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MALLINCKRODT CHEMICAL WORKS

URANIUM DIVISION

AEC RESEARCH AND DEVELOPMENT REPORT

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PROCESS DEVELOPMENT QUARTERLY REPORT
PART I - LABORATORY WORK

edited by

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by authority of OTD 7-29-59

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GENERAL SUMMARY

Work during the first quarter of 1959 continued on acid dissolution of uranium metal, raw material projects, the green salt process, dingot process, and on various plant assistance projects. An X-ray spectrographic method was investigated for the determination of uranium in aqueous and organic solutions.

Specific studies are summarized as follows (Roman numeral refers to the section on which the summary is based):

II. Aqueous entrainment in the extract from the first refinery pumper-decanter was found to range from 0.7 to 2.4 volume per cent. About an order of magnitude better decontamination for sodium and similar impurities is obtained by centrifuging the organic extract.

III. The amount of water sorbed by green salt under equilibrium conditions is a linear function of the uranyl fluoride content. Uranium tetrafluoride could not be dried in air above 400°C without serious decomposition.

IV. Experiments with "isothermal" laboratory-scale bombs indicate that preignition charge temperatures above about 300°C are necessary for production of low-hydrogen uranium. An upper limit of about 400°C on this heating was necessary to minimize premature ignition. The thermoconductivity of a laboratory bomb charge was increased by replacing part of the normal granulated magnesium with magnesium strips or larger chips.

The lowest ignition temperature of heated, stirred magnesium-green salt mixtures was found to be 393°C. This indicates that preheated bomb charges could probably be handled safely at temperatures below about 300°C. A high-voltage spark discharge ignited a cold mixture of UF_4 in magnesium.

The replacement of normal bomb lids and MFL charge caps with either porous graphite or firebrick produced uranium with lower hydrogen than normal bombs fired under similar conditions.

Molten uranium poured through atmospheres of hydrogen, water vapor, and hydrogen fluoride picked up approximately the same amount of hydrogen from all three gases under comparable conditions.

V. The thermal diffusivity of most MFL materials at 650°C was found to be approximately 2.0×10^{-3} cm²/sec. An initially high diffusivity (3×10^{-3} cm²/sec.) was found in measurements on regular MFL, but this higher diffusivity decreased to a limiting value upon heating. No significant variation in thermal diffusivity was found from lot to lot of regular MFL.

VI. The rate of dissolution of uranium in nitric acid has been shown to depend on nitrous acid concentration, consistent with previous postulates of the dissolution mechanism.

VII. The occurrence of an unexpectedly vigorous reaction between uranium metal and nitric acid in the plant metal dissolver has been tentatively traced to a conditioning of the metal in a "treated water" containing small amounts of sodium dichromate, sodium triphosphate, and sulfuric acid. The conditioning process apparently produces sensitized patches of the massive pieces of uranium which react with nitric acid with greater than normal activity.

VIII. The X-ray spectographic determination of uranium through use of strontium as the internal standard has been successfully applied to the analysis of aqueous and organic solutions. The precision at the 95% confidence limit is ±1.3% relative for aqueous solutions at a uranium concentration of 1.0 g/l and ±1.9% relative for organic solutions at a concentration of 2.0 g/l.

Pilot plant work for this quarter will be reported in Part II as a separate volume.

AQUEOUS ENTRAINMENT IN THE REFINERY EXTRACTION STREAM AND ITS EFFECT ON DECONTAMINATION FACTORS. PART II

by

E. N. Nelson

G. P. Lang

Summary

The degree of aqueous entrainment in the various organic streams of the MCW uranium refinery has been measured on ten different occasions. The level of entrainment in the extract from the first pumper-decanter was found to be in the range of 0.7 to 2.4 volume per cent. Overall decontamination factors for sodium, iron, aluminum, magnesium, molybdenum, silicon, and vanadium were found to be affected by this concentration of aqueous entrainment in the organic extract. About an order of magnitude better decontamination for sodium was obtained by centrifuging the uranium-laden extract.

Differences between the analysis of laboratory re-extracted uranium and refinery re-extracted uranium for copper, nickel, and tin, together with an indicated retention of iron in refinery solvent, make it appear that refinery solvent contains some unknown complexing agent which is affecting the distribution coefficients of these elements.

Introduction

This report is a continuation of work begun in the last quarter pertaining to the effect of aqueous entrainment in the TBP-hexane extract on product purity.[2] At that time the Weldon Spring refinery extraction stream was sampled during normal operation and while processing a feed material which caused relatively stable emulsions in the extraction units. It was shown that, when aqueous entrainment in the extract was relatively high, a major portion of the impurities found in the uranium product was carried in by the entrainment. The purpose of the current investigation is to collect additional information as to the effect of entrainment on the decontamination factors of various elements in the extraction process.

Experimental and Results

The refinery extraction streams were sampled at various points on each of ten different operating days and the aqueous entrainment in the various organic stream samples was measured. The entrainment values are given in Table I.

[2] Nelson, E. N., and Lang, G. P., *Process Development Quarterly Report, Part I, MCW-1425* (January 2, 1959), p 17

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Table I

Aqueous Entrainment in the Refinery Extract

Date	Aqueous Entrainment ml/l		
	D-1 Extract	Wash Column Feed	Washed Extract
Nov. 21	11.25	5.5	1.5
Nov. 24	12.25	6.0	1.0
Nov. 25	17.0	8.5	<0.5
Nov. 26	12.25	6.5	0.5
Dec. 1	18.0	9.0	0.5
Dec. 2	19.5	10.5	8.3
Dec. 3	24.3	11.5	17.5
Dec. 4	11.5	7.0	0.8
Dec. 5	7.5	5.0	1.0
Dec. 8	8.3	5.0	0.5

The overall effect of entrainment on product purity was determined by the following comparison. The sample of washed extract was centrifuged and the uranium re-extracted with six equal volumes of water. This re-extracted uranium was compared by spectrographic analysis with the NOK liquor produced in the refinery re-extraction column at the same time the washed extract was sampled. A comparison of the parallel samples is given in Table II.

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Table II

Effect of Entrainment on Product Purity

Contaminant Concentration, ppm (Uranium basis)

Element	Nov. 26		Dec. 1		Dec. 2		Dec. 3		Dec. 4		Dec. 5		Dec. 8	
	Centrifuged NOK[a]	Refinery NOK[b]	Centrifuged NOK[a]	Refinery NOK[b]	Centrifuged NOK[a]	Refinery NOK[b]	Centrifuged NOK[a]	Refinery NOK[b]	Centrifuged NOK[a]	Refinery NOK[b]	Centrifuged NOK[a]	Refinery NOK[b]	Centrifuged NOK[a]	Refinery NOK[b]
Ag	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Al	<10	<10	<10	<10	<10	<10	<10	30	<10	<10	<10	<10	<10	<10
As	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Be	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bi	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Co	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cr	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Cu	2	<1	1	<1	1	<1	2	<1	2	<1	<1	<1	1	<1
Fe	<15	<15	<15	30	<15	15	<15	40	<15	<15	<15	<15	<15	15
In	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Mg	<10	15	<10	15	<10	20	<10	40	<10	20	<10	40	<10	40
Mn	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Mo	<10	<10	<10	<10	<10	<10	<10	30	<10	<10	<10	<10	<10	<10
Ni	3	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Pb	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Sb	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
Si	<15	30	<15	20	<15	15	<15	80	<15	<15	<15	<15	<15	<15
Sn	3	<1	1	<1	1	<1	1	<1	<1	<1	<1	<1	<1	<1
V	<20	<20	<20	<20	<20	20	<20	50	<20	<20	<20	<20	<20	<20
Zn	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50

[a] Uranium re-extracted from centrifuged, washed extract by the laboratory re-extraction procedure.

