15

X-822

MASTER

OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE NUCLEAR COMPANY
Division of Union Carbide Corporation
UCC
Post Office Box X
Oak Ridge, Tennessee

EXTERNAL TRANSMITTAL AUTHORIZED

ORNL CENTRAL FILES NUMBER

59-1-115

COPY NO. 36

DATE: January 30, 1959

SUBJECT: DISSOLUTION OF ZIRCONIUM MATRIX FUELS IN MOLTEN FLUORIDE SALTS (To be presented at the American Chemical Society's Nuclear Technology Symposium, Boston, April 5-10, 1959)

TO: F. L. Culler, Jr.

FROM: R. W. Horton
M. E. Whatley

ABSTRACT

The application of the Volatility Process for reprocessing spent reactor fuels to zirconium fuel elements requires the conversion of the fuel to a fluoride form. This conversion can be accomplished by the dissolution of such fuels in a bath of molten fluoride salts with a hydrogen fluoride sparge. Studies with dummy zirconium fuel elements showed dissolution rates averaging 2 mg/sq cm-min. The effect of submergence, geometrical configuration, and HF impingement rate appeared more significant than the effect of temperature. Experiments with partially submerged elements have indicated that at temperatures in the neighborhood of 700°C the gas phase reaction rate can exceed the salt phase rate. The use of the process involves problems with corrosion, with entrainment of solids in the off gas, and with the recovery and recycle of the hydrogen fluoride. Tentative solutions to these problems have been studied.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

810 01

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

DO NOT DISCOUNT

1.0 INTRODUCTION

The hydrofluorination of zirconium-uranium alloy fuel elements in molten fluoride salts is the initial step in the recovery of uranium from these fuels by the Volatility Process.(1,2) This process is of interest because it provides a means of handling this type of fuel with a very small volume of waste, as compared to the conventional aqueous processes. Also, uranium hexafluoride is produced directly whereas aqueous recovery processes require several intermediate conversion steps to produce the hexafluoride.

The second step of the process, following hydrofluorination is the one from which the name "Volatility" is derived. In this step, the melt which contains uranium and zirconium tetrafluorides in addition to fission product fluorides and the inert fluorides originally present is sparged with elemental fluorine. The uranium is fluorinated from the tetrafluoride to the hexafluoride which is volatile and leaves the melt as a gas. Some fission product fluorides, notably molybdemum, ruthenium, and niobium also have high vapor pressures at the prevailing melt temperature, and they are also present in the off-gas stream along with some unreacted fluorine. The gas stream is then passed through adsorption beds at a controlled temperature such that uranium and fission products are held on the bed, allowing fluorine and some nitrogen used for purge to pass through the beds.

When the uranium has been completely removed from the molten salt, fluorination is stopped, the temperature of the adsorption beds is raised, and the uranium hexafluoride is selectively desorbed. It passes to product cold traps and eventually to storage cylinders. The product is of sufficient purity to be used as feed in the gaseous diffusion cascade or to be reduced to metal for reforming. The barren salt melt remaining contains the majority of the fission product waste and is dumped into waste cans and allowed to solidify. In this form, the waste is in a compact cake and can be buried for disposal. The sorption beds can be used for several batches before they become loaded with fission products. At this time they must be disposed of as waste and new beds put in use.

The product decontamination step may also be accomplished by fractional distillation of uranium hexafluoride from fission product fluorides instead of using the sorption-desorption beds. Considerable work has been done on this method at Argonne National Laboratory.

The fluorination of a fused salt fuel and sorption-desorption decontamination of product UF_6 have been operated in a pilot plant at Oak Ridge National Laboratory. Uranium loss to the barren salt was 0.03% and the 132 kg of product met the specifications for feed to the gaseous diffusion cascade.(3)

This processing method is particularly attractive for application to zirconium matrix fuels which are characterized by a high weight ratio (20 to 1) of zirconium metal to uranium metal in the form of long thin fuel plates stacked parallel and closely spaced in bonded sub-assemblies. This type of construction does not lend itself to "decladding" procedures which may be used to remove an excess of inert cladding metal from uranium. Therefore it is necessary to react, or dissolve, all of the metal in order to produce chemical forms which will permit separation.

2.0 DISSOLUTION STUDIES

The method studied in the Unit Operations Section of the Chemical Technology Division at Oak Ridge National Laboratory has been hydrofluorination in a molten salt bath. The reaction, producing the tetrafluorides of uranium and zirconium, is:

$$4HF + U \xrightarrow{650°C} UF_4 + 2H_2 + 165 \text{ KCal/gm mole}$$

$$4HF + Zr \xrightarrow{650°C} ZrF_4 + 2H_2 + 163 \text{ KCal/gm mole}$$

The molten salt used in this work has been a mixture of sodium and zirconium fluorides, one of several suitable mixtures. The major functions of the salt are to retain all of the reaction products in a liquid phase at moderate temperatures, and to keep the products (largely zirconium tetrafluoride) removed from the reacting surface.

This study is concerned with the determination of the hydrofluorination rate under conditions approximating those predicted for a pilot processing unit. The rate is reported in terms of weight of zirconium dissolved per unit area in unit time. It was assumed for the sake of calculation that the initial surface existed until dissolution was complete. The assumption seems reasonable for thin plates until 80% or more of the total weight has reacted. The rates reported are recognized as empirical. The relationships reported in addition to others now being obtained may eventually lead to fundamental rate expressions.

A description of the experimental results should follow a discussion of the flow sheet of the processing cycle as shown in Fig. 1. The fuel element is placed in the dissolver vessel, resting on the gas distribution plate, and the vessel is closed, purged with nitrogen, and heated. Molten fluoride salt at 650°C is then transferred from the salt preparation tank to the dissolver by nitrogen pressure on the preparation tank. The proper depth of

