

AEC RESEARCH AND DEVELOPMENT REPORT

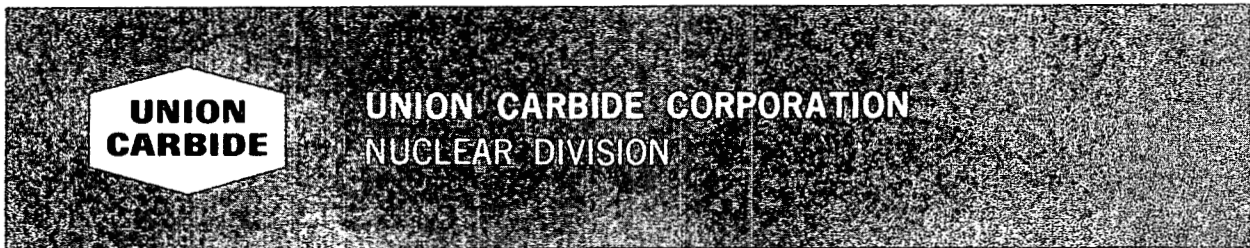
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AN IMPROVED THERMOBALANCE REACTOR
FOR THE STUDY OF
REDUCTION AND HYDROFLUORINATION
OF URANIUM FEED MATERIALS

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Date of Issue: September 16, 1964

Report Number: K-1617

Subject Category: TECHNOLOGY -
FEED MATERIALS
TID-4500 (32nd. Ed.)

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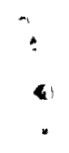
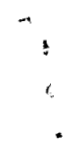
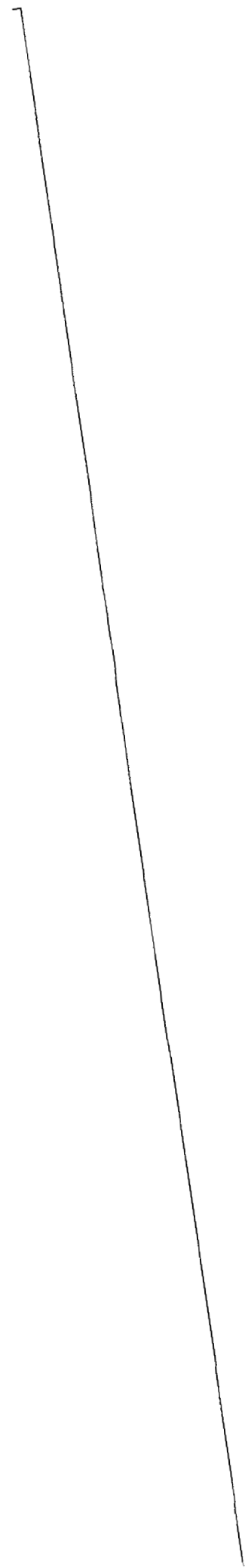
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and E. J. BarberA B S T R A C T

Two thermobalances have been constructed which make use of an improved reactor design for the study of gas-solid reactions as they apply to the conversion of uranium oxide materials to uranium tetrafluoride. Since temperature has been recognized as one of the most important rate-governing factors for both of the reactions involved in this transformation, the reactor design provides for maintaining the sample temperature constant to $\pm 1.0^\circ\text{C}$. at any selected temperature over the range 100° to 600°C . Rate-controlling variables such as reaction temperatures, gas flow rates, pre-heating time and bed depth have been studied in order to establish the ranges over which small variations in these factors can be ignored.

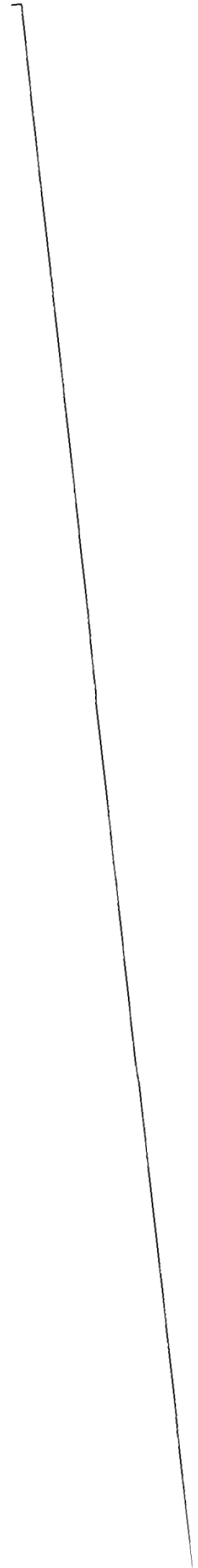
* Deceased.



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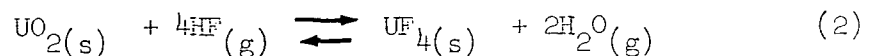
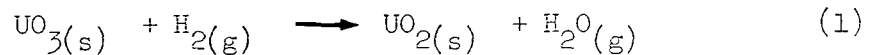
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AN IMPROVED THERMOBALANCE REACTOR FOR THE STUDY OF REDUCTION
AND HYDROFLUORINATION OF URANIUM FEED MATERIALS

Numerous investigators have used some type of thermobalance in their search for correlations between intrinsic physical differences of various uranium oxide preparations and their chemical reactions with gases. A lack of consistency among the fundamental data so obtained has retarded general progress in this direction. Comparative evaluations of similar preparations in different laboratories have not always resulted in complete agreement. While some of these differences may be due to real but unidentified differences in the materials, occasionally we have been unable to agree with other investigators upon the observed behavior of duplicate samples of the same material.

The gas-solid reactions represented by the equations,



are of particular interest, since the uranium tetrafluoride product is an important intermediate in the production of both uranium metal and uranium hexafluoride. This is especially true in the latter case in view of the suggested use of thermobalance data as a basis of acceptable reduction rate performance (24) and the interest shown in the potential utility of thermobalance hydrofluorination rate data in determining the most favorable process conditions for efficient production of feed for the gaseous diffusion plants.

Since temperature is apparently the most important single rate-determining factor in both of these reactions, accurate control and measurement of this variable could eliminate much of the discrepancy observed among thermogravimetric rate data. The design of the equipment used by Petretic and Bertram (22) incorporated features for accurate measurement of the sample temperature. However, the same design limited usage to pelletized samples, whereas most of the pot-produced feed materials were in powder form.

The thermobalance reactor design described in this report was developed to study and thereby eliminate or at least minimize the effects of potentially critical operational variables in a rate study of the reduction and hydrofluorination of uranium oxides. Provisions were made so that either powdered or pelletized samples could be used and precise control of temperature in the reaction zone was incorporated with accurate temperature measurement.

Using precise control of the temperature, the effects of (a) temperature, (b) hydrogen flow rate, (c) sample preheating time, and (d) sample bed depth upon the reduction rate of uranium trioxide in hydrogen were

studied in detail. Rate effects attributed to these operational variables have been cited most frequently by experimentalists investigating the reduction of uranium trioxide. The effect of temperature upon the reduction rate has received attention in the work of Kewish and Fry (5); Kuhlman (8); Moore and Maness (19); Petretic, Lerner, and Beaumont (21); and in this laboratory (20). Lasovick and Walsh (13) and Petretic and Bertram (23) have reported that the reduction rate is influenced by hydrogen flow rate. Preheat time, variously described as thermal dissociation or dehydration of a hydrated oxide, has been treated as an operational variable by Goldbeck and Rodden (4); Kuhlman (12); LeGassie, Roszkowski, Bertram, and Petretic (14); and Lister (15). Bed depth has been associated with sample temperature as a rate-determining factor during reduction by Petretic and Bertram (23) and by Swinehart (25).

By the same criteria (a) reduction temperature, (b) hydrofluorination temperature, (c) hydrogen fluoride flow rate and (d) sample bed depth were selected as operational variables in the hydrofluorination of uranium dioxide worthy of more detailed study. Bertram (2); DeMarco, Bonfer and Abbott (3); Kewish and Fry (5); Kuhlman (10); and Swinehart (25) have shown that the temperature employed in the reduction of uranium trioxide may affect the subsequent hydrofluorination rate of the resulting uranium dioxide. The temperature at which the hydrofluorination is performed has also been shown to have a rate-controlling effect by Kewish and Fry (5); Klingel (6); Kuhlman (7); Ludwig (16); Voisinet (27); and in this laboratory. The dependence of the hydrofluorination rate of uranium dioxide upon the reactant gas supply has been studied by Ludwig (17) from the viewpoint of hydrogen fluoride flow rate. In the deeper beds of uranium dioxide the dependence has been observed in terms of completeness of reaction or extent of bed temperature elevation by Bard, Fry, and Kewish (1); Kewish and Fry (5); Klingel (6); Lasovick and Walsh (13); Ludwig (16,17); and Petretic and Bertram (23).

In this report, following the description of the apparatus and the procedures employed in its operation, the results of studies involving each of the potentially important variables mentioned above are presented and discussed in an effort to differentiate between inherent differences in oxide reactivity and those incurred as a result of equipment limitations.

SUMMARY

An improved thermobalance reactor has been designed and tested. With this reactor the temperature at the sample location may be controlled to within $\pm 1.0^\circ\text{C}$. of a constant predetermined value in the operating range of 100° to 600°C . The temperature differential between the inner wall of the radiation shield and the shield axis at the sample location did not exceed 5°C . and a constant temperature was maintained along the axis of the radiation shield for 5 inches on either side of the sample location. The temperature of a duplicate reactant sample and the temperature of the gas in the immediate vicinity of the reactant sample being weighed were measured accurately with bare thermocouples.

The performance of the thermobalance and the effect of variations in temperature, reagent flow rates, and clean-up procedures upon this performance were evaluated using a pot-calcined uranium trioxide and uranium dioxide produced from this trioxide.

The hydrogen reduction rate of uranium trioxide varied by a factor of 20 over the temperature range of 480° to 700°C. When the rates were measured at 20° intervals, the temperature dependence was greatest in the lower part of the range. Change of the hydrogen flow rate from 800 to 3000 std. cc./min. increased the rate of reduction of uranium trioxide. A fixed gas flow would eliminate this variable for most rate comparison studies; the larger gas flow should be employed for studies of reaction kinetics so that limitation of the reaction rate by hydrogen availability or water vapor removal is minimized. Preheating the pot-calcined uranium trioxide at the reduction temperature in an inert gas atmosphere for periods of 5 to 60 minutes prior to reduction produced relatively small rate variations. Adoption of a standard preheat time of 10 minutes completely eliminated this factor as an operational variable. Bed depth exerted considerable influence upon the reduction rate, primarily as a result of poor dissipation of the heat of reaction from the deeper beds. Increasing bed depths from 0.5 to 4.0 mm. resulted in observed increases in bed temperature as large as 140°C. Corresponding times required for reduction were decreased by a factor of three as a consequence of the higher reaction temperature. Limiting bed depth to 0.5 mm. or essentially a single layer of powder particles eliminated practically all of the bed depth effect.

The hydrofluorination rate of uranium dioxide is influenced by the reduction temperature employed in its formation. Reduction conditions optimized to give a minimum time for hydrofluorination of one oxide are not necessarily optimum for other oxide preparations. The rate of hydrofluorination of a uranium dioxide powder is particularly sensitive to reaction temperature variation in the range of 500° to 600°C. The effective reactor temperature controls of this improved reactor design reduced the undesirable effects of hydrofluorination temperature variation to a minimum. Hydrogen fluoride flow rates in the range of 250 to 1000 std. cc./min. for a 0.5-gram oxide sample gave essentially duplicate hydrofluorination rates for a particular oxide. A flow of 500 std. cc./min. was made standard procedure so that minor fluctuations would not exceed the limits of the range investigated. Diffusion was a rate limiting factor in the hydrofluorination of deeper uranium dioxide beds. The influence of this variable was maintained at an acceptably low level by use of the minimum bed depth consistent with accurate observation of weight change, namely a bed 0.5 mm. in depth.