[b] Normal refinery NOK liquor obtained from the refinery re-extraction column at the same time the above washed extract sample was taken.

The concentration of iron and sodium was measured directly in the centrifuged washed extract by a flame spectrophotometric method. Decontamination factors for iron and sodium from aqueous feed to centrifuged washed extract were calculated on the basis of these values. Comparative iron and sodium decontamination factors from aqueous feed to the uranium product re-extracted from centrifuged washed extract and to refinery NOK liquor were also calculated. These comparisons are given in Table III for iron and in Table IV for sodium, and in Figure 1 the iron decontamination factor is plotted as a function of aqueous entrainment in the D-1 extract.

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Table III

Iron Decontamination Factors in the Refinery

Date	Aqueous Feed PPM Fe (U basis)	Refinery NOK[a]		Centrifuged NOK[b]		Centrifuged Wash Extract[c]	
		PPM Fe (U basis)	Decontamination Factor	PPM Fe (U basis)	Decontamination Factor	PPM Fe (U basis)	Decontamination Factor
Nov. 21	6,100	14	440	--	-	--	--
Nov. 24	5,400	17	320	-	--	-	--
Dec. 1	7,700	30	260	<15	>510	96	80
Dec. 2	5,700	28	200	<15	>380	109	52
Dec. 3	6,400	53	120	<15	>430	148	43
Dec. 4	5,200	20	260	<15	>350	30	173
Dec. 5	7,400	15	490	<15	>490	--	--
Dec. 8	11,000	22	500	<15	>730	--	-

[a] Normal refinery NOK liquor obtained from the refinery re-extraction column at the same time the washed extract sample was taken.

[b] Uranium re-extracted from centrifuged washed extract by the laboratory re-extraction procedure.

[c] Refinery washed extract was centrifuged and the iron concentration measured directly in the extract by a flame spectrophotometer procedure.

Table IV

Sodium Decontamination Factors in the Refinery

Date	Aqueous Feed PPM Na U basis	Refinery NOK[a] PPM Na U basis	Refinery NOK[a] Decontamination Factor	Centrifuged Washed Extract[b] PPM Na U basis	Centrifuged Washed Extract[b] Decontamination Factor
Nov. 21	11×10^4	25	4,400	-	-
Nov. 24	4.6×10^4	17	2,700	-	-
Dec. 1	13×10^4	39	3,300	3.5	37,000
Dec. 2	13×10^4	67	1,900	23.	5,700
Dec. 3	8×10^4	35	2,300	3.5	23,000
Dec. 4	13×10^4	25	5,200	3.5	37,000
Dec. 5	8×10^4	14	5,700	-	-
Dec. 8	2.9×10^4	15	1,900	-	-

[a] Normal refinery NOK liquor obtained from the refinery re-extraction column at the same time the washed extract sample was taken.

[b] Refinery washed extract was centrifuged and the sodium concentration measured directly in the extract by a flame spectrophotometric procedure.

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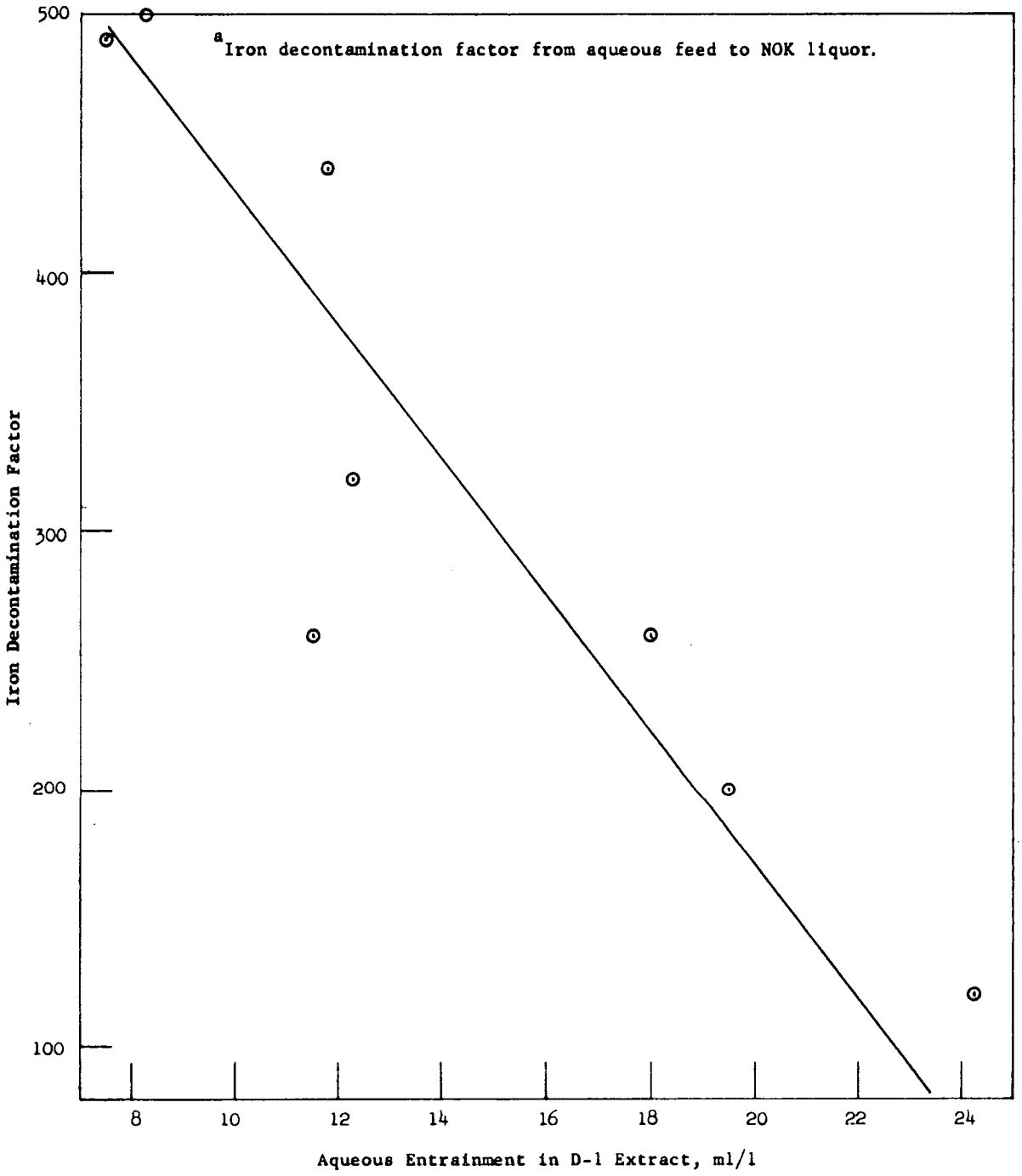
Figure 1

IRON DECONTAMINATION FACTOR AS A FUNCTION OF AQUEOUS ENTRAINMENT IN D-1 EXTRACT[a]



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Discussion

Aqueous entrainment in the extract from the first pumper-decanter was found to be in the range of 7.5 to 24.3 ml/l (0.75 to 2.43 volume per cent). Approximately one-half of this entrainment settles out in the small de-entraining or break tank between the first pumper-decanter and the wash column. The entrainment level in the washed extract is generally quite low (~ 0.1 volume per cent) but on two occasions the entrainment level was much higher and may indicate a minor upset in the wash column at the time those samples were taken.