UNCLASSIFIED
ORNL-LR-DWG 35261

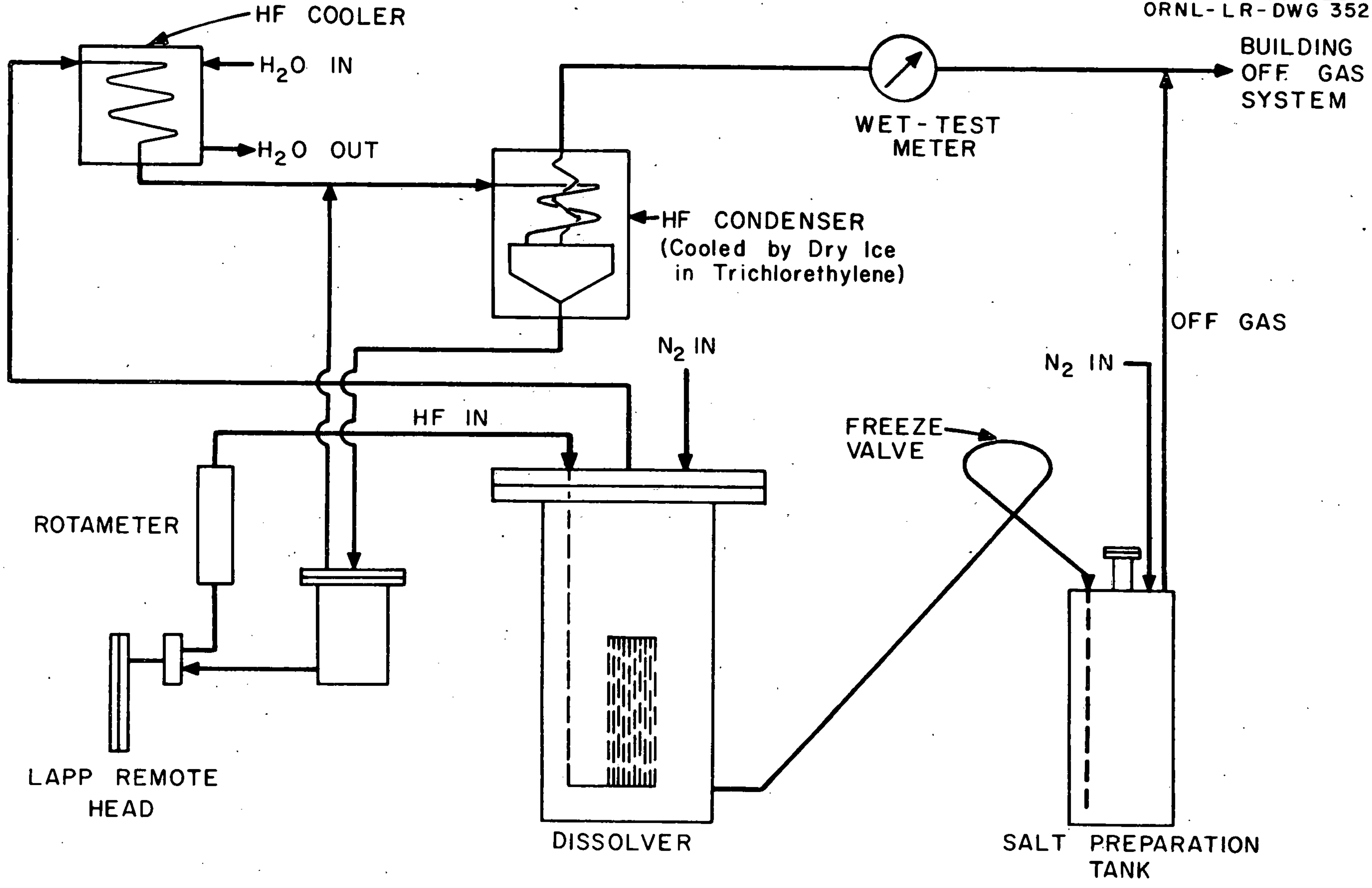


Fig. 1. Hydrofluorination Process Flow Sheet

salt in the dissolver is determined by liquid level measurement using a nitrogen bubbler dip tube and a differential pressure cell.

With the molten salt and the dummy fuel element in the dissolver and the temperature at 650°C, anhydrous hydrogen fluoride is then introduced to the gas distribution plate at a metered rate. The hydrogen produced by the reaction plus the unreacted hydrofluoric acid and a small quantity of purge nitrogen pass to the off-gas system where the acid is condensed and collected for recycle. The non-condensable hydrogen and nitrogen pass through a "wet-test" gas meter and thence to waste.

Some of the equipment mentioned is shown in Fig. 2. The dissolver vessel is a section of six inch schedule 40 stainless steel pipe lined with one-eighth inch thick copper and closed at the top with Inconel flanges sealed with a copper ring gasket. The off-gas line is one inch copper tubing, the acid inlet line is three-eighths inch copper tubing. The condenser consists of a 20 liter copper receiver and a condensing worm of one inch copper tubing immersed in a trichlorethylene bath cooled with dry ice to an operating temperature of -78°C.

The balance of the hydrofluoric acid system, not shown, consists of a recycle system: a steel tank which supplies the remote pumping head of a Lapp diaphragm pump unit. The pump and valve assembly are fabricated entirely from Monel metal, and are refrigerated to 0°C to eliminate vapor binding. This pump has given reliable service for about 100 hours of operation and will meter reproducibly through the range of stroke adjustments. The pump discharges to a steam heated boiler which vaporizes the hydrofluoric acid and thence to a superheater unit which raises the gas temperature to about 100°C before it is again metered through a fluorothene tube rotameter as it passes to the dissolver vessel. The rotameter is useful in providing a visual check on the acid system operation.

The fuel elements used are dummies fabricated from Zircaloy-2 and Zircaloy-3 to simulate STR type fuels in thickness and spacing of fuel plates. The relatively close spacing of plates makes dissolution rate measurement difficult because of the uncertainty of contacting all possible reacting surfaces. In all rate determinations, it has been assumed that the entire exposed area was available and all calculations were made on that basis. The simulated assemblies have ranged in weight from one and a half to eleven pounds and in area from one-half to six square feet.