EXPERIMENTAL

Apparatus

Preheater-Reactor. The reactor and preheater were built as a single unit as illustrated in figure 1 because of the valving problems and the thermal

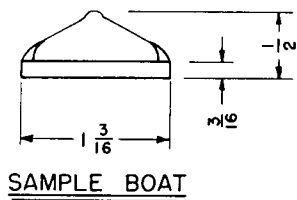
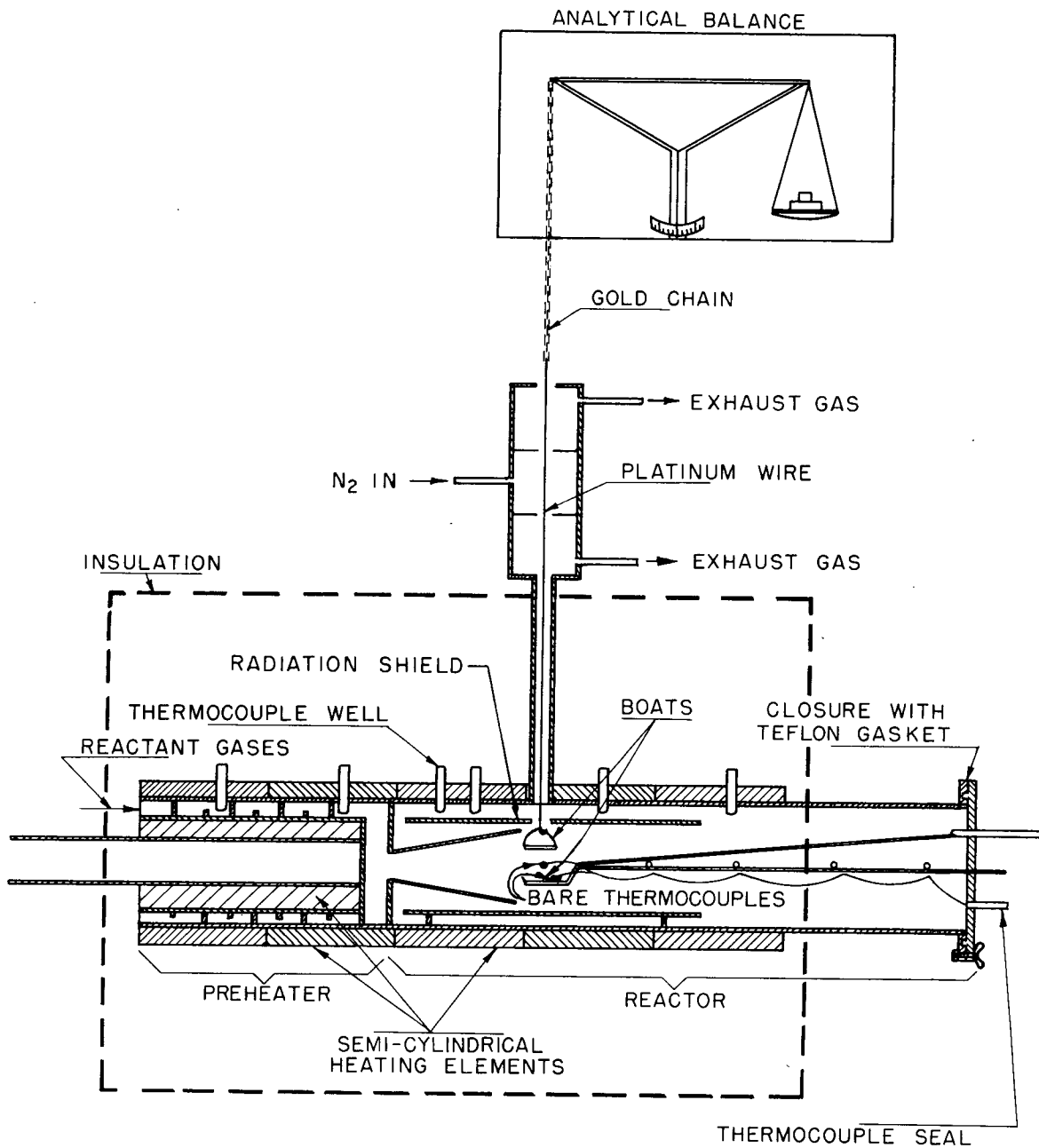


Figure 1
THERMOBALANCE REACTOR AND PREHEATER

losses that would be encountered with separate preheaters for each gas at the elevated operating temperatures. Use of an annular preheater with baffles decreased the volume and improved the surface-to-volume ratio in the preheater. The outer wall of the cylindrical unit was fabricated from 4-inch, heavy wall Monel tubing. The unit was divided into five independently heated outer zones spaced as shown by the location of the heating elements in figure 1. Ten semicylindrical, ceramic embedded, 35-ohm, resistance heating elements*, made to the specifications of the preheater-reactor unit, were attached directly to the reactor wall. A pair of 1-1/4-inch commercial tube furnace heating elements placed inside the inner wall of the baffled preheater served to offset the greater heat losses from the preheater zone. Controls for these heating zones, which are described later, gave a uniform reactor temperature over an axial distance of about ten inches at the center of which the sample was suspended. The radiation shield used in conjunction with the external heaters and the conical gas distributor allowed the temperature differential between the radiation shield wall and the axis at the sample location to be maintained within a range of 5°C. Under these conditions the sample temperature remained constant within $\pm 1^\circ\text{C}$.

Since it was impractical to measure the temperature of the sample being weighed, provision was made for supporting a duplicate sample and boat in an equivalent geometrical position below the weighed sample. A bare chromel-alumel thermocouple placed in the duplicate sample permitted measurement of the sample temperature during reaction. A second thermocouple located between the two sample boats measured the gas temperature. Leads for both couples were passed through ceramic insulators suspended from a Monel tube attached to the removable flange plate from which they were electrically insulated by Teflon gaskets held in place by 3/8-inch compression couplings which were silver soldered into the four plate openings.

Firebrick preshaped to fit the installed reactor heaters and encased in a metal outer shell served as thermal insulation for the preheater-reactor assembly. This insulating case was constructed in two parts so that the insulation could be opened on hinges to allow more rapid cooling of the reactor. The furnace and flanged end of the reactor, located beneath the balance table, are visible in the view of the complete assembly shown in figure 2.

The preheater-reactor unit was of all-welded Monel construction to resist the corrosive attack of hydrogen fluoride-water vapor mixtures. The 4-inch diameter of the unit was chosen as the minimum standard size of Monel tubing which would accommodate two sample boats inside a radiation shield spaced 3/8 inch from the reactor wall. The 26-inch length was determined by three factors: (a) adequate preheating of the reactant gases, (b) placement of the sample location a minimum of 10 inches from the ends of the furnace where radiant heat losses were greatest, and (c) need to

* Made by the Cooley Electric Manufacturing Corp., Indianapolis, Indiana.

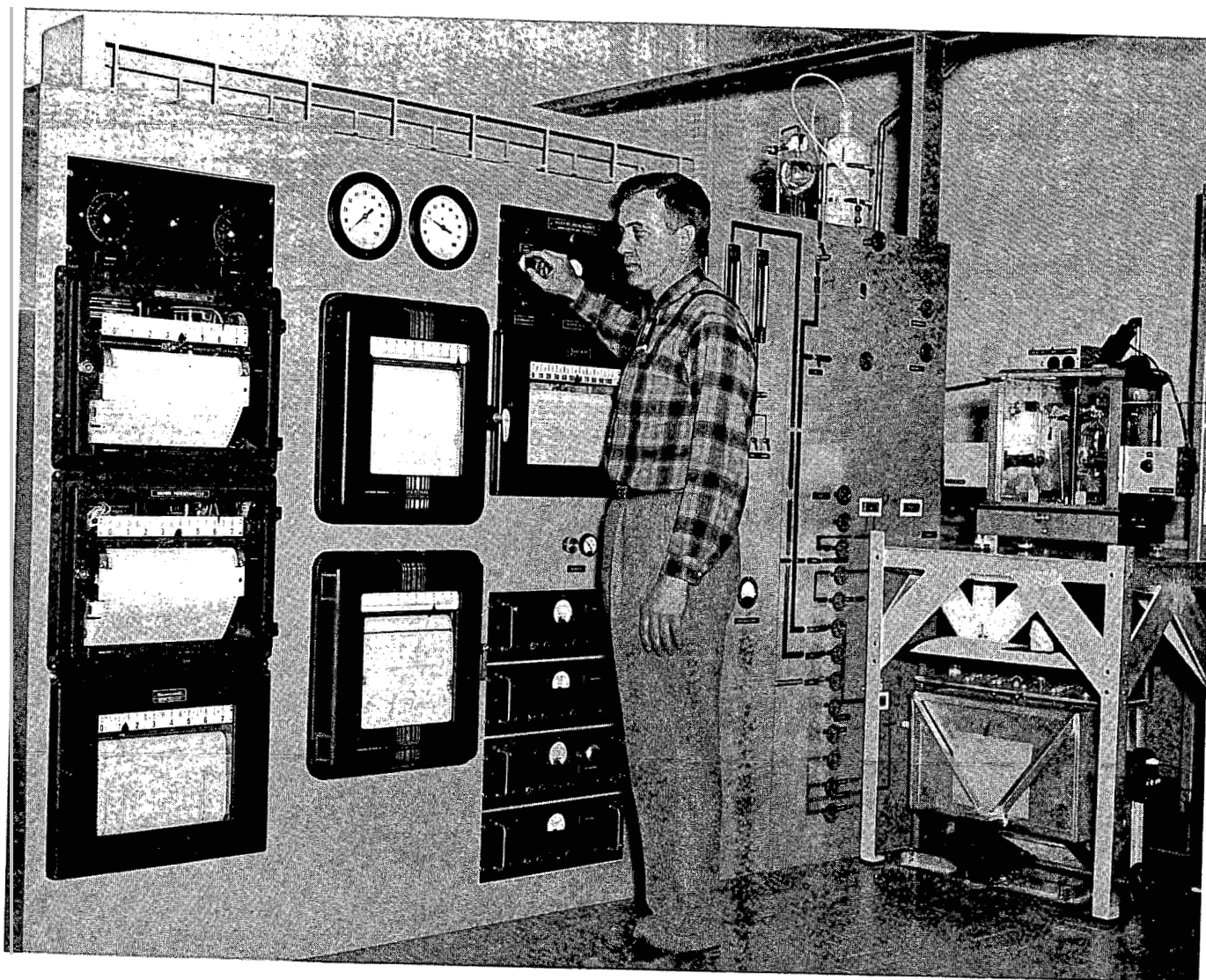


Figure 2
AUTOMATIC RECORDING THERMOBALANCE INSTALLATION

extend the flanged end of the reactor far enough from the furnace to prevent overheating of the Teflon gasket and thermocouple insulators.

The nitrogen seal chamber, which had only one compartment in the original design, was later divided into three sections to decrease the possibility of room air diffusing into the reactor or reactant gases escaping into the room.

Temperature Controls. An electronic absolute temperature regulator, having the circuitry shown in figure 3, was used to control the heat input to the pair of heating elements immediately to the left of the sample as shown in figure 1. The sensing device for this null-seeking control was a simple chromel-alumel thermocouple circuit, one junction of which was kept at 0°C. A 10-turn potentiometer inserted in one branch of the thermocouple circuit opposing the potential of the couple could be set in the range of zero to 50 millivolts. An unbalanced potential of ± 0.005 millivolts in this circuit activated a relay in the power circuit supplying the primary control zone.

The two heating zones to the right and one immediately to the left of the primary control zone were individually controlled by three differential thermal regulators. Each of these regulators had the same circuitry and sensitivity as the absolute regulator, except that the 10-turn potentiometer was omitted. The reference junctions of these thermocouple circuits were inserted in a common thermowell located in the primary control zone while the other junctions were each placed in the thermowell of one of the individually controlled zones. Thus, each of these regulators controlled a relay which supplied power to the corresponding pair of heating elements and which was activated when the potential of the measuring junction was less than that of the reference junction. This arrangement provided very sensitive control of four heating zones and automatically maintained the temperature of the central 10 inches of reactor wall essentially constant at the preset level.

The heating zone at the left end of the preheater-reactor unit and the internal heater were each controlled independently by a Brown temperature controller-recorder having a range of 0° to 700°C. Chromel-alumel thermocouples were employed as sensing elements. All power circuits controlled by temperature regulators included a variable voltage transformer for which settings had been established to provide the best control at the desired operating temperature. All control thermocouples were made by fusion of 20-gauge duplex thermocouple wire. A six-point Brown potentiometer recorded the temperature of all six heating zones. A Sangamo electric time switch operated a master relay for the primary power supply to all heaters and electronic control circuits. By presetting this switch the system could attain thermal equilibrium before the working day was scheduled to begin.