A comparison of the concentration of impurities found in uranium re-extracted from centrifuged washed extract with the concentration of impurities found in a parallel refinery NOK sample is shown in Table II. The concentrations of most elements are too low to measure and the measurable values are underlined. The values for aluminum, iron, magnesium, molybdenum, silicon, and vanadium all show a lower concentration in the strip solution from centrifuged samples than in the refinery NOK samples. It is believed that the difference can be attributed to entrained aqueous in the extract. The opposite result was found for copper, nickel, and tin. The centrifuged extract was higher in these elements than the plant NOK. Since the re-extraction procedure used in the laboratory on centrifuged washed extract was more complete (more stages) than is obtained in the refinery re-extraction column, it is believed that these elements were stripped more completely by the laboratory procedure than by the plant procedure.

In Table III, an effect similar to that for copper, nickel, and tin is shown for iron. However, iron is held so tightly that neither stripping procedure removes significant quantities from the extract. The iron values for the extract are much higher than the values obtained on either of the strip solutions, indicating that much of the iron cannot be easily stripped from the organic.

To explain these results it has been postulated[3,5,6] that the degradation products of the solvent contain ligands which form easily extractable complexes with these metals. These degradation products have never been identified but their effect on uranium and zirconium distribution coefficients have been previously observed and the magnitude of their effect has been used as a measure of solvent quality.

The effect of aqueous entrainment on iron decontamination factor values is also demonstrated by the values in Table III, and in Figure 1 where these results are plotted against the amount of

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[3] Nelson, E. N., Weidman, S. W., and Lang, G. P., *Process Development Quarterly Report, Part I, MCW-1412* (April 1, 1958); p 35-43

[5] Moore, R. H., *Investigation of Solvent Degradation Products in Recycled Uranium Recovery Plant Solvent*, Hanford Atomic Products Operation, *HW-34502 (Rev.)* (April 28, 1955)

[6] Siddall, T. H., III, and Wallace, R. M., *Effect of Solvent Degradation on the Purex Process*, E. I. du Pont de Nemours and Company, Savannah River Laboratory, *DP-286* (May, 1958)

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entrainment measured in the D-1 extract. A fair correlation is obtained. Furthermore, the strip solution from the centrifuged extract (Table III) contains too little iron to measure, showing that almost all of the iron in plant NOK is carried over by the aqueous entrainment in the extract.

The effect of aqueous entrainment on the decontamination factor for sodium is even more pronounced than for iron as can be seen in the results shown in Table IV. Decontamination factor values about ten times higher are obtained when the extract is centrifuged before re-extraction. It is evident that if more decontamination is necessary it can be easily obtained by centrifuging the extract.

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WATER VAPOR SORPTION BY GREEN SALT

by

W. F. Finch
J. A. Kennelley

Summary

The equilibrium water sorption by UF_4 is a function of the UO_2F_2 concentration in the UF_4 and may be represented mathematically by the relationship,

$$y = m(x - a), \qquad (1)$$

where y is the % water, m is the slope, x is the % UO_2F_2 in UF_4, and a is the x intercept (0.75%). At 33.5°C the value of m is 0.625 for a vapor pressure of 38.0 mm, 0.185 for 29.9 mm, and 0.013 for 7.8 mm. At 7.4°C m is 0.409 for a water vapor pressure of 7.8 mm. It should be emphasized that this relationship is valid only for UF_4 having UO_2F_2 concentrations between 0.8% and 6.0%.

The water-green salt heat of sorption was calculated to be approximately 9 kcal/mole.

The highest temperature for drying UF_4 in air without serious decomposition is around 400°C. Above this temperature decomposition may proceed in two ways:

$$UF_4 \xrightarrow[600^\circ]{H_2O} HF + UO_2 \xrightarrow{O_2} U_3O_8 \qquad (2)$$

or

$$2UF_4 + O_2 \xrightarrow{800^\circ} UF_6 + UO_2F_2 \,. \qquad (3)$$

Introduction

One of the most likely sources of hydrogen contamination in uranium metal is the water vapor adsorbed on the green salt and magnesium. The object of this experimental work was to measure the equilibrium sorption of water vapor by green salt and to determine the effect of green salt composition, water vapor pressure, and temperature, on this sorption.

Experimental

Samples of green salt having UO_2F_2 contents of 0.72% to 5.66% and no significant variation in surface area were placed in weighing bottles and dried for four days at 130°C under a vacuum of 0.5 μ. The bottles were then capped in a dry box and placed in a hygrothermostat which contained an analytical balance. A weighing bottle was placed on the balance and weighed with the cap in

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place. At zero time the cap was removed and placed on the balance pan. The subsequent increase in weight with respect to time was recorded and was assumed to be a measure of the water sorbed by the sample. A blank run with no sample in the weighing bottle showed that the weight gained by the bottle was insignificant when compared to the weight gained by the sample. Weight gain measurements were made under relative humidities of 98%, 77%, and 20% at 33.5°C and 7.4°C. In addition, a brief study of the conditions necessary to dry green salt was made.