The fluoride salt mixture used in this survey was 38 mol per cent zirconium fluoride and 62 mol per cent sodium fluoride at the start of the dissolution. This composition, for the Na-Zr fluoride system, is chosen because of the melting point, as shown in Fig. 3. This figure is a phase diagram for

9006 018

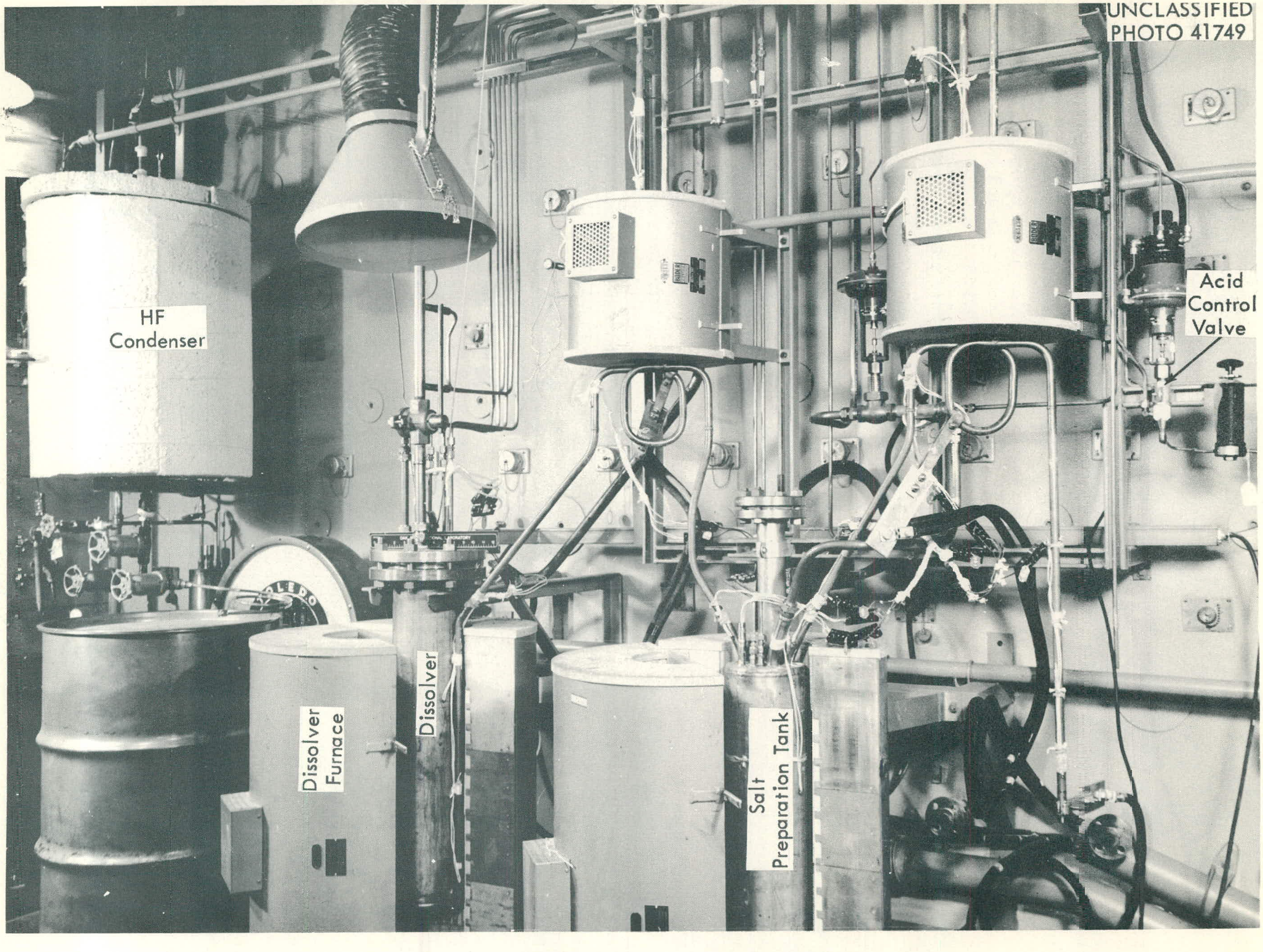
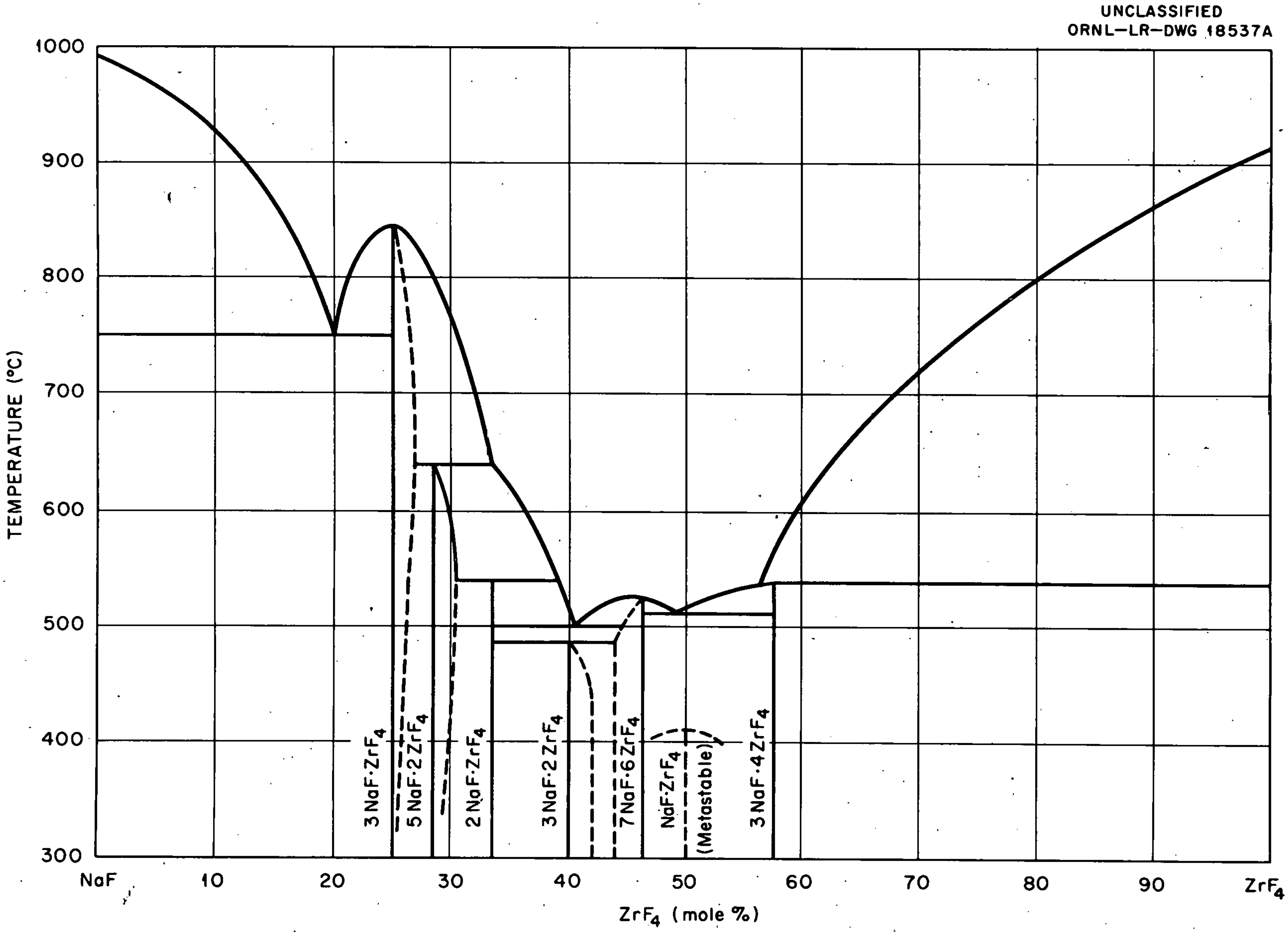


Fig. 2. Dissolver and Related Equipment.