Even though the thermocouple wells extended into the gas stream, the temperatures monitored were essentially those of the reactor and preheater walls. Since the sample temperature was of primary interest,

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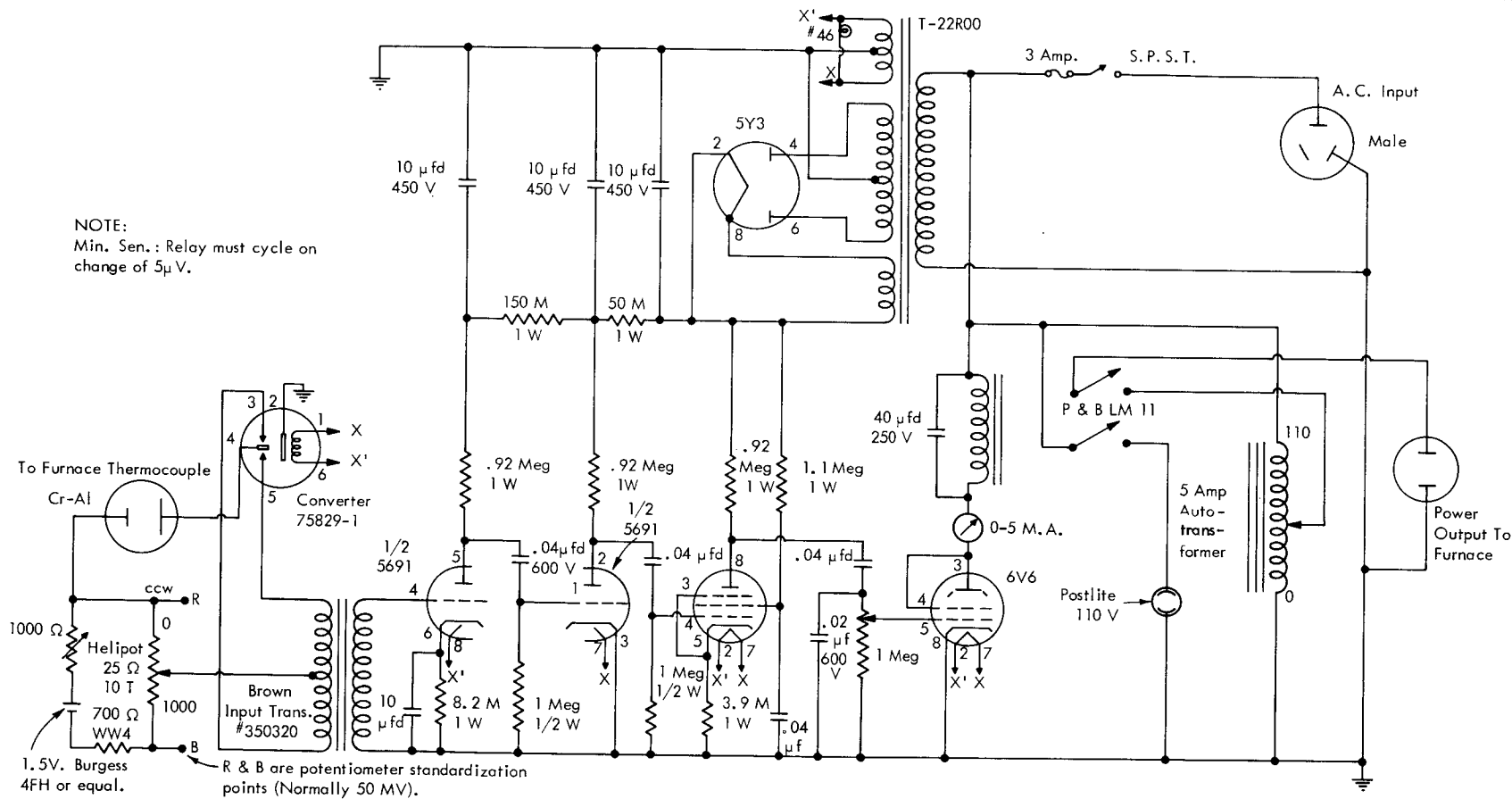


Figure 3
ABSOLUTE TEMPERATURE REGULATOR

the regulators were arbitrarily set to yield the desired value in the lower sample. The sample temperature and that of the gas stream were identical when the system had reached equilibrium. These temperatures were usually 10° to 25°C. lower than the reactor wall temperature. Most of this temperature differential was between the wall and the radiation shield. The magnitude of the temperature differential was dependent upon the operating temperature level and upon the thermal properties of the reactant gas. The sample and gas temperatures were recorded by a Leeds and Northrup Speedomax and Micromax, respectively. Each instrument received its signal from a bare 28-gauge chromel-alumel thermocouple with a reference junction at 0°C. The full-scale sensitivity of each of these recorders was 10 millivolts. Incorporation of an opposing potentiometer circuit with each instrument enabled the recorder zeros to be shifted in 5-millivolt increments for a total span from 0 to 55 millivolts.

Supply and Exhaust Manifolds. The gas supply and exhaust manifolds, shown schematically in figure 4, consisted of (a) a noncorrosive gas supply system, (b) a corrosive gas supply system, (c) an exhaust system, and (d) a water vaporizer.

The noncorrosive gas system supplied nitrogen, argon, helium, and hydrogen gases to the reactor through 0.25-inch copper lines as indicated. Nitrogen was also supplied to the seal chamber. Flow rates were measured by Fisher and Porter laboratory type rotameters calibrated for the various gases and were controlled by properly combining commercial high pressure gas cylinders, pressure reducing valves and Ideal needle valves. Hoke toggle valves 1 through 5 and Hoke needle valves 9 and 10 were used for off-on control.

The corrosive gas system used for introduction of controlled flows of anhydrous hydrogen fluoride to the reactor was constructed of silver-soldered Monel components. These included a 36-mil orifice for metering the gas flow, Hoke style M-342 needle valves in which the standard stainless steel needles had been replaced by needles machined from Monel, and 0.375-inch diameter Monel tubing. Teflon was substituted as an inert packing for these valve stems. The differential pressure across the metering orifice was measured by a corrosion resistant, closed system, remote reading, mechanical pressure transmitter, DBM-1, with a pressure range of zero to 0.5 psi. This transmitter is designated 206RF-3 by the manufacturer.* The entire corrosive gas system was enclosed in a constant temperature air bath maintained at 125°C. This assured that hydrogen fluoride would be metered as the molecular monomer.

Since the reactor is open to the atmosphere where the sample boat support wire enters, a nitrogen gas seal and a system of balanced flows were used to prevent oxidizing air from entering the reactor and to prevent

* The Taylor Instrument Company, Rochester, New York.

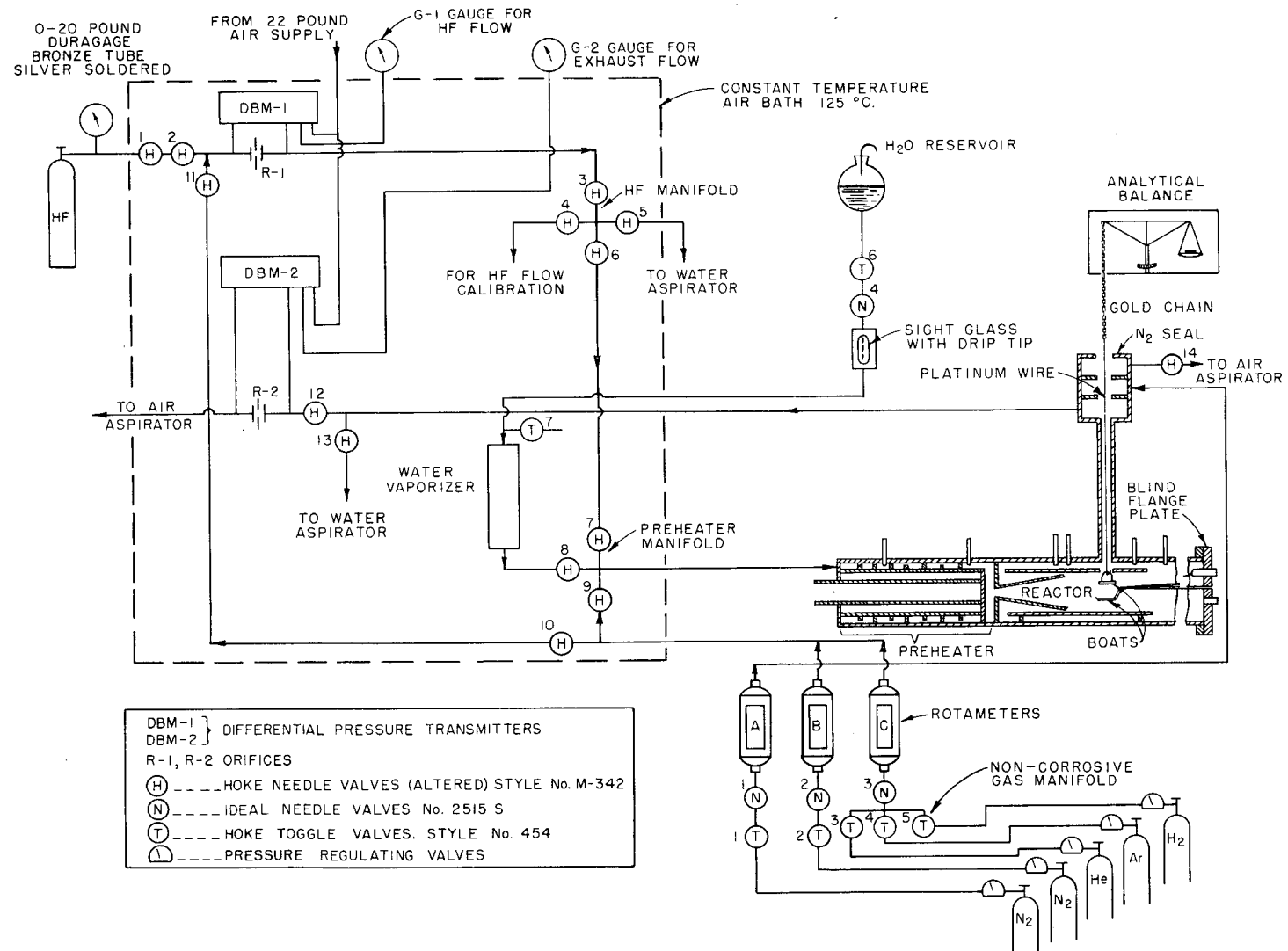
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Figure 4

THERMOBALANCE SUPPLY AND EXHAUST MANIFOLDS

explosive hydrogen or toxic hydrogen fluoride from escaping into the room. This was accomplished by regulating the exhaust flow at a level larger than the reactant gas flow alone but smaller than the combined flows of reactant gas to the reactor and nitrogen to the seal chamber. An air-operated aspirator performed satisfactorily for exhausting the noncorrosive gases, the exhaust flow being metered through a preset valve acting as a variable orifice. The pressure differential across this orifice was measured by another Taylor transmitter, DBM-2. When anhydrous hydrogen fluoride was being fed to the reactor it was necessary to exhaust the excess reactant gas diluted with water vapor formed as a reaction product. The corrosive nature of the aqueous hydrogen fluoride vapor caused plugging of the orifice and air aspirator so that another means of exhausting this gas was devised. A reliable exhaust of hydrogen fluoride from the reactor was achieved by use of a water aspirator without a direct metering device. Instead, a provision for indirect metering was made in which Hoke valve 13 to the water aspirator was adjusted so that the sample weight in an inert gas remained the same with exhaust by water aspirator as it was with the metered exhaust by the air aspirator. This adjustment was essential for proper operation of the balance since any appreciable variation in gas flow would result in an apparent change of the sample weight and might upset the balanced flow volumes excessively. All exhaust lines, valves, and associated metering devices were enclosed in the 125°C. constant temperature air bath to prevent condensation of hydrogen fluoride-water azeotrope from the exhaust gases. The supply lines from the air bath to the preheater-reactor unit and the exhaust lines from the nitrogen seal chamber were heated by coils of insulated resistance wire which were controlled by Fenwal bimetallic thermal regulators (No. 17,000).

A water vaporizer system was used for hydrolytic decontamination of the reactor after hydrofluorination since steam of greater purity could be prepared from the vaporization of tap water than was available in the building steam lines. Controlled by an Ideal needle valve, water dropped from a beveled drip tip, sealed in a tubular sight glass, into a cool tube which conducted it in a steady flow to a continuous evaporator inside the 125°C. air bath. Supplementary heat was supplied to the evaporator as needed by a wrapping of insulated resistance wire to which power was supplied from a 7.5-ampere variable voltage autotransformer. A metered liquid flow of 17 drops per minute provided delivery of 1000 cc. of water vapor per minute to the reactor. Calibration of the rate of water vapor generation over a range allowed use of the vaporizer unit to provide steady generation of water vapor for make-up of reactant gas mixtures of known dilutions.

Balances. Two different balances were used during the study of the reaction variables discussed in this report. One was an Ainsworth magnetically damped chainomatic analytical balance which had been modified as previously described (20) for manually weighing a sample suspended into an external reactor. This balance initially had a sensitivity of ± 0.05 mg. which was decreased to ± 0.2 mg. by the modifications. All hydrofluorinations and certain indicated reduction experiments were performed with this equipment.

During the course of this investigation a Mauer recording balance (18) which had been constructed for this laboratory by the Niagara Electron Laboratories of Andover, New York, was received. This modified Ainsworth balance had essentially the same sensitivity as the manually operated Ainsworth balance after modification, but by electronic conversion provided for strip chart recording of continuous automatic weighing instead of the intermittent direct observations made with the manually operated balance. The recording balance was installed with a new reactor and furnace built to the same design specifications as the one already in use. This assembly, which is shown in figure 2, was limited in this investigation to the study of the reduction rates of uranium trioxides in hydrogen. Because this reactor was not used for hydrofluorination studies, the reduction data tabulated later under the heading "clean reactor" indicates the use of this thermobalance assembly.