Results and Discussion

The most significant information gained from this study is that the amount of water sorbed by green salt is definitely related to the amount of UO_2F_2 present in the green salt. This effect is illustrated in Figure 1. The equilibrium water sorption by green salt appears to be a linear function of UO_2F_2 contents between 0.75% and 6%, although there is a slight hysteresis effect at higher atmospheric water contents. If one neglects the hysteresis effect, the equilibrium water content of green salt may be approximated by the relationship,

$$y = m(x-a), \qquad (1)$$

where y is the % weight gain, m is the slope, x is the % UO_2F_2 in green salt, and a is the x intercept. It should be emphasized that this relationship is valid only for green salt having UO_2F_2 concentrations between 0.80% and 6.00%. The value of a has been empirically determined to be 0.75%. Table I shows the variation of the value of m with pressure and temperature changes. Calculation of the equilibrium

Table I

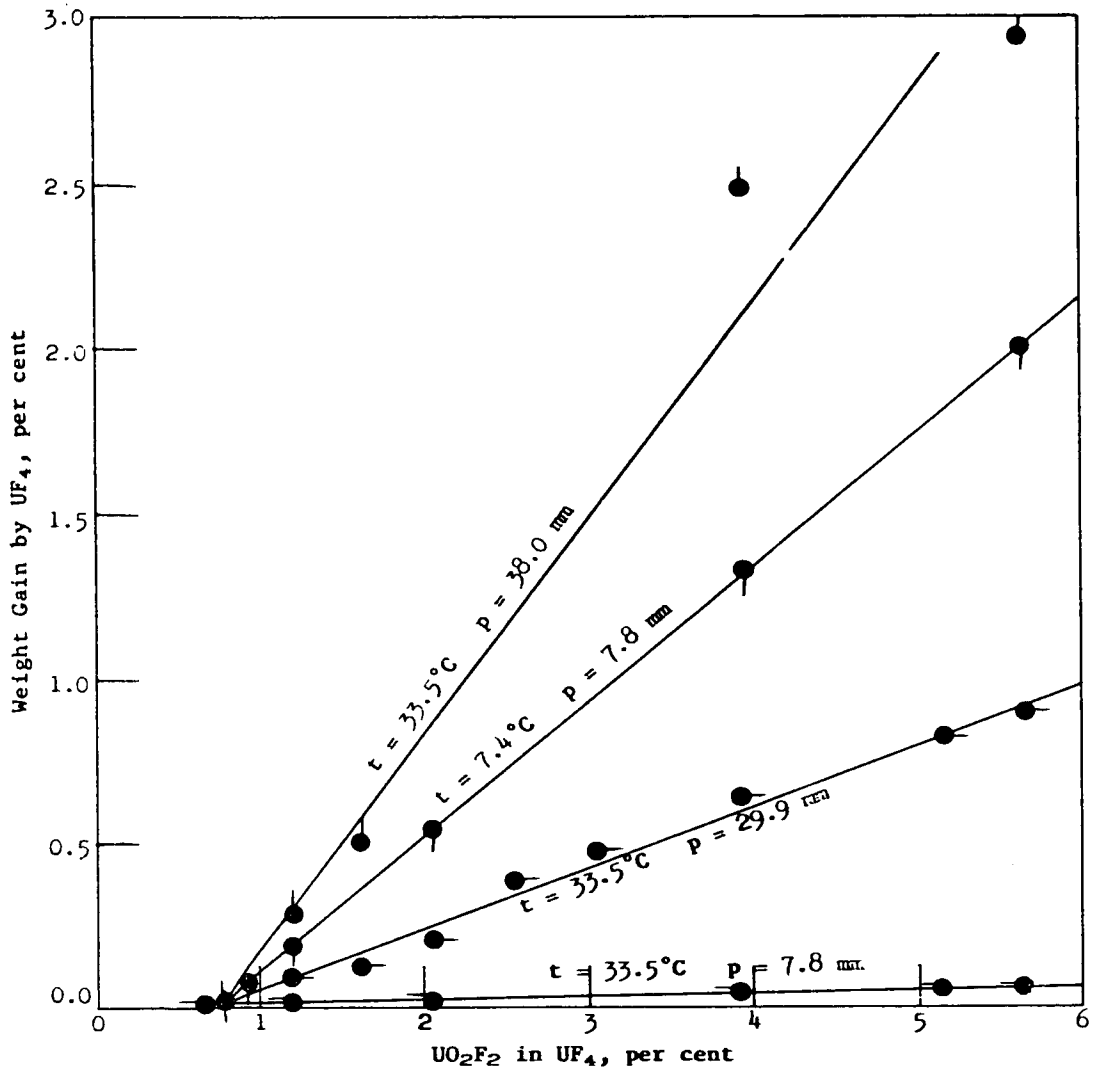
The Effect of Various Atmospheric Conditions on the Slope (m) of the Relationship, % water = m(% UO_2F_2 in green salt - 0.75%)

m	Temperature, °C	Relative Humidity, %	Vapor Pressure, mm Hg
0.652	33.5	98	38.0
0.185	33.5	77	29.9
0.013	33.5	20	7.8
0.409	7.4	98	7.8

water content in green salt from the information presented in Table I is accurate to ± 0.02%.

Figure 1

THE EFFECT OF THE UO_2F_2 CONTENT ON THE SORPTION OF WATER VAPOR BY GREEN SALT



In order to help determine the nature of the water-green salt bond, the Clausius-Clapeyron equation[1] was applied to experimental isosteres to give an approximation of the heat of sorption. The calculated heat of sorption is $\sim$9 kcal/mole. According to Trapnell,[2] the maximum heat of physical adsorption of water vapor is 14 kcal/mole, and it is generally understood that the minimum heat of chemisorption (if one exists) is below 3 kcal/mole. It seems then that the 9 kcal/mole heat of sorption may be due to physical and/or chemical bonding.

Another clue to the type of bonding may be obtained from the sorption rate. In general, the rate of physical sorption is independent of the temperature, while chemisorption proceeds more slowly at lower temperatures. Figure 2 shows an effect of temperature on sorption rate which is characteristic of chemisorption. Chemisorption, however, can never occur in more than a monolayer, which corresponds roughly to a weight gain of 0.01% to 0.02% for green salt having a UO_2F_2 concentration of less than 6%. Therefore it is likely that multilayer physical absorption occurs on top of any chemisorbed monolayer that may exist.

In a brief study of the conditions favorable for drying green salt, a series of UF_4 samples was equilibrated with water vapor and dried for increasing times in air at 230°C. The water concentration dropped from 0.16% (180 ppm H_2) to 0.043% (48 ppm H_2) in less than 1/2 hour. Loss of water thereafter was extremely slow, reaching 0.023% (26 ppm H_2) after 72 hours. The samples could not be further dehydrated at this temperature. Drying of similar samples at 400°C in air resulted in decreasing the water content to 0.0025% (2.8 ppm H_2) in 30 min. An attempt at drying at 600°C in air resulted in pyrohydrolysis of the UF_4 as illustrated in the reaction,

$$UF_4 \xrightarrow[600^0]{H_2O} HF + UO_2 \xrightarrow{O_2} U_3O_8 \,. \qquad (2)$$

Etching of the glassware was evident. One attempt at drying UF_4 at 800° resulted in the following reaction:

$$2UF_4 + O_2 \longrightarrow UF_6 + UO_2F_2 \qquad (3)$$

It seems evident that 400°C is the maximum useful temperature for drying UF_4 in air without considerable decomposition. It may be possible to dry UF_4 at around 200°C until most of the water is gone and then raise the temperature above 400° without pyrohydrolysis, but only then if the atmospheric water content is low.