The System NaF—ZrF_4.

Figure 3

the system which shows that to avoid extremely high melting points the zirconium concentration must be kept in the approximate range of 40 to 60 mol per cent. High temperature is undesirable because of the increased rate of equipment corrosion and also because of the appreciable vapor pressure of zirconium fluoride above 700°C.

3.0 TEST RESULTS

The initial series of dissolution tests was made to scout the temperature dependence of the reaction rate. The results, Fig. 4, indicate that the temperature effect is relatively small.

The next test series explored the effect of acid addition rate. The results of this series when plotted as shown in Fig. 5 indicate that the specific dissolution rate is proportional to the rate of acid addition, expressed in terms of superficial velocity. The specific dissolution rates, in mg/sq cm min, ranged from 0.2 to 0.6 in the first series and 1.0 to 1.3 in the second.

The second curve indicates results obtained following a modification of the dissolver which was made to reduce splash and entrainment difficulties. The slopes of the two curves are essentially the same although they are displaced. This result led to the formulation of this expression:

$$R = K \log \frac{G}{G_o}$$

R = Specific dissolution rate

K = Proportionality constant

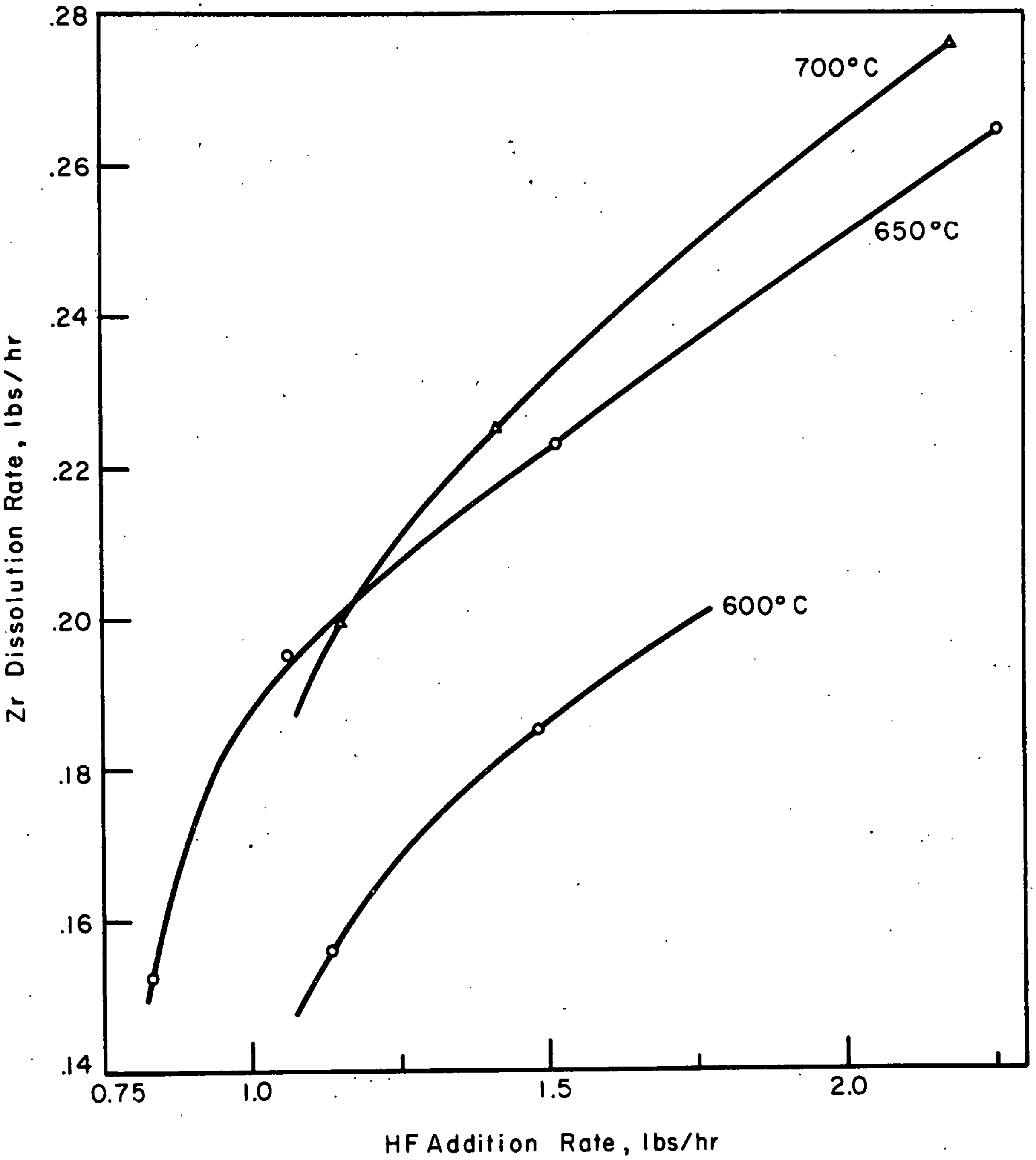
G = HF mass flow rate

G_o = Geometric factor

The specific rate is directly proportional to the logarithm of the acid addition rate divided by a geometric factor G_o (in consistent units) which expresses the physical configuration of a particular dissolver vessel. In this expression, the G_o factor could be interpreted as the acid addition rate for zero dissolution; however, extrapolation of plotted results indicates no real meaning for this interpretation.