Sample Boats. The sample boats, detailed in figure 1, were made from 1.4-inch squares of 12-mil platinum sheet with one pair of the diagonally opposite corners rounded. A boat was shaped by forcing the sheet into a circular, flat-bottomed female die with a one-inch cylindrical rod. Clearance between the two components of the die was about $3/32$ inch. The untrimmed corners of the shaped boat were bent toward the center and were joined by 55-mil platinum wire spot welded between them. The edges of the boat were bent downward to the outside to form a smooth edge. Sample boats prepared as described weighed between 6.5 and 7.0 grams. Similar sample boats of the same diameter but greater depth were required for the experiments with bed depth as a variable.

Intermediate Gases. While the thermobalance reactor was being heated to the predetermined operating temperature, a flow of nitrogen was originally maintained through the reactor and the nitrogen seal, and the air aspirator was in operation. Due to the relatively large differences in the thermal conductivities of nitrogen and the reactant gases, whenever a direct change of gas was made an attendant gas temperature change was observed. The magnitude of the change varied from a rise of 30°C . when nitrogen was replaced with hydrogen to a drop of 70°C . when hydrogen was replaced with hydrogen fluoride. To avoid this temperature effect, an inert gas having a thermal conductivity similar to that of the reactant gas to be introduced was fed immediately prior to changing to the reactant gas. Hence, following the initial heating of a sample of uranium trioxide in a nitrogen atmosphere, this gas was replaced by helium and the reactor was allowed to reach temperature equilibrium before reduction with hydrogen was started. Similarly, after the reduction was completed, the hydrogen atmosphere was replaced by argon and temperature equilibrium was again established before hydrofluorination of the uranium dioxide was started. Using helium and argon as intermediate gases, momentary gas temperature changes of less than 5°C . were observed and there was no detectable change in the sample temperature associated with the change from intermediate gas to reactant gas.

The inert gas manifold was so arranged that either of the intermediate gases or nitrogen could also be employed as diluents for the hydrogen fluoride.

Gas Flow Calibrations. Hydrogen, nitrogen, helium, and argon supplied to the reactor as well as the nitrogen supplied to the reactor seal were metered through rotameters which had been calibrated directly with a wet test meter under operating conditions. The metered flow of gas in the air-aspirated exhaust line was calibrated directly by use of a wet test meter. The anhydrous hydrogen fluoride metering system was first calibrated with a nitrogen flow through a wet test meter. Conversions to the corresponding hydrogen fluoride flows were made on the basis of fundamental relationships between the two gases. Finally, direct measurement of a few hydrogen fluoride flows was made by chemical neutralization of the hydrogen fluoride passed in a specified interval of time. Periodic rechecks were made of the hydrogen fluoride flow calibration by means of nitrogen passed first through a rotameter then through the hydrogen fluoride metering orifice.

The water vaporization system supplying the preheater manifold was used during hydrolytic cleanup of the reactor following a hydrofluorination reaction. A rough calibration was achieved by counting the drops from the drip tip for a definite time interval and weighing the water collected. Seventeen drops of water upon vaporization produced approximately 1000 cc. of saturated steam at atmospheric pressure.

In order to establish the appropriate corrections for buoyancy effects and temperature variations, the empty boat was weighed in each gas under the proposed operating conditions.

Materials

Blended samples of uranium trioxide from several sources were used as starting materials for determining the variables which affect the reduction rates in hydrogen. These were representative of production lots prepared by the pot calcination of uranyl nitrate hexahydrate at the Savannah River Laboratory of E. I. duPont de Nemours and Company, the Mallinckrodt Chemical Works at Weldon Springs, and the Hanford Atomic Products Operation of the General Electric Company. The samples, according to origin, were given the respective designations, SRP, MCW, and HPC. A fourth sample, designated HPCS, was representative of a Hanford lot to which sulfate had been added as sulfuric acid prior to the denitration process.

Procedure

Preliminary. At the beginning of each reduction experiment, the tare weight of the sample boat was determined on the thermobalance under the conditions of temperature and gas flow selected for the experiment. The boat was removed from the reactor and an approximately weighed sample of oxide was transferred into it on an auxiliary analytical balance. The boat containing the sample was then resuspended in the preheated reactor of the thermobalance and the closure was bolted into place. The sample was allowed to preheat in a flow of helium for 10 minutes at the selected reduction temperature; selection of this particular preheat interval is discussed later in this report. An accurate weighing of the sample and boat was then made in place, to which a predetermined correction for the

difference in the buoyancy effects of flowing helium and hydrogen upon the weight of the boat was applied. Subtraction of the tare weight from this corrected weight gave a difference which was recorded as the initial weight of the sample corresponding to zero time in hydrogen.

Reduction. When the helium flow was replaced with a flow of hydrogen, reduction of the sample began. While the temperature and the gas flow were controlled at the predetermined values, weighings on the manually operated balance were made periodically and recorded at 0.5- to 2-minute intervals depending upon the rate of reaction; the faster the rate the more often weighings were made and recorded. When the Mauer balance was used the strip chart weight record was continuous. In either case the experiment was continued until a minimum constant weight was observed over a 10-minute interval of time.

Calculations. A theoretical weight change could have been calculated for the reduction of a known weight of pure uranium trioxide. However, the uranium oxides used for this investigation were prepared under calcination conditions which left small but varying amounts of water and nitrate as contaminants. When the sample was heated in the reactor at 560°C., the contaminants were gradually expelled simultaneously with some thermal decomposition of the oxide, making it impractical to determine directly the true weight of uranium trioxide involved. Hence, a preheat time of 10 minutes at the reduction temperature was established as an empirical standard because it was adequate to allow the sample to attain thermal equilibrium and it was reproducible. Considering then the total weight change observed from zero time in hydrogen to represent complete reduction to uranium dioxide, the average reduction rate for any portion of the reaction could be derived by calculating the time related intermediate fractions of uranium oxide reduced from the following empirical expression:

$$F_{\text{red.}} = \frac{\Delta W_i}{\Delta W_t} \quad (3)$$

where $F_{\text{red.}}$ is the fraction reduced in a specified interval of time,

ΔW_i is the weight lost by the sample during this interval and

ΔW_t is the total weight lost by the sample during the entire reaction from time zero.

In this report comparisons are made on the basis of the times required for complete reduction in hydrogen or some arbitrarily chosen fraction thereof.

Intermediate Procedure. When hydrogen reduction of the uranium trioxide was completed, the hydrogen flow was exchanged for one of argon; the temperature controls were set for the desired hydrofluorination temperature; and the gas and sample were allowed to reach thermal equilibrium. Exhaust of gases from the reactor was changed from the air aspirator to the water aspirator and an accurate weighing of the sample in argon

was made. To this, a predetermined correction in weight for the buoyancy variation involved in changing from argon to hydrogen fluoride was applied. The corrected sample weight so obtained was recorded as the weight of uranium dioxide at zero time in hydrogen fluoride.

Hydrofluorination. Conversion of the uranium dioxide to uranium tetrafluoride began when argon was replaced by a flow of anhydrous hydrogen fluoride. With the reactor temperature controlled at the predetermined value, manual balance weighings were made and recorded at 0.5- to 15-minute intervals depending upon the rate of reaction. This procedure was continued until 99 percent of the weight change calculated for complete conversion of the uranium dioxide sample to the tetrafluoride was observed or for a period of 180 minutes, whichever period was shorter.

Reactor Decontamination. After terminating the hydrofluorination experiment, it was necessary to clean the reactor to prevent hydrogen fluoride poisoning during subsequent reduction reactions (9). Residual hydrogen fluoride gas was purged from the reactor by a flow of nitrogen for a period of five minutes before the sample and boat were removed. When the reactor was again closed after sample removal, it was heated to 650°C. and treated with steam flowing at a rate of approximately 1000 std. cc./min. for a period of 20 minutes. The reactor was then purged with nitrogen for five minutes to remove the remaining water vapor and traces of hydrogen fluoride produced by the pyrohydrolysis of metal fluorides on the preheater-reactor walls. The exhaust flow was returned to the air aspirator and a flow of hydrogen was substituted for the nitrogen flow. The decontamination was completed by treating with hydrogen for 20 minutes at 650°C. To prevent any reoxidation, the flow of hydrogen was continued while the reactor cooled to the selected reduction temperature, which in these studies was 560°C. The total cycle time was approximately one hour in the normal case.

Meanwhile the sample boat was emptied, washed with water or with a 0.5-N sodium hydroxide solution containing a few drops of 30 percent hydrogen peroxide, and finally dried in an oven at 110°C. After decontamination of the reactor was completed, the dried sample boat was replaced in the reactor and a tare weight was obtained for the next experiment.

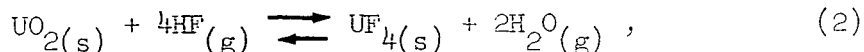
The reactor decontamination described was sufficient to give subsequent rates comparable to those obtained in an uncontaminated reactor provided the hydrofluorination temperature had not been in excess of 550°C. The reactor of the manually operated thermobalance was used over a period of about one month to determine hydrofluorination rates at 600°C. Following these experiments, a decontamination treatment about 20 times as long as normal would permit reproducible reduction rates to be obtained although these rates were somewhat slower than those obtained using an uncontaminated reactor as shown in table I.

TABLE I

EFFECT OF TEMPERATURE ON THE HYDROGEN REDUCTION RATE OF URANIUM TRIOXIDES

Sample	Gas Temp., °C.	Time to Achieve Indicated Completion, min.			Number of Determinations	
		In Reactor Contaminated by HF at 600°C.		In Clean Reactor	In Contaminated Reactor	In Clean Reactor
		97 per cent	100 per cent	100 per cent		
MCW	480	---	---	26.5	--	1
	500	---	---	16.0	--	1
	520	---	---	9.9	--	1
	540	15	18	8.5	1	1
	560	8.9 ± 1.7	12.7 ± 4.0	4.8 ± 0.5	10	5
	580	8.5	10.0	3.9	1	1
	600	4.5	6.0	2.3 ± 0.3	1	2
	625	2.9	3.5	---	1	--
	650	1.9	2.0	---	1	--
	675	1.4	1.5	---	1	--
700	1.0	1.0	---	1	--	
HPCS	480	---	---	22.5	--	1
	520	---	---	11.5 ± 0.5	--	2
	540	15.5	17.0	---	1	--
	560	10.1 ± 0.8	11.9 ± 1.0	5.4	10	1
	580	7.7	10.0	---	1	--
	600	5.3	7.0	2.5	1	1
	650	2.1	3.0	---	1	--
	700	1.9	2.0	---	1	--
HPC	480	---	---	21	--	1
	520	---	---	9.3	--	1
	540	14.0	16.0	---	1	--
	560	9.8	12.0	4.0 ± 0.0	1	2
	600	5.7	7.0	1.9	1	1
	650	1.9	3.0	---	1	--
	700	1.9	2.0	---	1	--
SRP	480	---	---	20	--	1
	520	---	---	11.8	--	1
	540	16.1	18.0	---	1	--
	560	9.5	12.0	5.7 ± 2.3	1	2
	600	4.8	6.0	2.3	1	1

Calculations. A stoichiometric solids weight change for the reaction,



was calculated based upon the weight of the uranium dioxide sample measured in hydrogen at the end of the reduction reaction. The average reaction rate for any portion of the hydrofluorination could then be derived by calculating the time related fractions of uranium dioxide converted to uranium tetrafluoride by use of the following expression:

$$F_{\text{hydf.}} = \frac{\Delta W_i}{\Delta W_{\text{st}}}, \quad (4)$$

where $F_{\text{hydf.}}$ is the fraction converted in a specified interval of time,
 ΔW_i is the weight gained by the sample during this interval and
 ΔW_{st} is the stoichiometric solids weight gain for conversion of the uranium dioxide to uranium tetrafluoride.

In this report the accumulated fractions converted from time zero in hydrogen fluoride are presented graphically as first order reaction rate plots with respect to unreacted uranium dioxide although the hydrofluorination reaction is obviously not first order in its entirety.

RESULTS AND DISCUSSION

Reduction Variables

Temperature. As noted earlier in this report several investigators have shown that temperature is a rate-controlling factor in the hydrogen reduction of uranium trioxide. However, in much of the previous work the reduction rates apparently have been related to the skin temperature of the reactor. In the work of Petretic, Lerner, and Beaumont (21) on pellets of hydrated uranium trioxide, and in the preliminary stages of the present investigation, a significant difference has been observed between the temperatures of the sample and the reactor wall in the vicinity of the sample. Consequently, an improved thermo-balance reactor was essential to establishing a reproducible relationship between reduction rate and sample temperature in the range 480° to 700°C. Using 0.5-gram samples of uranium trioxide with a bed depth of about 0.5 mm., the sample temperature remained practically constant during reaction and was essentially the same as that of the reactant gas. The data obtained from the four samples studied are summarized in table I.

In the range studied, 480° to 700°C., the reduction rate of all samples increased as the reaction temperature was increased. Differences among the behaviors of the four samples which were primarily attributable to sample differences were small. The effect of incremental temperature changes upon the time required for reduction varied not only with the magnitude of the change but was also influenced by the temperature region

in which the change was made and to a large extent by the condition of the reactor. Reduction at comparable temperatures was completed in a clean reactor in one-third to one-half the time required for reduction in a reactor which had been previously used for hydrofluorination reactions at 600°C.