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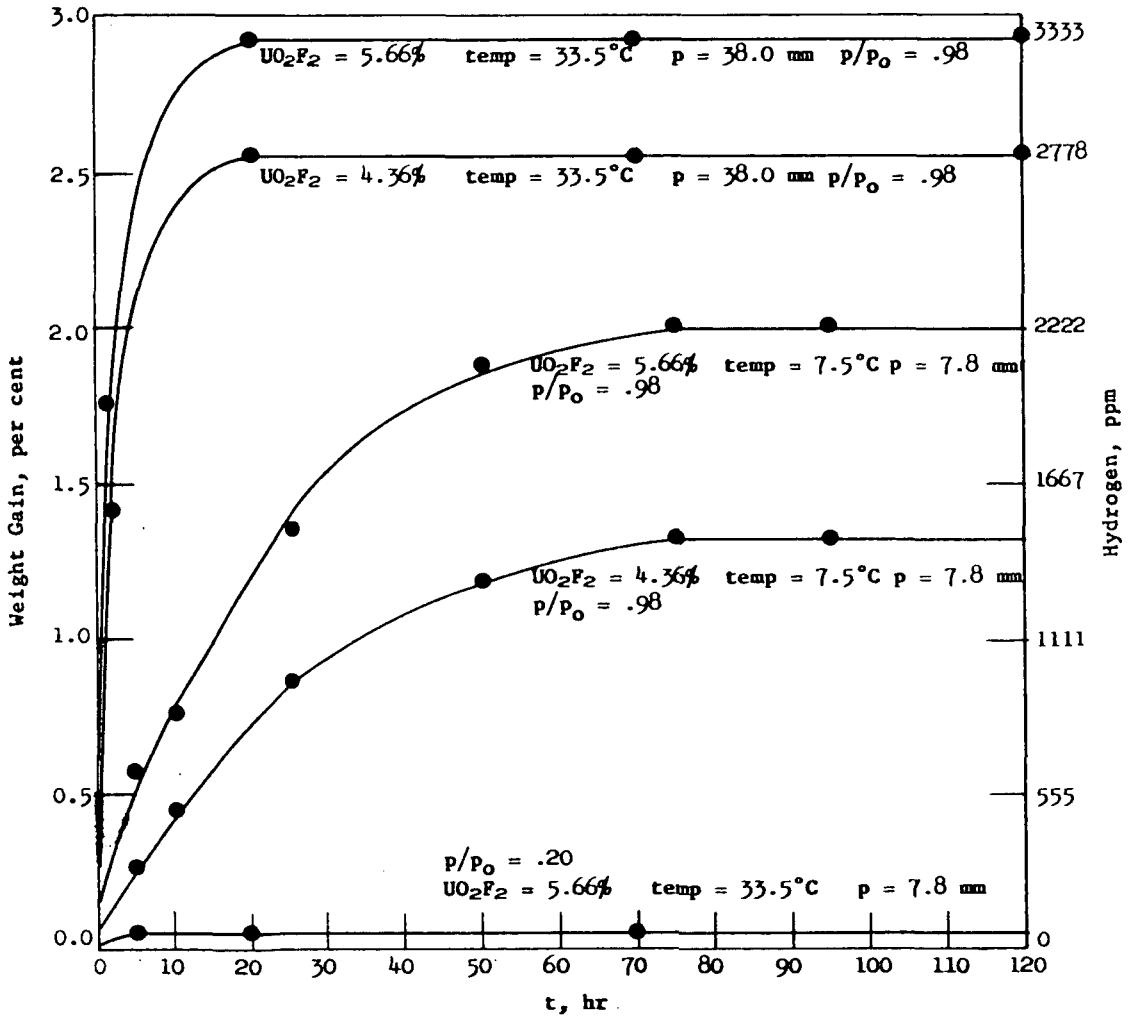
[1] $\frac{(\partial p)}{(\partial T)_V} = \frac{q}{RT^2}$ or $q_{isosteric} = \frac{\ln (P_1/P_2) \times R}{1/T_2 - 1/T_1}$

where v is the volume of gas adsorbed, p is the pressure of the gas, and T is the absolute temperature

[2] Trapnell, B.M.W., "Chemisorption," *Butterworth's Scientific Publications*, London, 1955, p 144

Figure 2

THE INFLUENCE OF TEMPERATURE ON THE RATE OF WATER VAPOR SORPTION BY GREEN SALT



HYDROGEN IN URANIUM

by

R. F. Leifield
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I. Summary

A. Effects of Various Bomb Heating Patterns on the Hydrogen Content of As-Reduced Uranium

Bombs heated to 300°C or higher before ignition have shown decreases of hydrogen in the resulting uranium with both increasing time and temperature. Bombs heated at temperatures below 250°C showed no decrease in uranium hydrogen content with increasing time at these temperatures before ignition. These results indicate that plant procedures utilizing longer times at temperature before ignition would best be carried out at temperatures above 300°C. An upper limit of 400°C is necessary to minimize premature ignition.

B. Accelerating Bomb Charge Heating Rates

Bomb charge thermal conductivity can be increased by replacing part of the normal granulated magnesium with either magnesium strips or larger chips. Charge center heating rates have been increased 15 to 40 per cent using these techniques. Crude yields, however, are affected when excessive amounts of large size magnesium are used.

C. Reduction of Green Salt Containing Added Water

Water additions to bomb charges have been used to produce hydrogen-in-uranium values above normal. Low-hydrogen uranium has been produced from green salt containing added water by increasing the time at temperature before initiation of the reduction reaction. The results are interpreted as indicating that plant procedures utilizing longer times at temperature to control hydrogen in uranium at low levels will not be affected by seasonal variations in UF_4 water content.

D. Ignition Temperatures of Stirred Magnesium and Green Salt Mixtures

The lowest ignition temperature of heated and stirred magnesium-green salt mixtures was

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found to be 393°C (740°F). These results indicate that handling preheated bomb charges would probably be safe at temperatures below 300°C. However, high voltage spark discharges ignited even cold mixtures of UF_4 and Mg.

E. Porous-Top Bombs

Replacing normal MFL bomb lids and charge caps with either porous graphite or firebrick and a vented bomb lid produced uranium with hydrogen contents lower than normal bombs fired under similar conditions. This technique offers a possible means of producing low-hydrogen uranium with a shorter furnace residence time.

F. Hydrogen Pickup by Molten Uranium

Molten uranium poured through atmospheres of hydrogen, water vapor, and hydrogen fluoride picked up approximately the same amounts of hydrogen from all three gases.

II. Introduction

Laboratory work on the hydrogen-in-uranium problem in the past quarter has concentrated on bomb reduction studies. Effort was expanded on evaluation of the beneficial effects of increasing bomb charge temperature before initiation of the reduction reaction. This work included variations in heating patterns caused by alteration of furnace practice and also by improving the thermal conductivity of the charge. Experiments in this area were also carried out to determine if the beneficial effects produced by increased charge temperatures would persist at water levels greatly increased over normal within the bomb. Finally, studies were made of the rate of hydrogen pickup by molten uranium when poured through $HF_{(g)}$, $H_2O_{(g)}$ and $H_{2(g)}$ atmospheres.

III. Effects of Various Bomb Heating Patterns on the Hydrogen Content of As-Reduced Uranium

A. Summary

The uranium produced from 4-kg bombs which had been heated at 300°C or higher showed a decrease in hydrogen content with increased heating time, while the uranium from bombs heated at 250°C or lower showed no such decrease with increased heating time.