In the temperature and addition rate experiments the dummy element was fully submerged in fused salt. In an attempt to determine the rate for areas

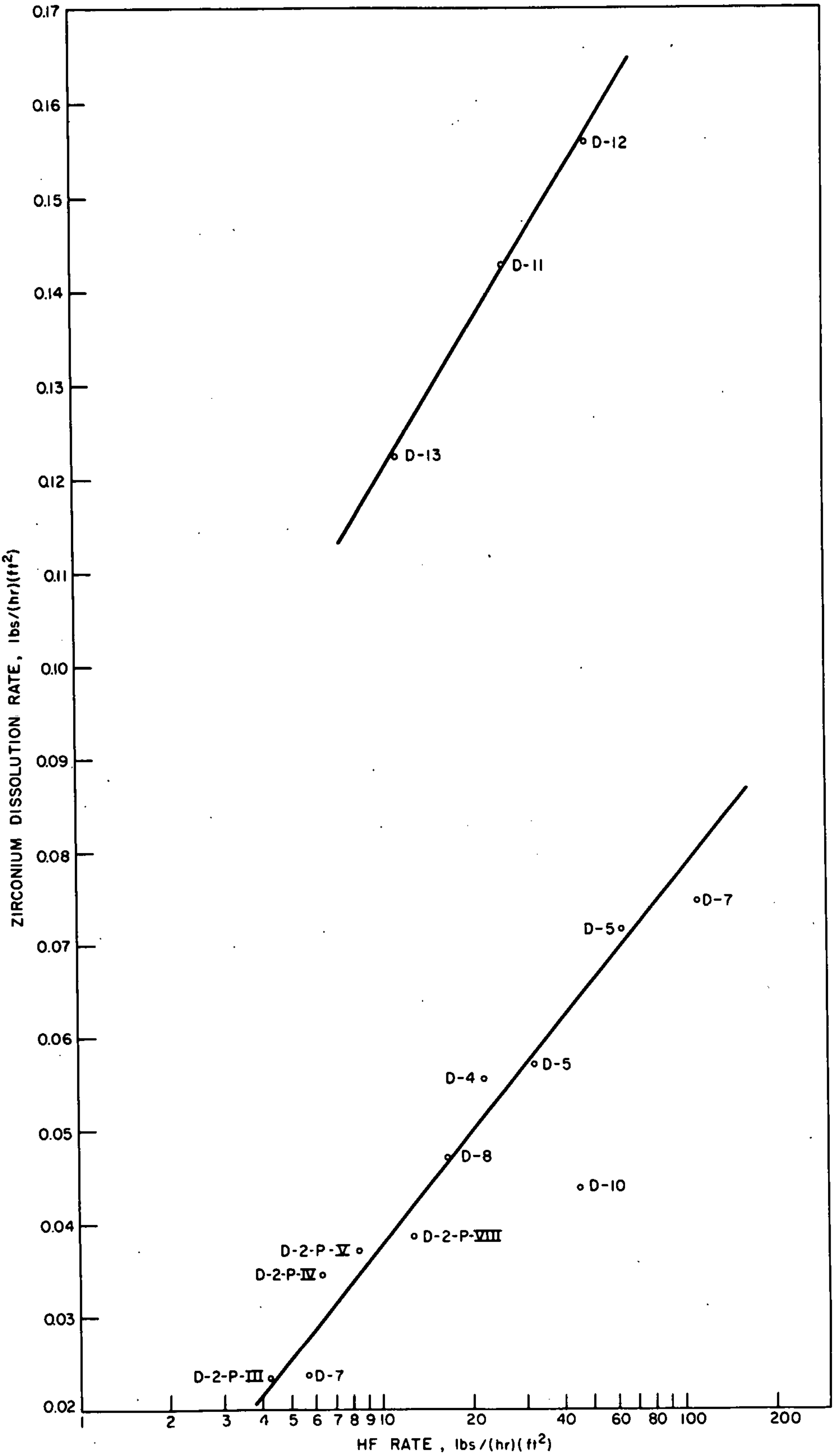
UNCLASSIFIED
ORNL-LR-DWG 28705



HF-Fused Salt Dissolution of Zirconium. Test D-2 12-12 and 12-13 1957 Zr dissolution rate vs HF addition rate.

Figure 4

UNCLASSIFIED
ORNL-LR-DWG 29588



The Effect of HF Addition Rate on the Zirconium Dissolution Rate in Molten NaF-ZrF_4 at 650° C.

Figure 5

not submerged in salt, three test dissolutions were made with non-reactive (copper) dummy elements interspersed with zirconium dummies, as shown in Fig. 6. It may be seen that the rates for the three cases were increasingly higher as the distance above the salt increased. The reactions were complete in all cases and the high rate for the third case indicated that direct gas-phase hydrofluorination might offer high dissolution rates. A test was made using no salt in the dissolver and the same acid rate as used in three previous tests. The initial rate was high as shown in Fig. 7, but fell off to zero when the amount of hydrogen evolved was equivalent to 40% dissolution of the metal.

On examination of the element at the end of the test the condition noted in Fig. 8 was found. All surfaces of the element, except the bottom which was exposed to the gas stream, were completely blocked by a dense layer of crystals which analysis proved to be zirconium tetrafluoride. It was concluded that higher ambient temperatures in the dissolver were required to prevent the reaction zone from cooling below 900°C, which is the temperature at which the vapor pressure of the tetrafluoride is atmospheric. An additional experiment with the gas phase reaction resulted in complete hydrofluorination at an average rate of 6.0 mg/sq cm/min. Additional work on this reaction is scheduled.

These tests have proven that complete hydrofluorination of massive zirconium metal assemblies is possible at reasonable reaction rates in both fused salt dissolutions and the dry reaction. The fused salt method is best suited for immediate use with Volatility processing and is now being refined. Some of the problems associated with the process are those of corrosion and of solids contamination of the off-gas stream.

The major corrosion problem exists in the reaction vessel which operates at approximately 700°C wall temperature and is exposed to hydrofluoric acid as well as molten fluoride salts. The effect appears particularly troublesome at the gas-salt interface region, possibly because a protective film is not maintained in this area. Several high nickel alloys are being investigated for use by a group at Battelle Memorial Institute. The most promising appears to be INOR-8, an alloy developed by the Metallurgy Division at Oak Ridge National Laboratory and the International Nickel Company.