It was found that an hour decontamination cycle was sufficient to decontaminate a reactor following its use for hydrofluorination at temperatures no higher than 410°C.; a decontamination treatment of longer duration was required following a hydrofluorination at 550°C. However, after hydrofluorination reactions at 600°C., a complete decontamination of the reactor was not achieved with the standard procedure at 650°C. even when applied repetitively for a total period of 24 hours.

While these data confirm Kuhlman's observations (9) regarding the poisoning effects of traces of hydrogen fluoride, they also show that reproducibility among individual determinations is better when fluoride contamination is not a factor. Thus, when more limited reduction rate studies are to be made thermogravimetrically, a reactor which has not been used previously with hydrogen fluoride is preferable.

The pronounced effect of temperature upon the hydrogen reduction rates of uranium trioxides, especially at the lower temperatures, attests to the importance of adequate control of the sample temperature during such rate studies. Control of the sample temperature to within $\pm 1.0^\circ\text{C}$. is possible with this equipment even though the control instruments respond to variations in the reactor wall temperature which is different from that of the gas stream and sample; the difference remains essentially constant after the sample has been brought to temperature in flowing helium. Less adequate maintenance of a known sample temperature probably accounts for the lack of agreement among previous investigations of the reduction rates of standard uranium trioxide samples in hydrogen. For this reason there is insufficient basis for any direct comparison of the data from this study with those reported earlier (20) since neither the Mallinckrodt uranium trioxide samples nor the equipment used in the two investigations are the same.

Every effort has been made in the design of this improved thermobalance reactor to eliminate uncontrolled temperature variations as a barrier to detecting and evaluating other experimental variables as potential rate-controlling factors in the conversion of uranium trioxide feed materials to uranium dioxide then to uranium tetrafluoride.

Hydrogen Flow Rate. Lasovick and Walsh (13) state that the rate of hydrogen flow has an effect on the reduction rate of uranium trioxide. Petretic and Bertram (23) found that flows of five to ten liters of hydrogen per minute gave higher reduction rates than they obtained when a one-gram pellet of hydrated uranium trioxide was reduced with a flow of three liters per minute.

Hydrogen flow rate was examined as an operational variable in the present study using 0.5-gram samples of unhydrated uranium trioxide powder. With

the experimental flow rates employed, the hydrogen supplied to the reactor each minute represented 18, 35, and 70 times the stoichiometric amount of hydrogen required for complete reduction. The experimental results are given in table II. It should be noted that the data are for reduction at 560°C. in the contaminated reactor and at 520°C. in the clean reactor.

As was observed in the experiments performed to study the effects of temperature variation, fluoride contamination of the reactor again resulted in lower uranium trioxide reduction rates. In both reactors the reduction time decreased as the hydrogen flow was increased. In view of the large excesses of hydrogen employed in all of these reduction experiments the differences must be partially attributable to the dilution effect observed by Kuhlman (11). Another flow dependent reaction variable is the time required to replace the helium in the pre-heater volume, about 1000 cc., with gas having a sufficiently high concentration of hydrogen to initiate reduction of the sample. The significance of this factor was verified by a series of experiments in which the hydrogen flow rate was reduced after a uniform reduction rate had been attained with a high rate of flow. When parallel reductions were started with initial hydrogen flows of 3000 std. cc./min. and completed with flows of 3000 and 1500 std. cc./min., respectively, the times required for the total reduction of each sample were identical. However, when the hydrogen flow was reduced from 3000 to 800 std. cc./min. after reduction was underway, the time required to complete the reaction was extended. This shows that a hydrogen flow of 800 std. cc./min. was insufficient to maintain reduction of the sample at a maximum rate.

The limiting factors revealed by these parallel experiments indicate that identical flow rates should be employed in any empirical comparison of the reduction behaviors of various uranium trioxides. For kinetic studies of uranium trioxide reduction performed in this equipment upon 0.5-gram samples, a minimum flow of 3000 std. cc. of hydrogen per minute is needed to eliminate flow as a rate-controlling variable.

Sample Preheat Time. Preheat time is here defined as the interval between the time the uranium trioxide sample is placed in the hot reactor with helium flowing and the time at which reduction is initiated by replacing the helium with a flow of hydrogen. Although this interval has not been previously called preheat time, the dependence of an optimum preheat time upon the rates at which a particular uranium trioxide sample undergoes dehydration and thermal decomposition has been observed by Kuhlman (12); LeGassie, Roszkowski, Bertram, and Petretic (14); Lister (15); and Goldbeck and Rodden (4).

In the present work, preheat times of 5, 10, 20, 30, 40 and 60 minutes were investigated. Studies were made at 520° and 560°C. in the clean reactor and at 560°C. only in the fluoride-contaminated reactor. The preheated samples were then reduced at the preheat temperature with hydrogen flowing at a rate of 1500 std. cc./min. The results are given in table III.

TABLE II

EFFECT OF HYDROGEN FLOW RATE ON THE REDUCTION TIME OF
URANIUM TRIOXIDES

Sample	Hydrogen Flow Rate, std. cc./min.	Time for Complete Reduction, min.*		Number of Determinations	
		In Contaminated Reactor at 560° C.,	In Clean Reactor at 520° C.	In Contaminated Reactor	In Clean Reactor
MCW	800	19.8 ± 3.8	20.5	6	1
	1500	12.7 ± 4.0	9.9	10	1
	3000	9.8 ± 2.2	9.0	6	1
HPCS	800	18.0 ± 2.0	14.5	5	1
	1500	11.9 ± 1.2	11.1 ± 0.4	5	2
	3000	7.0 ± 0.5	7.6	5	1
HPC	800	15.0	13.0	1	1
	1500	12.0	9.5 ± 0.3	1	2
	3000	7.0	7.0	1	1
SRP	800	17.0	13.0	1	1
	1500	12.0	11.8	1	1
	3000	8.0	8.0	1	1

* 0.5 gram samples were used in all cases.

TABLE III

EFFECT OF PREHEAT TIME IN HELIUM UPON THE HYDROGEN REDUCTION
RATE OF URANIUM TRIOXIDES

Sample	Preheat Time, min.	Time for Complete Reduction, min.			Number of Determinations		
		at 560°C.		at 520°C.	at 560°C.		at 520°C.
		In Contaminated Reactor	In Clean Reactor	In Clean Reactor	In Contaminated Reactor	In Clean Reactor	In Clean Reactor
MCW	5	14.8 ± 2.2	5.3	12.0	4	1	1
	10	12.7 ± 4.0	4.8 ± 0.5	9.9	10	5	1
	20	15.3 ± 1.7	5.0	---	4	1	-
	30	14.2 ± 0.8	4.5	11.5	5	1	1
	40	16.0 ± 4.0	4.5	---	5	1	-
	60	15.0 ± 1.0	5.0 ± 0.5	12.0	4	2	1
HPCS	5	14.7 ± 2.0	6.5	10.9	3	1	1
	10	11.9 ± 1.0	5.4	11.1 ± 0.4	10	1	2
	20	13.0 ± 0.5	5.0	---	3	1	-
	30	15.0 ± 2.0	5.0	12.0	4	1	1
	40	15.0 ± 0.5	4.8	---	3	1	-
	60	16.2 ± 1.8	5.3	11.8	5	1	1
HPC	5	11.0	3.8	10.2	1	1	1
	10	12.0	4.0	9.5 ± 0.3	1	1	2
	20	---	5.0	---	-	1	-
	30	12.0	4.0	10.0	1	1	1
	40	---	3.5	---	-	1	-
	60	15.0	3.8	11.0	1	1	1
SRP	5	12.0	---	---	1	-	-
	10	12.0	---	11.8	1	-	1
	30	14.0	---	---	1	-	-
	60	16.0	---	---	1	-	-

As before, there is a real difference in the reduction times required at a given temperature in the clean and the fluoride-contaminated reactors. These data, however, provide little guidance in the selection of a preheat time since the differences in reduction times after the various preheat periods are without statistical significance. Primarily on the basis of convenience a preheat period of 10 minutes was selected. Data obtained later showed that while a longer preheat time had but little influence on reduction time, the hydrofluorination of the dioxide obtained on reduction after long preheat periods required significantly longer times.

Bed Depth. Since the reduction of uranium trioxide with hydrogen is an exothermic reaction, the expected temperature elevations occurring in deep beds have been measured and reported by Petretic and Bertram (23), and Swinehart (26). One objective of this investigation was to minimize this stationary bed depth effect in the thermobalance in order that the data could be applied to engineering studies of fluidized bed reduction; thus, measurements were made which would establish the conditions necessary to achieve this objective.

Although the variable actually being controlled was sample weight, this was directly proportional to bed depth; a weight increase gave a corresponding increase in bed depth since the sides of the sample boat were perpendicular to its bottom and the smallest sample used covered the bottom. In these experiments the preheat time was increased to 15 minutes so that the larger samples would have adequate time to reach the reactor temperature; and the hydrogen flow rate was increased to 3000 std. cc./min. to minimize limiting the reaction rate by supplying the reactant gas at an insufficient rate. The bed depths for the four-gram samples were obtained by actual measurement and were identical to those calculated from the bulk densities of the samples and the dimensions of the boat.

The maximum temperature attained by each sample during reaction was measured in a duplicate sample supported directly beneath the sample being weighed and duplicating as near as possible its geometric location relative to the reactor wall. The temperature was measured continuously with a Speedomax recording potentiometer activated by a bare 28-gauge chromel-alumel couple buried in the lower sample. Hydrogen reduction times were determined with samples of 0.5, 1.0, 2.0, and 4.0 grams for each of the four uranium trioxides. The results are shown in table IV.

Both the sample temperature and the reaction rate increased as a function of increasing bed depth within the limits studied. This relationship probably would continue until some other factor, such as limited diffusion of gases into and out of deeper beds, becomes reaction rate controlling. Conversely, limiting the sample bed depth to less than 1.0 mm., from which the heat of reaction could be dissipated rapidly enough to avoid a significant temperature rise, enabled us to achieve the objective of reduction data essentially free of bed depth effects.

TABLE IV

EFFECT OF SAMPLE BED DEPTH ON THE TEMPERATURE AND RATE OF HYDROGEN REDUCTION OF URANIUM TRIOXIDES

Designation	Weight, grams	Bed Depth, mm.	Reaction Time at 560°C., min.		Temperature Rise, °C.		Number of Determinations	
			In Contaminated Reactor	In Clean Reactor	In Contaminated Reactor	In Clean Reactor	In Contaminated Reactor	In Clean Reactor
MCW	0.5	0.5	9.8 ± 2.5	4.8	4 ± 4	0	8	1
	1.0	1.0	10.0	5.8	7	14	1	1
	2.0	2.0	7.0	4.8	46	54	1	1
	4.0	4.0	2.1 ± 0.2	1.5	140 ± 15	128	4	1
HFCS	0.5	0.5	7.0 ± 0.5	---	2 ± 2	---	3	--
	1.0	1.0	7.5	6.0	6	8	1	1
	2.0	2.0	8.5	5.5	14	25	1	1
	4.0	4.0	4.5	1.5	100	106	1	1
HFC	0.5	0.5	7.0	---	0	---	1	--
	1.0	0.9	6.5	5.0	9	11	1	1
	2.0	1.8	5.5	4.5	27	57	1	1
	4.0	3.5	3.0	2.3	103	114	1	1
SRP	0.5	0.4	8.0	---	0	---	1	--
	1.0	0.8	7.0	---	10	---	1	--
	2.0	1.5	7.5	---	12	---	1	--
	4.0	3.0	6.5	---	77	---	1	--

One may observe by comparison of the data in tables I and IV that, where sizeable temperature rises occurred, the average adiabatic reaction rates approached those prevailing under isothermal conditions at temperatures somewhat below the maximum point of elevation. This would be predicted by integration of the adiabatic temperature curve presented by Petretic and Bertram (23). Hence, bed depth appears to be involved as a rate-controlling variable only in so far as the adiabatic conditions imposed are significant.

Variables Affecting Hydrofluorination Rates

Reduction Temperature. Bertram (2), DeMarco, Bonfer and Abbott (3), Kewish and Fry (5), Kuhlman (10), and Swinehart (25) have recognized that the temperature employed for reduction of a uranium trioxide powder usually affects the subsequent hydrofluorination rate of the resulting uranium dioxide. The effect has also been observed in this laboratory. All these investigators agree that the hydrofluorination rate of uranium dioxide derived from pot-calcined uranium trioxides increases as the reduction temperature used in its preparation is decreased. A typical example of this effect is shown graphically in figure 5. The three uranium dioxides were prepared for hydrofluorination by reduction of the same Mallinckrodt-produced uranium trioxide in hydrogen at 925°, 560°, and at 450°C. The magnitude of this effect is highly variable among samples of different origin, leading to the conclusion that the primary determining factors are the source of the uranium trioxide and the procedure used in its preparation.