B. Introduction

The hydrogen content of uranium from laboratory and plant bombs has been found, in previous work, to correlate with preignition heating time, bomb center temperature at firing, and temperature gradient between bomb center and edge. In the heating patterns normally used, all of these factors are so interrelated that it is very difficult to determine the

mechanism that effects the decrease in hydrogen content. In order to gain more information on the mechanisms involved as well as to establish criteria for determining optimum preheat times and temperatures for plant use, a series of 4-kg bomb runs has been made. The results obtained by two techniques--the "isothermal" bombs and the "preheated" bombs--are reported in this section.

C. Experimental and Results

This work involved the use of 4-kg dingot bombs charged with normal components by the usual techniques except for the use of electric igniters placed in the bottom of the bombs to permit ignition at the end of the desired time. These igniters were made from 3 feet of 26-gage asbestos-covered chromel wire wound into a helix of about 1-cm diameter and connected to a suitable power supply with 20-gage chromel wire. The bombs were ignited by supplying a current of 3-4 amps at 30-50 volts to the igniters. In some of the bombs thermocouples were placed in the charge to measure bomb center temperatures.

The technique used for the isothermal bombs was to soak the bombs at the desired furnace temperature for times ranging from the minimum time needed to approach isothermal conditions in the bomb (found to be 1½ hours by charge edge and center temperature measurements) up to 18 hours, and then ignite the bomb electrically. Temperatures studied by this technique ranged from 300°C to 450°C. The lower limit was imposed by the improbability of getting massive metal at lower temperatures and the upper limit by the probability of getting spontaneous ignition. Hydrogen results obtained by this technique are shown in Figure 1 as a function of soak time and in Figure 2 as a function of soak temperature.

The "preheating" technique permitted study of the effects of soak time at lower temperatures. In this series the bombs were preheated for the desired time at temperature and then transferred immediately to a 650°C furnace. There they were allowed to fire normally or were triggered electrically when they reached a given center temperature. In every case the bomb center temperature was measured to permit comparison of the hydrogen results obtained with those of normally fired bombs with equivalent center temperatures. The relationship between center temperature at ignition and hydrogen in the resulting uranium is shown in Figure 3. The relationship between preheat time at 250°C and hydrogen content of the uranium for a series of bombs fired at a 260°C center temperature is shown in Figure 4.