The problems of solids contamination of the off-gas stream arises from vapor phase transfer of zirconium tetrafluoride from the dissolver vessel at 650° to 700°C. The vapors condense in the cooler off-gas line as extremely small particles, possibly less than one micron, and are carried to the hydrofluoric acid condenser where they are trapped in the condensed acid. Over a period of time this entrainment could result in fouling of condenser

310 079

UNCLASSIFIED
ORNL-LR-DWG 35259

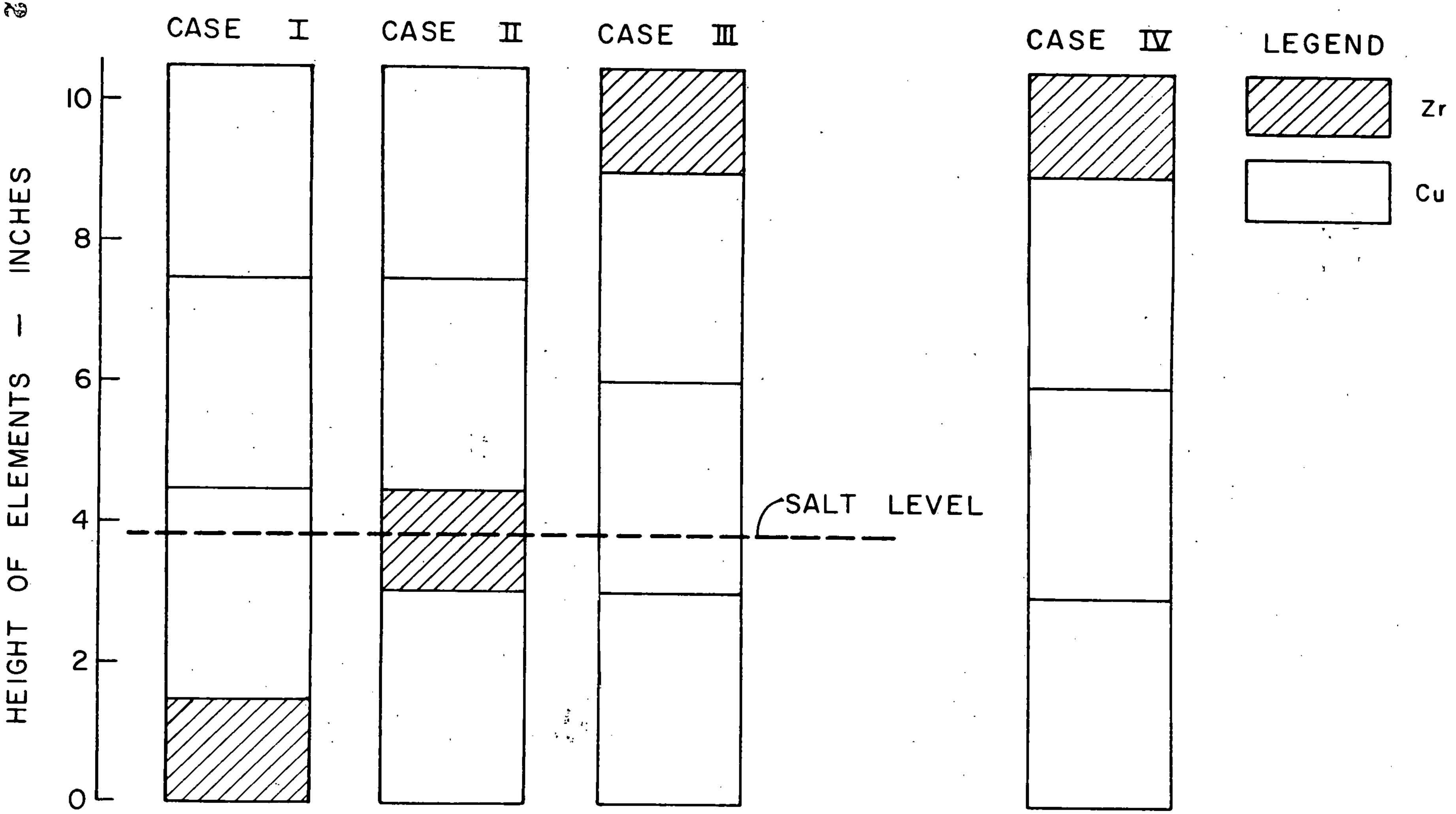


Fig. 6. Relative Positions of Test Elements in Dissolution Studies

UNCLASSIFIED
ORNL-LR-DWG 35260

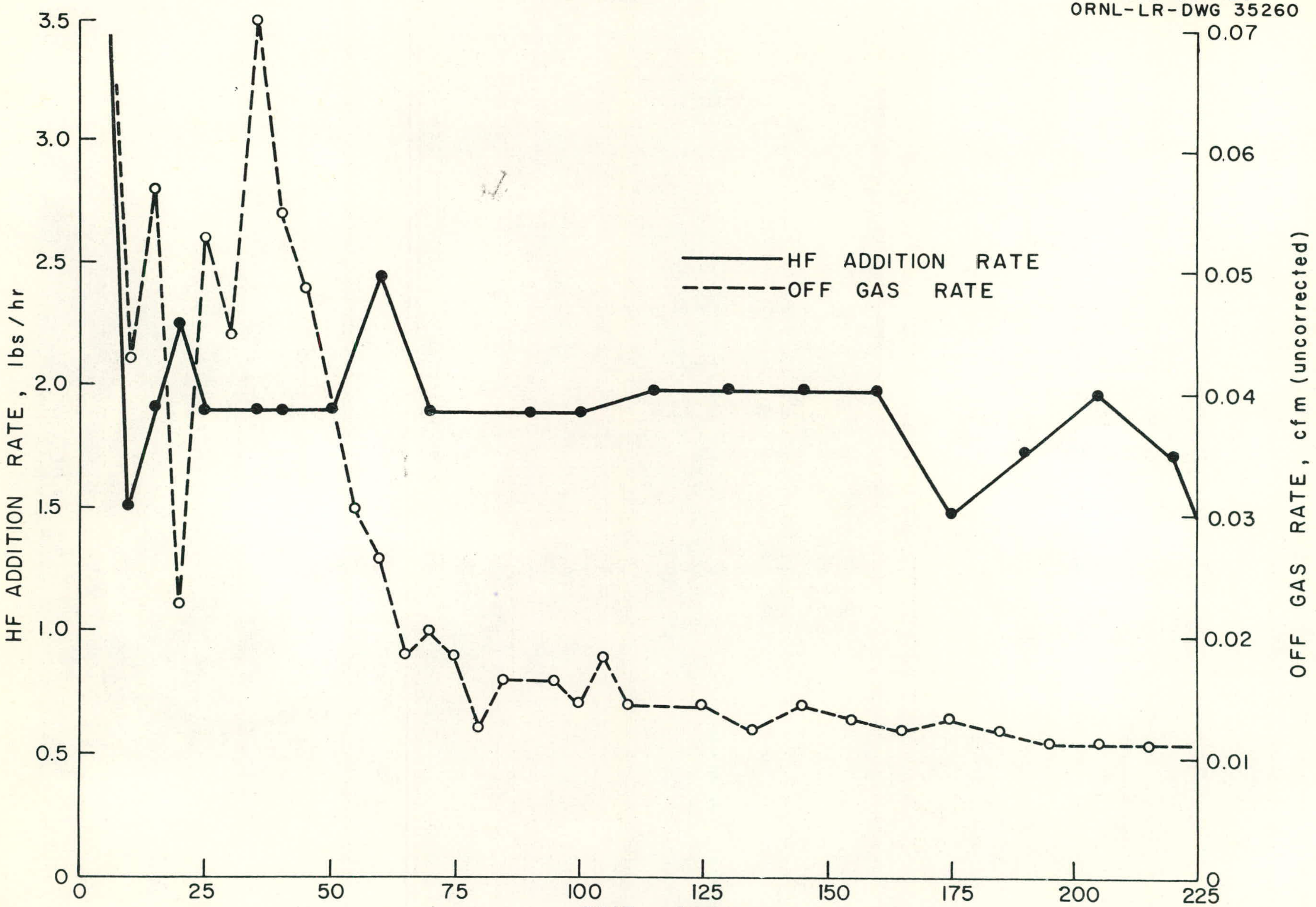
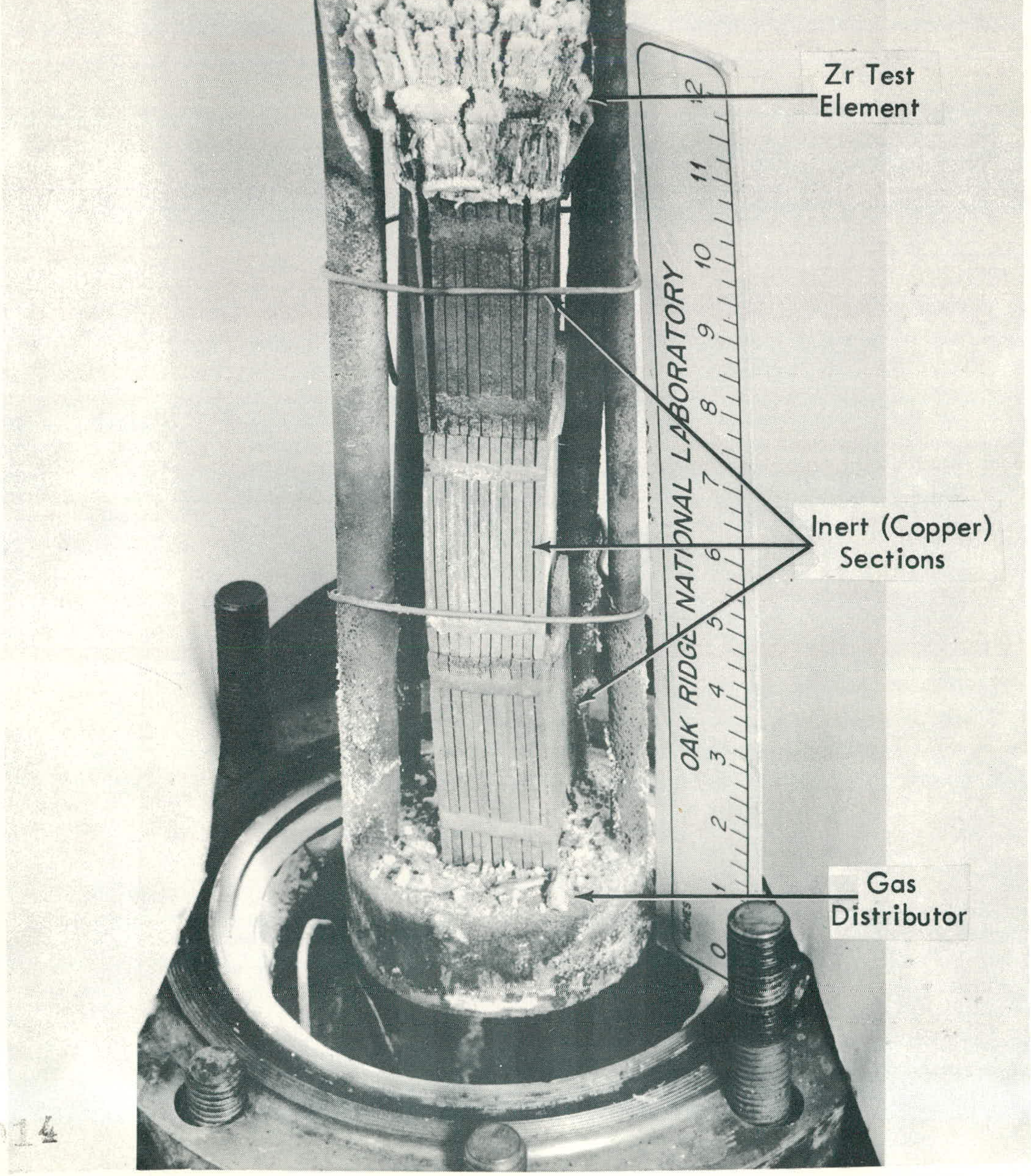


Fig. 7. Off Gas and HF Addition Rates in Absence of Fused Salt

310 013



310 014

Fig. 8. Test Element at End of Partial Dry Hydrofluorination Test.