Another indication of the influence exerted by the conditions of reduction upon the subsequent hydrofluorination rate was noted in a comparison of thermogravimetrically determined hydrofluorination rate data obtained in our laboratory and those obtained at the Paducah laboratory on duplicate samples of uranium trioxide from several sources. Agreement between the two laboratories varied from good to poor. Outside of equipment design differences the only known difference in the two procedures was that the Paducah investigators used a mixture of hydrogen and nitrogen for reduction rather than the undiluted hydrogen used here. The cases exhibiting the poorest agreement were those involving the hydrofluorination rates of oxides with the largest dependence upon reduction temperature. This could be attributed to the diluted hydrogen having an effect similar to the use of a lower reduction temperature; the reduction rates were slower with attendant increases in the subsequent hydrofluorination rates.

Although the qualitative effects of diluting the hydrogen during the reduction of various uranium trioxides are readily apparent, a generalized evaluation of the effects of dilution presents a formidable undertaking due to the indirect manner in which this variable functions and its dependent relationship to specific oxide characteristics and specific equipment geometries; consequently, it was impractical to include a study of dilution effects in the scope of this investigation.

Hydrofluorination Temperature. The number of investigators who have studied the effect of temperature on the rate of reaction between uranium dioxide and anhydrous hydrogen fluoride is indicative of the complexity

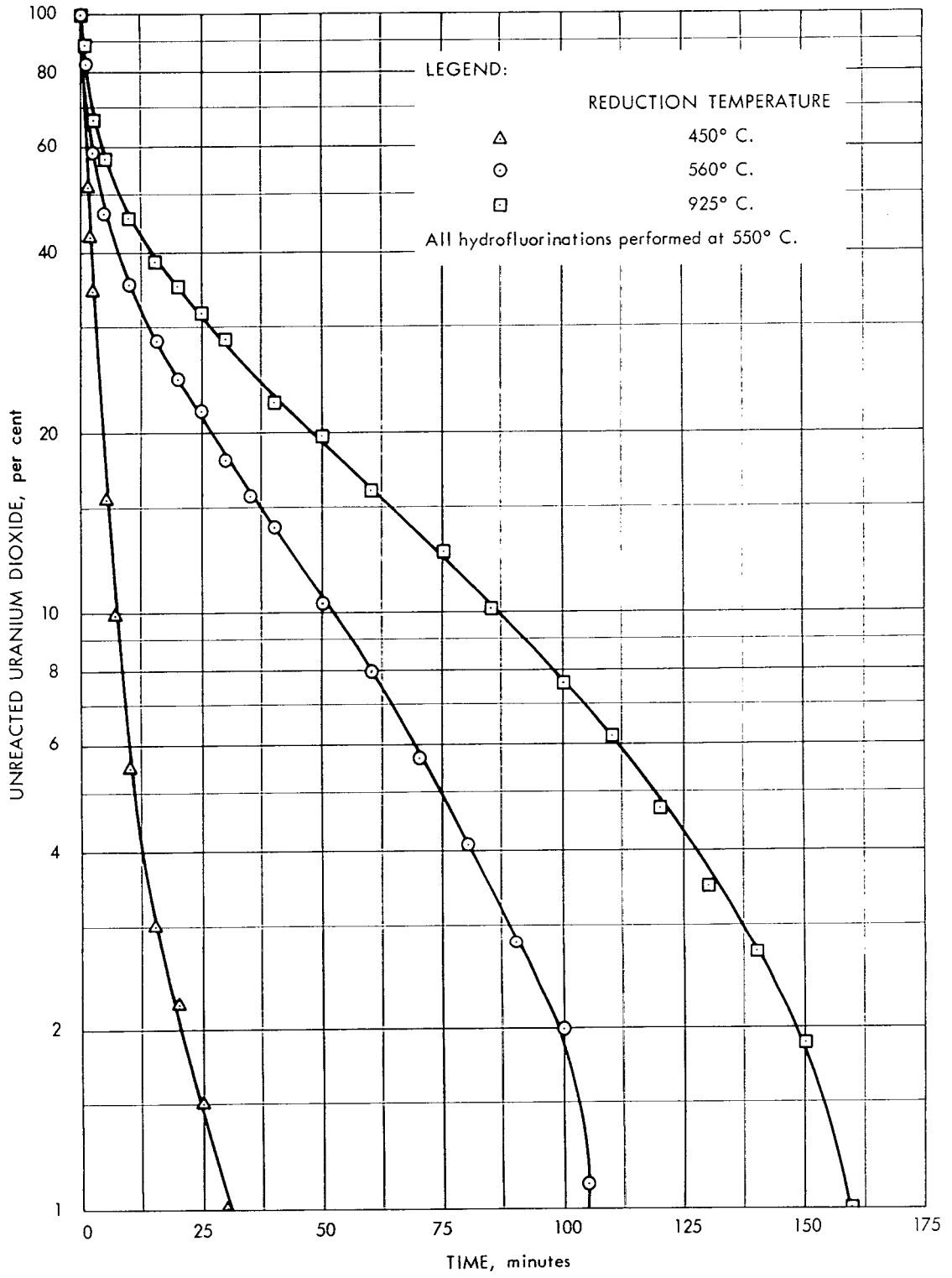


Figure 5
HYDROFLUORINATION OF URANIUM DIOXIDE SAMPLES
DERIVED BY REDUCING MALLINCKRODT URANIUM TRIOXIDE
WITH HYDROGEN AT VARIOUS TEMPERATURES

of the problem. All are agreed that this variable is rate controlling, but close agreement extends little further. Differences in the hydrofluorination rate response to temperature variations were often simply attributed to differences in the origin of the uranium oxide samples being studied. In some of the later work, the interrelationships among several reaction variables, such as have been demonstrated in this investigation, have been recognized.

Following reduction of the four uranium trioxides with hydrogen in a tube furnace reactor maintained at 925°C., temperature was studied as a hydrofluorination rate variable in the improved thermobalance reactor. Hydrofluorinations were performed at 500°, 550°, and 600°C. with the results shown in figures 6 through 9. The straightforward increase in average hydrofluorination rate with temperature elevation which the Mallinckrodt oxide exhibits (figure 6) probably accounts for its predictable processing behavior in the gaseous diffusion feed plants when both reduction and hydrofluorination were performed in tray and/or screwflight converters.

When one compares the plots in figure 6 with those in figures 7, 8, and 9, the average hydrofluorination rates exhibited by the various oxides under comparable conditions are somewhat different but the temperature dependence of the reaction rate is even more variable among these samples, e.g., the uranium dioxide produced from HPCS exhibits essentially the same hydrofluorination behavior at 550° and 600°C. in contrast to the large difference exhibited over the same temperature range by the dioxide produced from the HPC material. Voisinet (27) occasionally observed uranium dioxides which exhibited faster hydrofluorination rates at 1300°F. than at either 1000° or 1400°F. Examination of a very reactive oxide in this laboratory showed a similar maximum hydrofluorination rate at 500°C. with the slower rates at 400° and 600°C. being approximately equal. The hydrofluorination behavior of the HPCS-derived dioxide indicates that there is some relatively high temperature at which even these less reactive oxides would attain a maximum average reaction rate. The temperature at which this would occur is probably dependent upon the original particle size of the uranium dioxide and the temperature of the partially converted particle as its surface composition passes through the eutectic. If sintering occurs, diffusion of gases through the surface layer is impeded and continued reaction is retarded.

Bed Depth. Previously investigators have noted the effects of uranium dioxide bed depth upon hydrofluorination as evidenced by an abnormal temperature rise or a failure to achieve readily complete conversion of deep beds of uranium dioxide to uranium tetrafluoride. Like some of these investigators, our objective was to determine what bed depth during hydrofluorination would reduce the effect to a minimum.

To eliminate the previously discussed variable of bed depth during reduction, uranium dioxide for this study was prepared in an auxiliary reactor from the MCW uranium trioxide distributed in a large shallow tray so that the bed depth did not exceed 0.5 mm. After reduction, the dioxide was cooled to room temperature in a static atmosphere of hydrogen. Samples of the

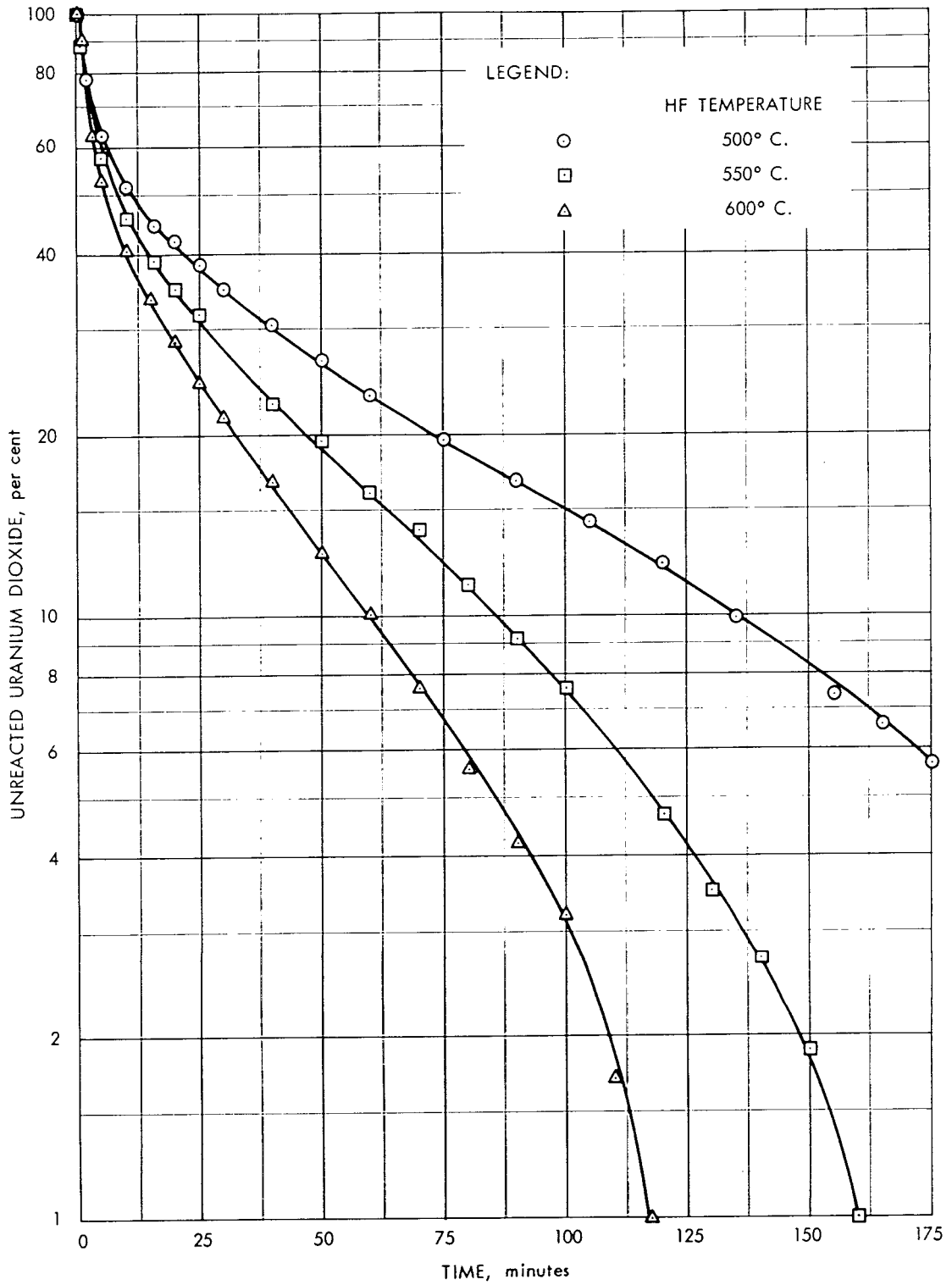


Figure 6
EFFECT OF TEMPERATURE ON THE HYDROFLUORINATION
RATE OF URANIUM DIOXIDE FOLLOWING REDUCTION
AT 925° C USING MALLINCKRODT URANIUM TRIOXIDE