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Figure 1

EFFECT OF PREIGNITION SOAK TIME ON HYDROGEN CONTENT OF URANIUM PRODUCED IN ISOTHERMAL 4-KG DINGOT BOMBS

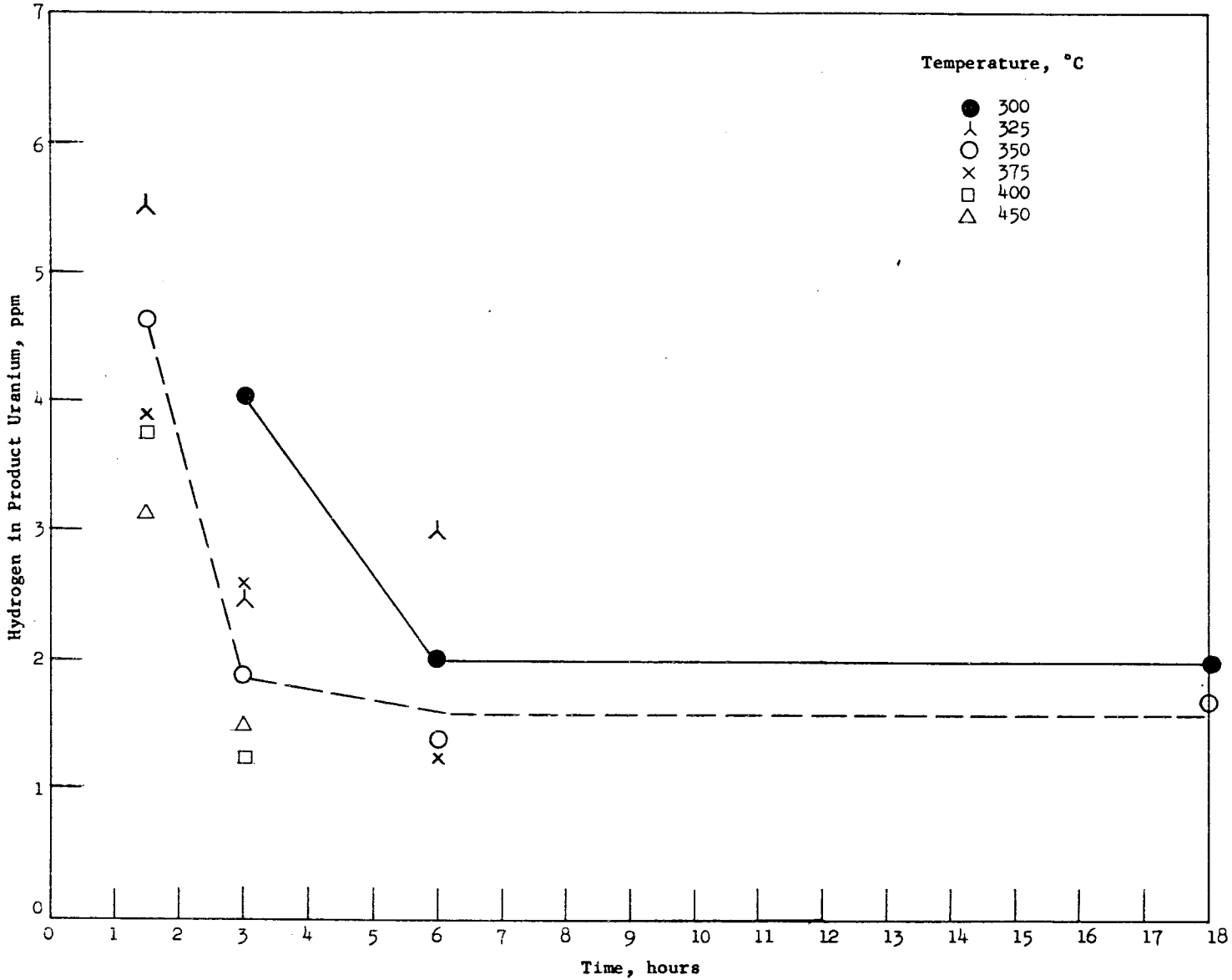


Figure 2

EFFECT OF PREIGNITION SOAK TEMPERATURE ON HYDROGEN CONTENT OF URANIUM PRODUCED IN ISOTHERMAL 4-KG DINGOT BOMBS

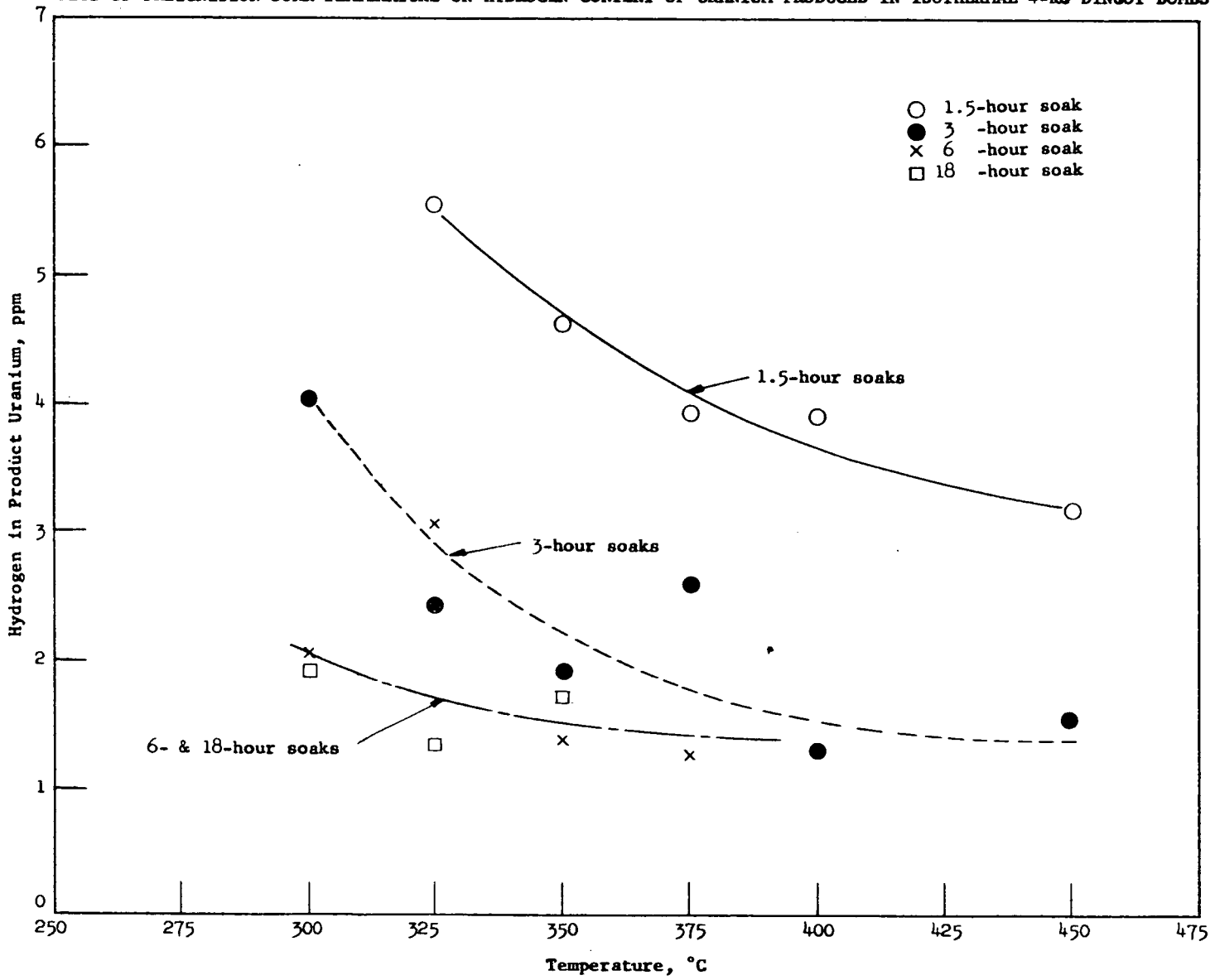


Figure 3

RELATIONSHIP BETWEEN CHARGE CENTER TEMPERATURE AND HYDROGEN CONTENT OF DINGOT URANIUM METAL

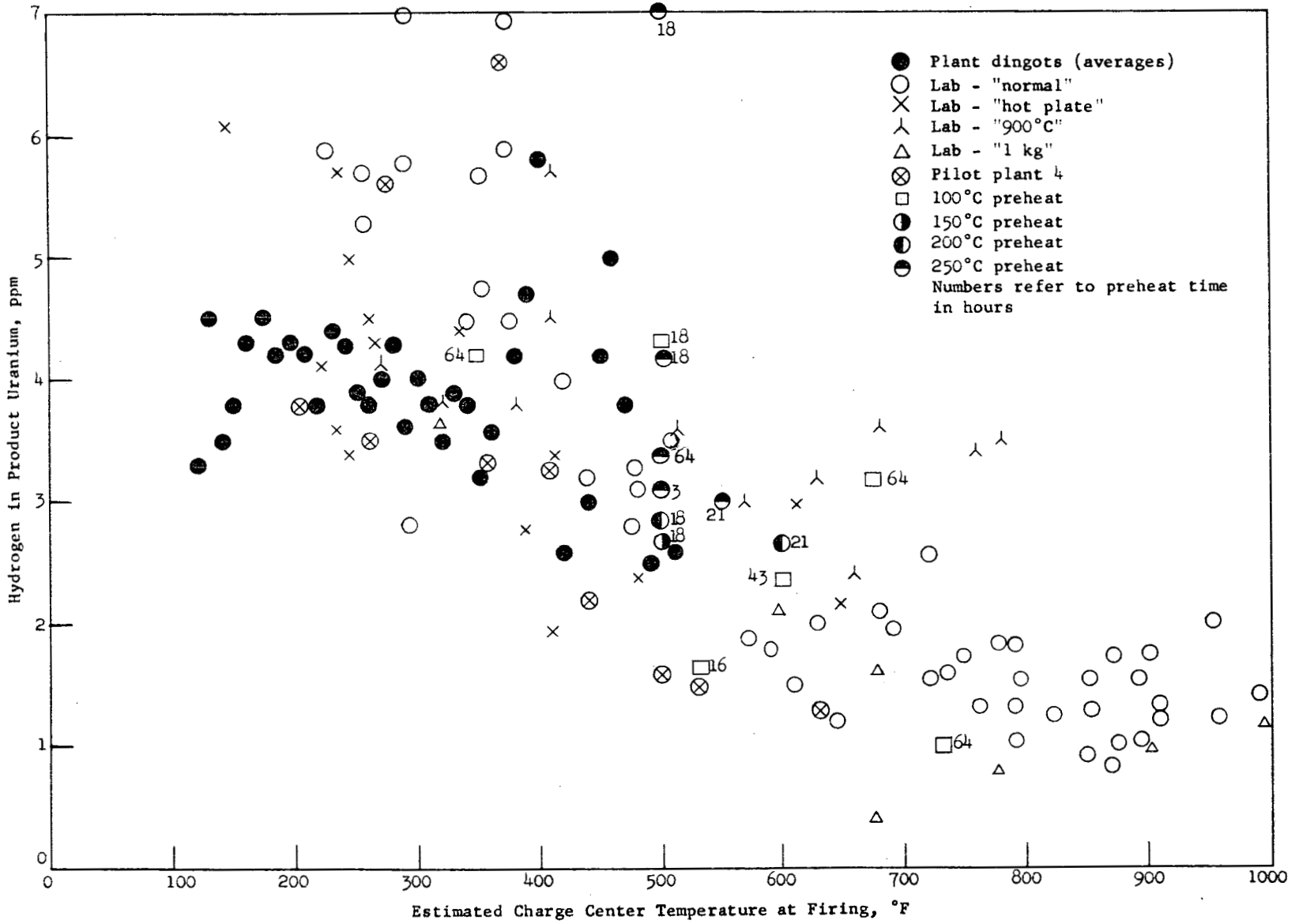
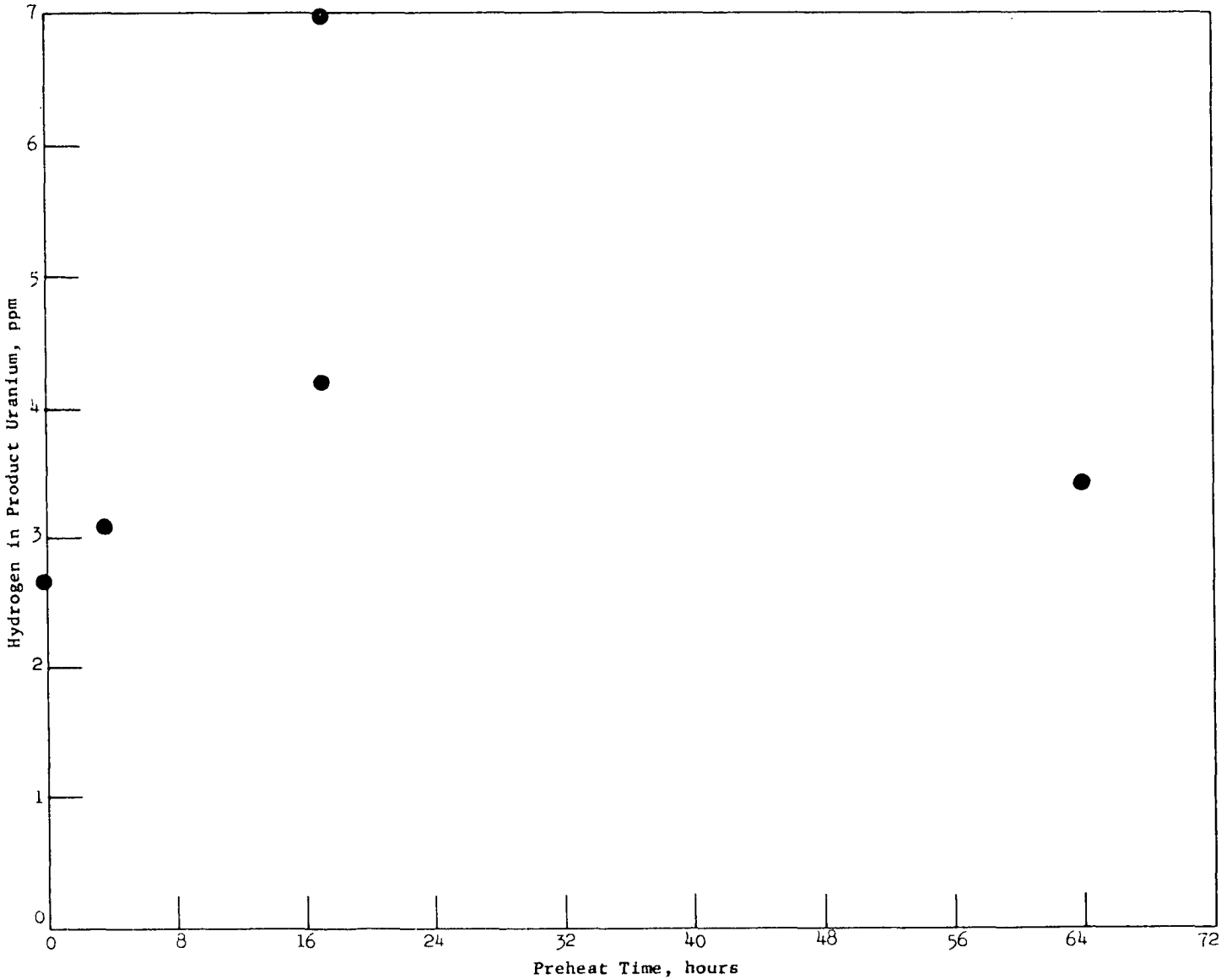


Figure 4

EFFECT OF PREHEAT TIME AT 250°C ON THE HYDROGEN CONTENT OF URANIUM PRODUCED IN 4-KG DINGOT BOMBS FIRED AT 260°C CENTER TEMPERATURE



D. Discussion

The decrease in hydrogen with increasing soak time and increasing temperature in the range 300°C to 450°C is probably the result of degassing the bomb components by evolution of water and/or hydrogen, which lowers the hydrogen remaining in the bomb at firing (c.f. section of this report on gas evolution from bombs). The fact that this decrease in hydrogen with increasing soak time was not observed in the preheated bombs at temperatures below 250°C indicates that there is a critical temperature needed for the degassing to occur. The chemical or physical process responsible for this is not known; it could be decomposition of a UF_4 hydrate, decomposition of $Mg(OH)_2$, or reaction of water with magnesium.

The fact that the time-temperature effects hold only above a hydrogen level of about 2 ppm is not surprising. The hydrogen remaining in the interstitial gas space in the bomb is more than enough to account for 2 ppm hydrogen in the metal. It seems likely that the factors controlling the hydrogen content in the range below 2 ppm are different from the factors involved at higher hydrogen levels.