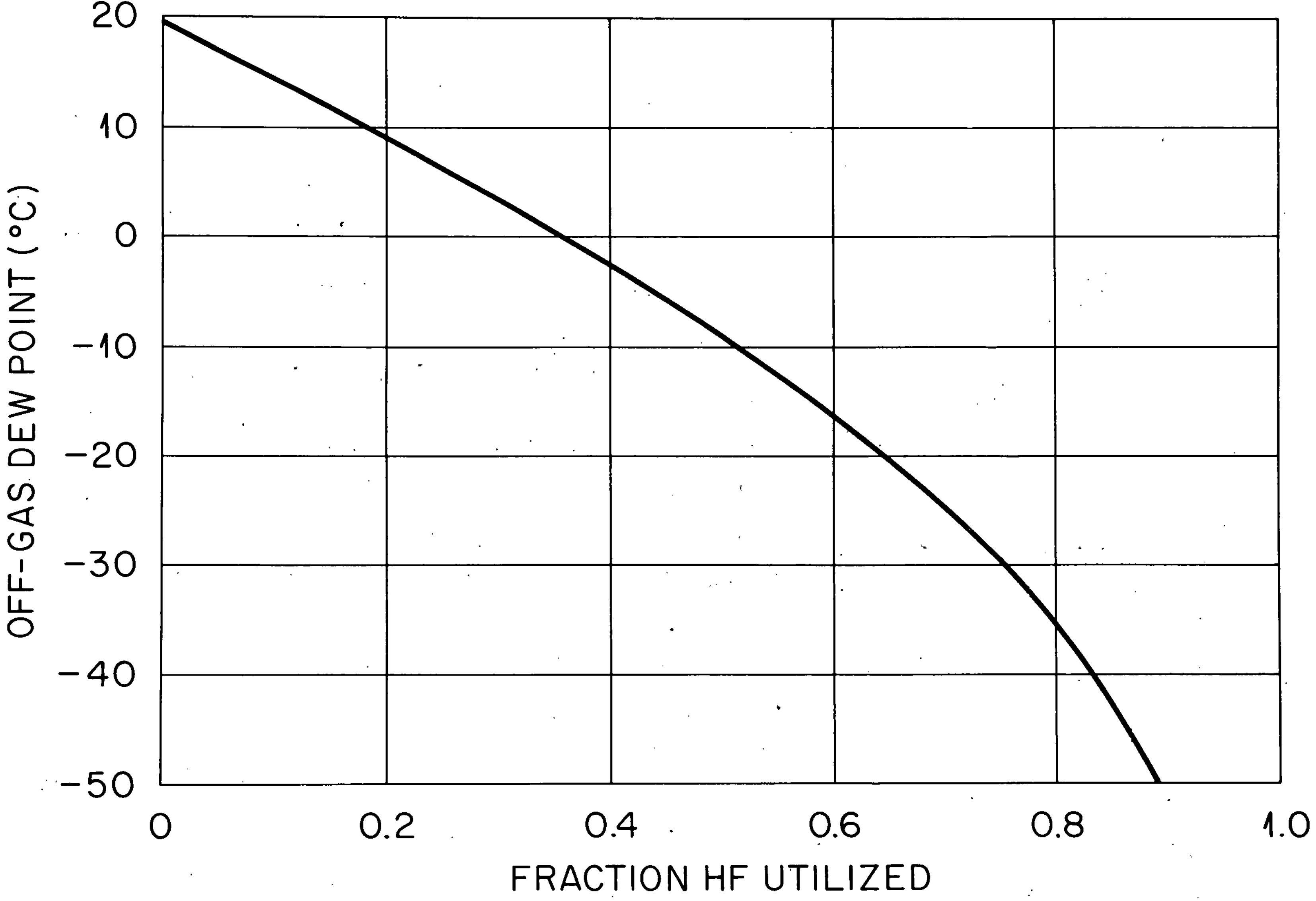
surfaces with a film of radioactive solids, and also would result in an accumulation of these solids in the hydrofluoric acid vaporizing stage of the acid recycle. Among the solutions of the problem under investigation is a scrubbing column in which hydrofluoric acid is refluxed to trap solids so that they can be returned to the dissolver vessel.

The physical properties of anhydrous hydrogen fluoride are such that operation of a reflux column is difficult. The particular properties involved are the high degree of association and the low heat of vaporization. The column operates on a gas stream containing hydrogen fluoride and hydrogen, with the hydrogen concentration varying from zero to sixty or seventy mol per cent. Since the association of hydrogen fluoride increases with decreasing temperature, variations in condensing temperature can cause large composition changes in the column exit gas stream and therefore create disturbances in the column liquid inventory. The relation between condensing temperatures and gas composition is shown in Fig. 9. In this figure, the dew-point is plotted against hydrogen fluoride utilization in the dissolution process; high acid utilization results in high concentration of hydrogen in the exit gas.

The reverse problem exists in an HF boiler, superheater and metering system. Because of the low heat of vaporization, boil-up rate requires close control, and the associative property makes it necessary to superheat the gas to a temperature sufficient to achieve complete dissociation before metering. At atmospheric pressure this temperature is about 70°C. For this reason, the primary metering for the dissolution studies is done in the liquid phase with the Lapp diaphragm pump.

310 916

UNCLASSIFIED
ORNL-LR-DWG 30904



Off-Gas Dew Point vs. HF Utilization.

Figure 9

REFERENCES

1. Cathers, G. I., Bennett, M. R. and Jolley, R. L., "A Uranium Hexafluoride Volatility Process for Fused Salts", ORNL-CF-56-9-21.

2. Gresky, A. T., Arnold, E. D. and Klatzbach, R. J., "Potentialities of Fused Salt-Fluoride Volatility Methods of Processing Irradiated Fuel", ORNL-1803.

3. Carr, W. H., "Volatility Processing of the HRE Fuel", ORNL-CF-58-11-60.

DISTRIBUTION

1. R. E. Blanco
2. J. C. Bresee
3. K. B. Brown
4. F. R. Bruce
5. W. H. Carr
6. G. I. Cathers
7-9. V. R. Cooper (Hanford Atomic Products Operation)
10. F. L. Culler
11. W. K. Eister
12. D. E. Ferguson
13. H. E. Goeller
14. A. T. Gresky
15. C. E. Guthrie
16. P. A. Haas
17. R. W. Horton
18. E. Lamb
19. R. B. Lindauer
20. A. P. Litman
21. J. T. Long
22. L. E. McNeese
23. R. P. Milford
24. E. C. Moncrief
25. E. J. Murphy
26. M. J. Skinner
27. S. H. Stainker
28. C. D. Watson
29. M. E. Whatley
30. C. L. Whitmarsh
31. Central Research Library
32. Document Reference Section
33-34. Laboratory Records
35. Laboratory Records (RC)
36-50. TISE, AEC

DO NOT PHOTOSTAT