-5



LEGEND

- 1. EXIT AREA
- 2. GAS BARRIER
- 3. THERMOCOUPLE WELL
- 4. THERMOCOUPLE SHEATH
- 5. REACTOR BODY
- 6. CHARGE SUPPORT GRATE
- 7. DISTRIBUTING PLATES
- 8. GAS DISTRIBUTOR
- 9. INLET PIPE

FIGURE 6-A
REACTOR DETAIL



LEGEND

- 1- TRAP JACKET
- 2- JACKET INLET
- 3- COIL INLET AND OUTLET
- 4- TRAP INLET ARM
- 5- TRAP OUTLET ARM
- 6- TRAP WASH PORT
- 7- ARM WASH PORT
- 8- JACKET BAFFLES
- 9- TRAP WASH OUTLET
- 10- JACKET OUTLET

FIGURE 7-A
COLD TRAP DETAIL

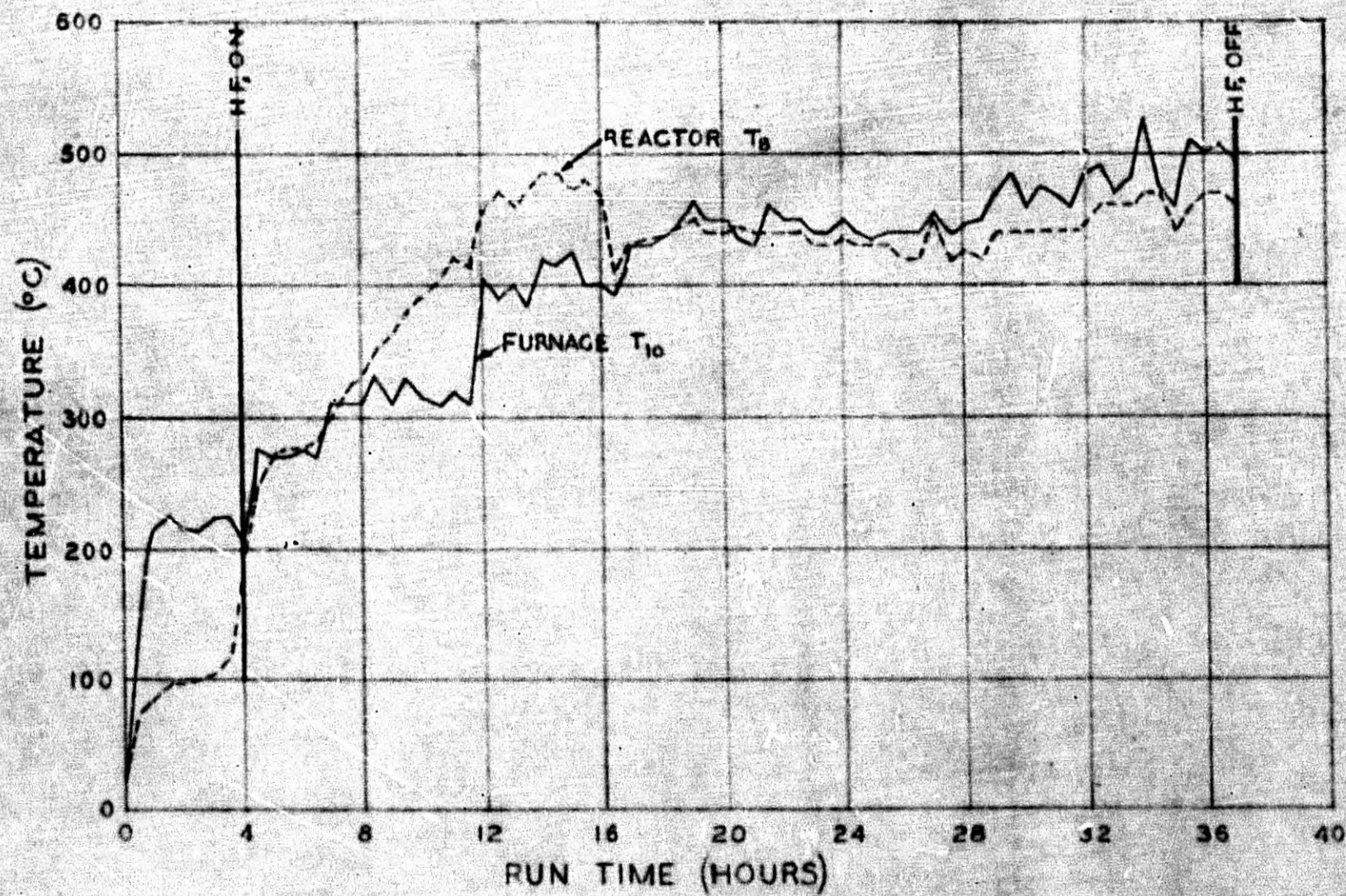


FIG. 9-A REPRESENTATIVE HF RUN TEMPERATURE HISTORY

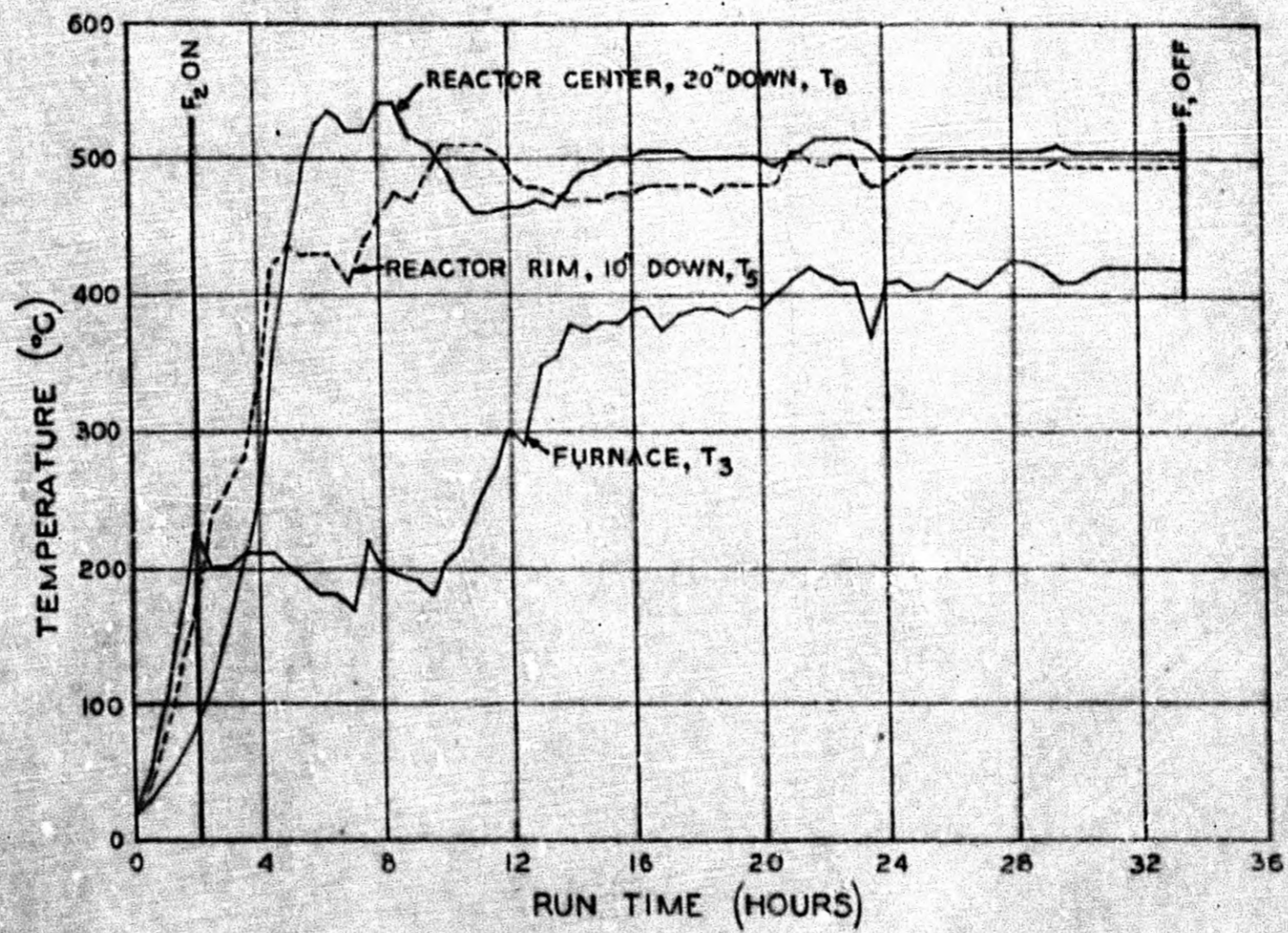


FIG.10-A REPRESENTATIVE F_2 RUN TEMPERATURE HISTORY

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UNCLASSIFIED

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