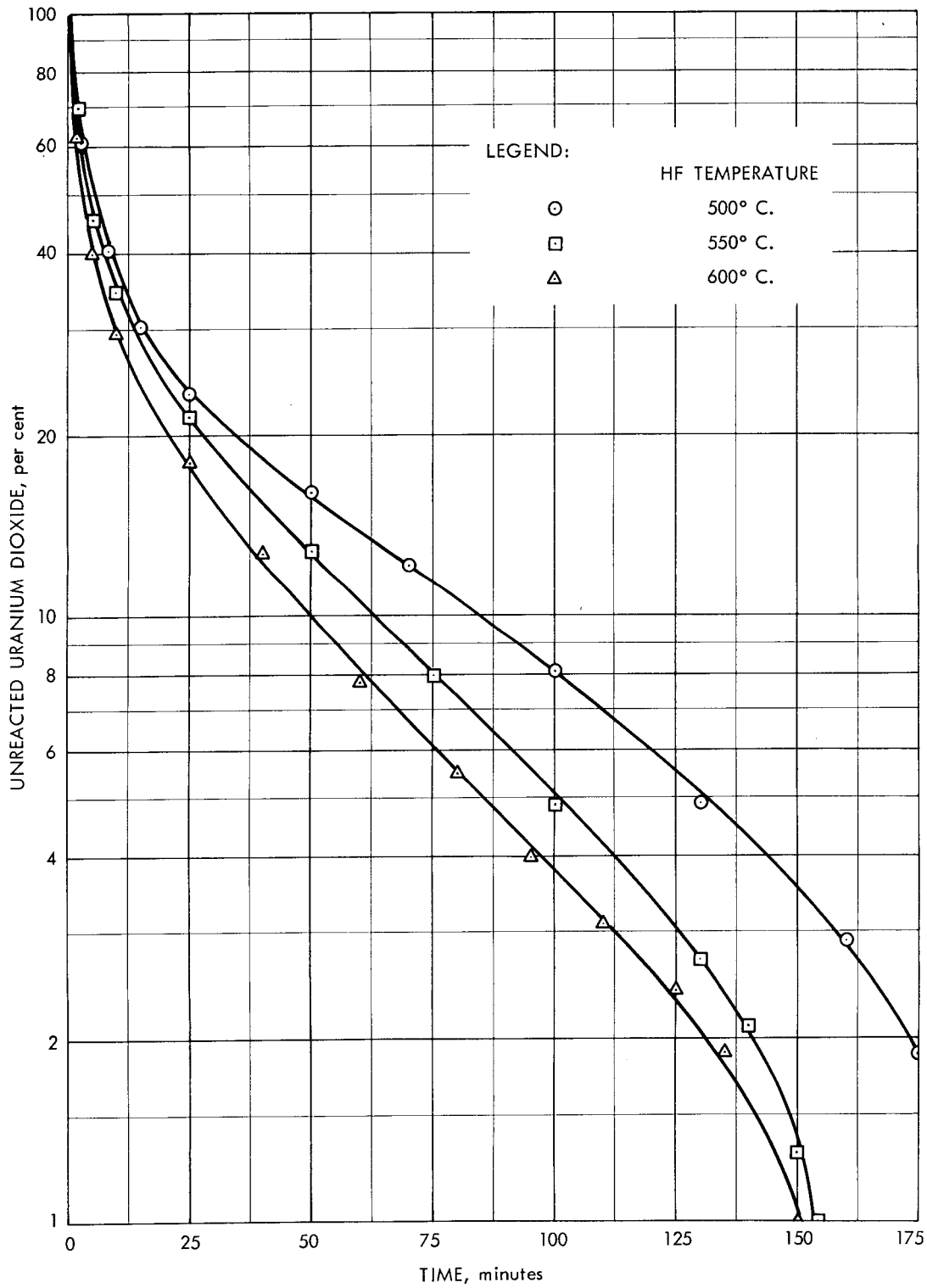


Figure 7
EFFECT OF TEMPERATURE ON THE HYDROFLUORINATION
RATE OF URANIUM DIOXIDE FOLLOWING REDUCTION
AT 925° C USING SAVANNAH RIVER POT CALCINED URANIUM TRIOXIDE

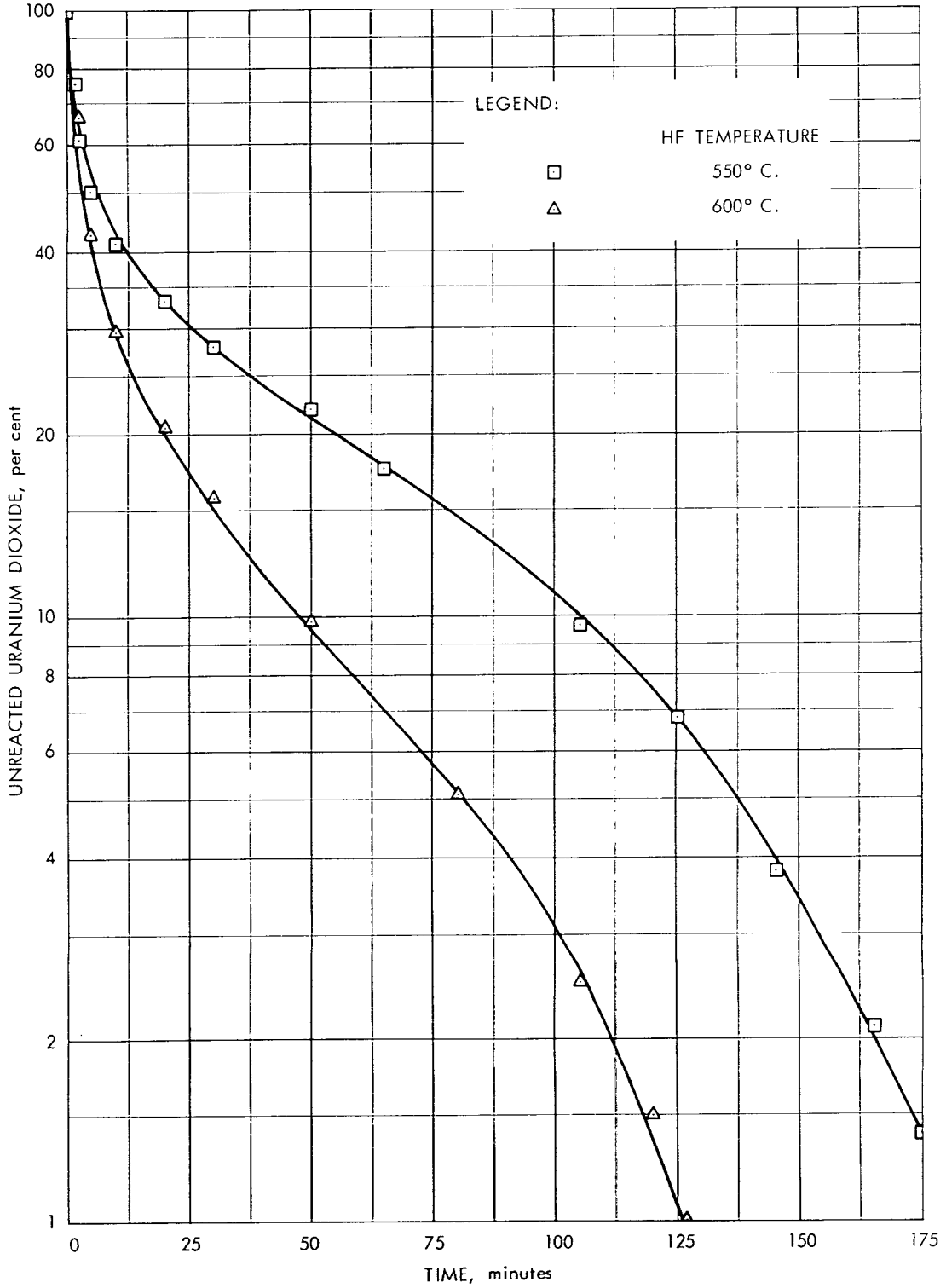


Figure 8
EFFECT OF TEMPERATURE ON THE HYDROFLUORINATION
RATE OF URANIUM DIOXIDE FOLLOWING REDUCTION
AT 925° C. USING HANFORD POT CALCINED URANIUM TRIOXIDE

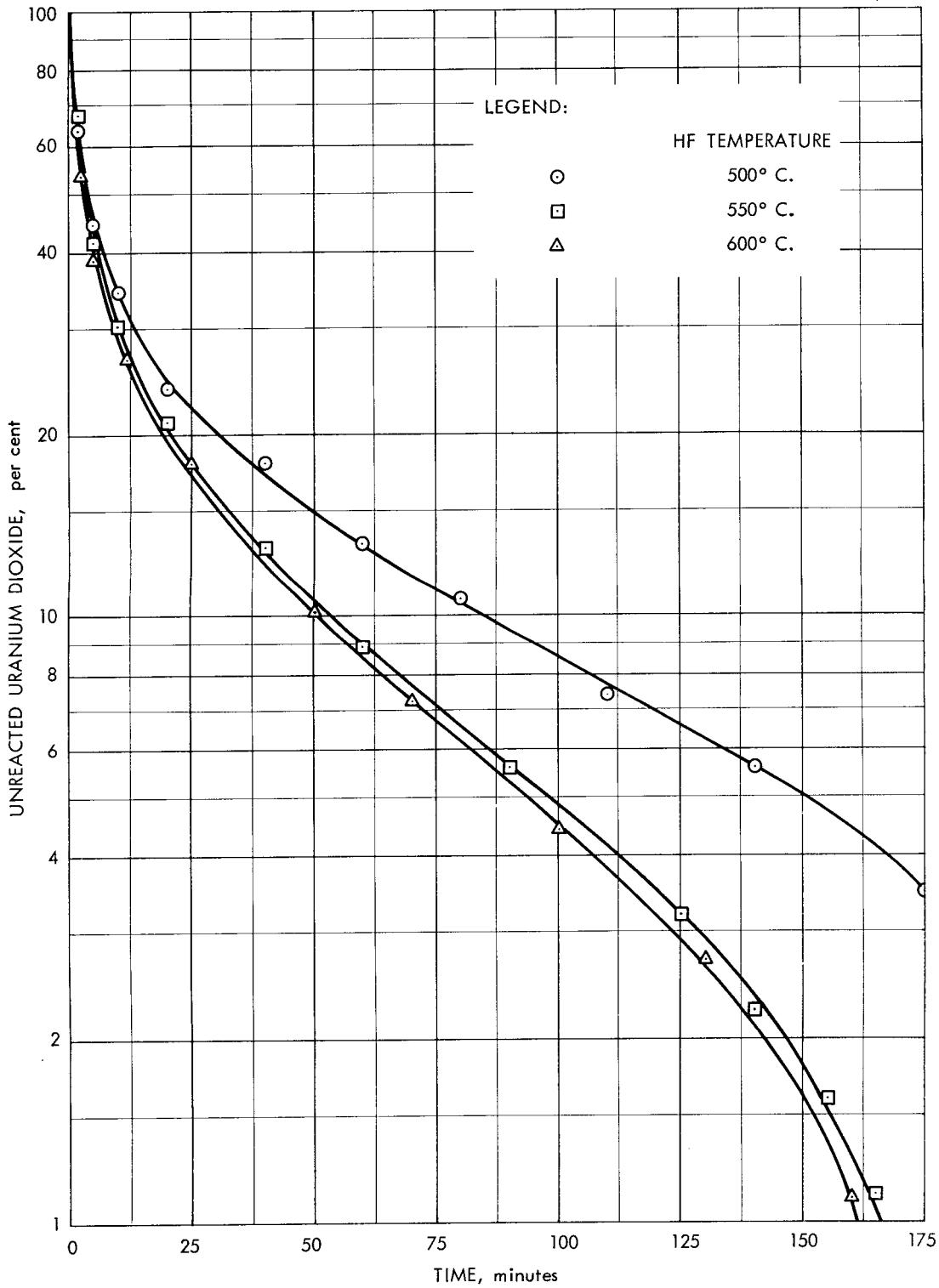


Figure 9

EFFECT OF TEMPERATURE ON THE HYDROFLUORINATION RATE OF URANIUM DIOXIDE FOLLOWING REDUCTION AT 925° C. USING HANFORD POT CALCINED URANIUM TRIOXIDE WITH ADDED SULFATE

uranium dioxide equivalent to original bed depths of 0.5, 1.0, 2.0, 4.0, and 7.0 mm. measured as the trioxide, were weighed into the thermobalance boat and heated from room temperature to the desired hydrofluorination temperature in an atmosphere of hydrogen. In this range of bed depth, hydrofluorination rates became slower and sample temperatures rose more with increasing bed depth. The data are shown graphically in figure 10 and figure 11.

One might expect the higher temperatures produced in the deeper beds during hydrofluorination to promote reaction at a faster rate; such was found to occur in the deeper beds during reduction. Since the average hydrofluorination rates experimentally observed were slower as bed depth was increased, other factors exerted a stronger influence upon the resulting reaction rate than did the temperature rise. The identity of two of these factors may be indicated by the results of a thermobalance investigation of hydrofluorination rates of uranium dioxide produced from hydrated uranium trioxide run in this laboratory. Although this particular oxide was much more reactive than the one being considered in the present investigation, the results of the earlier experiments indicate the possibility of thermal damage to reactivity toward anhydrous hydrogen fluoride as a result of particle sintering between 500° and 600°C. Furthermore, hydrogen fluoride dilution with water vapor, such as undoubtedly prevails in the deeper oxide beds where the water produced must diffuse out of the bed, has a definite retarding influence upon the rate of hydrofluorination. This effect increases rapidly as the concentration of water vapor is increased from 40 to 80 percent. In any event the interests of minimizing bed depth effects are best served by minimizing the depth of the bed itself.

Hydrogen Fluoride Flow Rate. Ludwig (17) has reported that a fourfold increase in hydrogen fluoride flow caused the reaction rate with uranium dioxide to increase during the first three-fourths of the reaction but caused a decrease during the remainder. Using hydrogen fluoride flow rates varying from 250 to 1000 std. cc./min. for the hydrofluorination of uranium dioxide produced from 0.5-gram samples of MCW uranium trioxide, we observed no dependence of reaction rate upon flow rate in this range. The three curves which result from plotting the data in figure 12 are practically identical. The absence of a detectable induction period similar to those observed at the beginning of the reduction experiments indicates that the hydrofluorination of uranium dioxide is initiated by the very low concentrations of hydrogen fluoride developed in the argon as soon as the hydrogen fluoride flow was started.

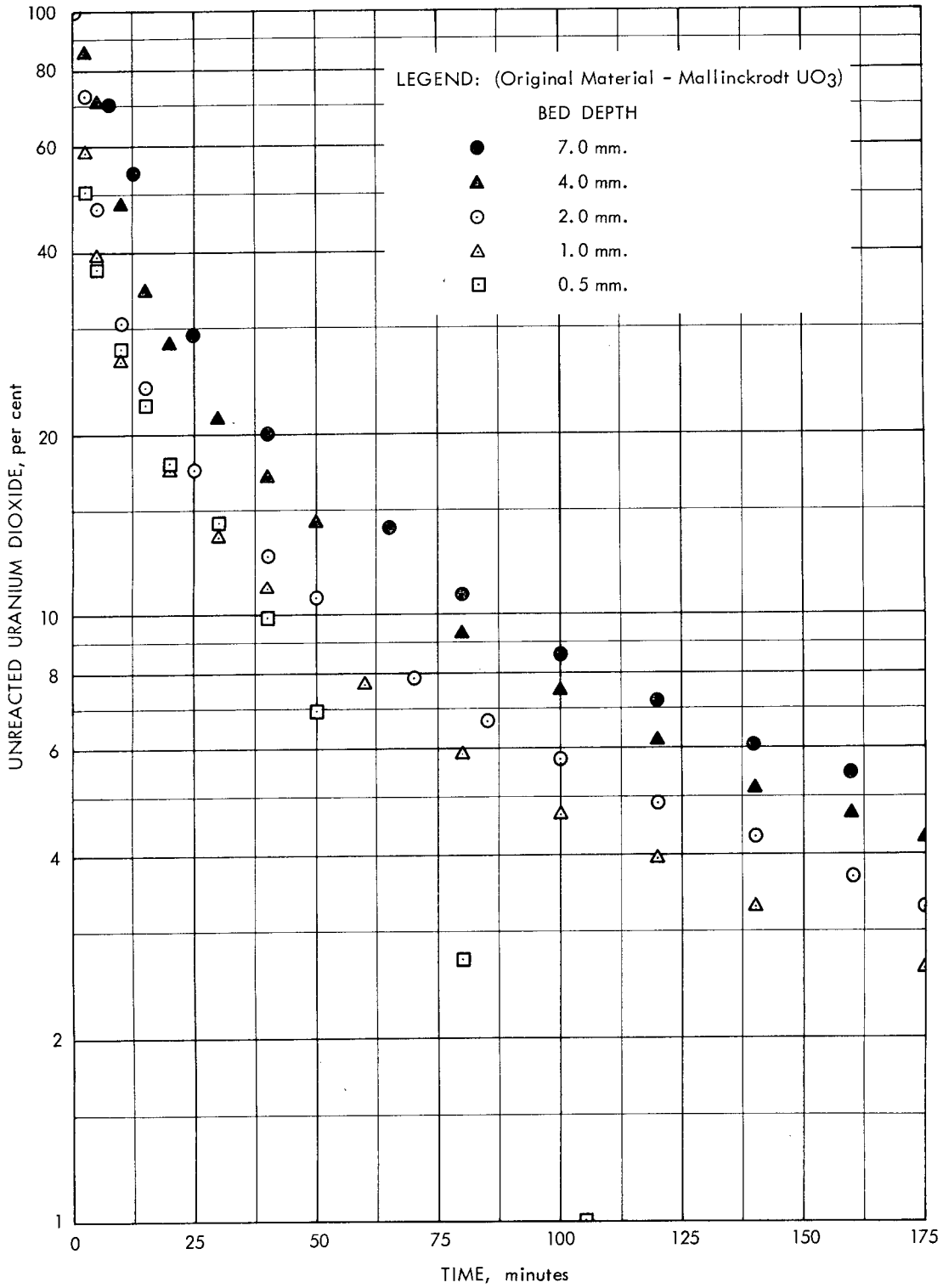


Figure 10
EFFECT OF BED DEPTH ON THE HYDROFLUORINATION
RATE OF URANIUM DIOXIDE AT 550° C.
FOLLOWING REDUCTION AT 560° C.

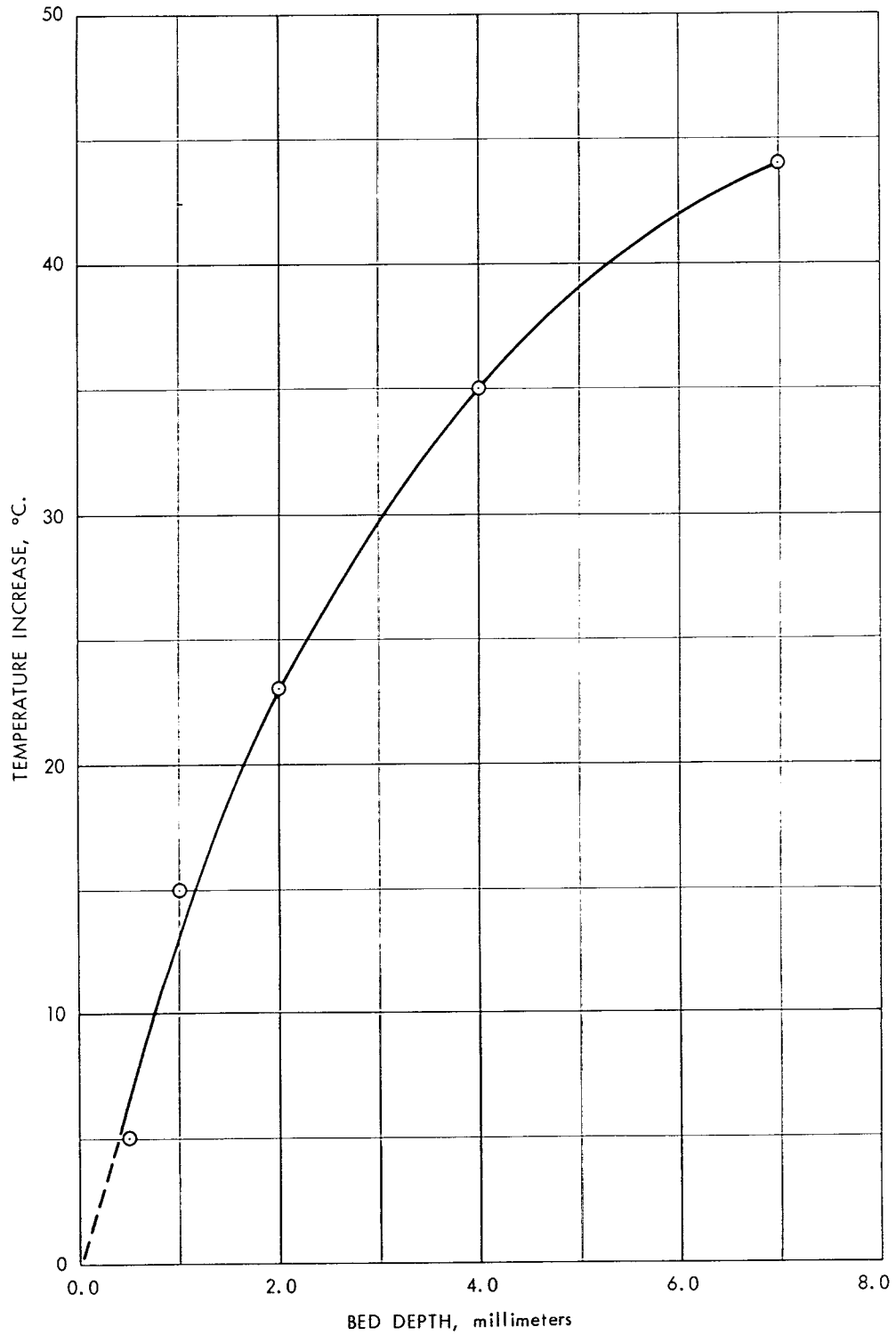


Figure 11
EFFECT OF BED DEPTH ON SAMPLE TEMPERATURE DURING
HYDROFLUORINATION OF URANIUM DIOXIDE AT 550° C.

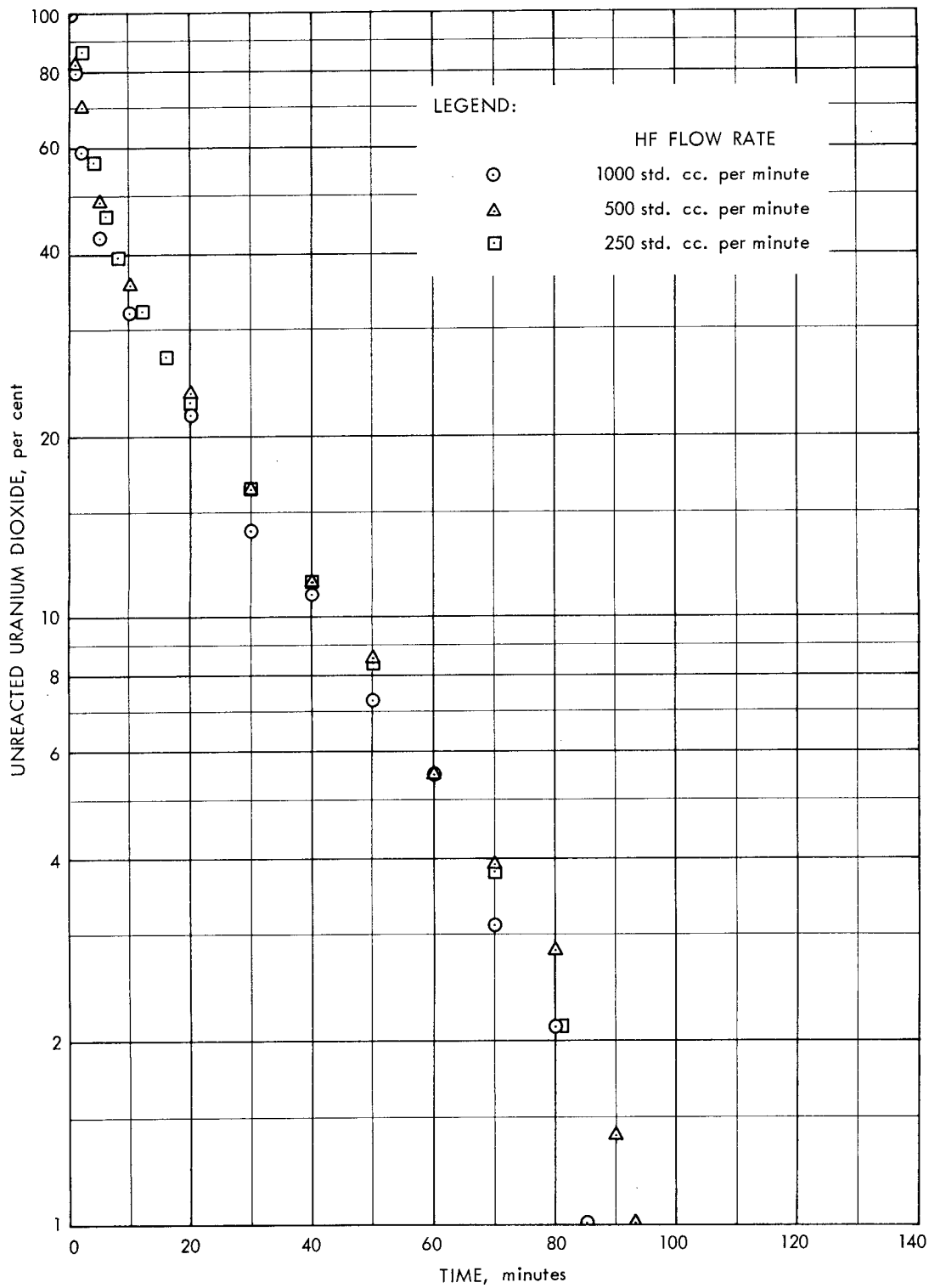


Figure 12
EFFECT OF HYDROGEN FLUORIDE FLOW ON
THE RATE OF HYDROFLUORINATION OF
URANIUM DIOXIDE AT 600° C.

ACKNOWLEDGEMENTS

Numerous individuals contributed to the success of this investigation. Mr. John Farquharson, in particular, made a major contribution in supplying the design and directing the installation of the electronic temperature control system. The work of draftsmen within our own Division, electricians, welders, sheet metal workers and insulators of the Maintenance Division made possible the construction of this well-built and reliable scientific apparatus.

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