It should be noted that, although preheating in the 100°C to 250°C temperature range did not lower the hydrogen content below that of metal from bombs with equivalent center temperatures, it did shorten the time required to reach a given temperature. This led to a higher mean charge temperature for a given center temperature for bombs preheated equivalent times. This may explain why some of the preheated bombs lie outside the normal hydrogen-center temperature range.

These data indicate that the observed correlation of hydrogen with center temperature and with preheat times is the result of degassing the bomb components when the components are heated above 300°C. Since the bomb center temperatures at firing and temperature gradients within the charge are also functions of preheat times and temperatures, these factors also correlate with the observed hydrogen level.

IV. Accelerating the Heating Rate of Bomb Charge Center

A. Summary

The thermal conductivity of bomb charges has been increased by replacing part of the regular Mg with Mg strips or turnings. Center temperatures have been increased by as much as 300°F compared to those of normal charges at equivalent times.

B. Introduction

Laboratory and plant work has shown that the charge center temperature at ignition is a useful control parameter in producing low hydrogen in the as-reduced metal. It was found that bomb center temperatures greater than 500-600°F at ignition are consistently related to metal with 2 ppm hydrogen or less.[1,2] Twenty to thirty-hour heat soaks are needed in the plant to allow the charge center to reach these temperatures under standard furnace conditions. Therefore, it is economically advantageous to bring the center temperature to the 500-600°F range more quickly. The work reported here concerns evaluation of increasing the center temperature heating rate by using Mg strips or turnings to replace part of the normal Mg. Previous work along these lines has been done using Mg plates.[3]

C. Experimental

Four-kg bombs, containing thermocouples at the liner-charge interface and in the charge center, were placed in a furnace set at 900°F. The interface and center temperatures were recorded until the center had reached 500°F, then the furnace temperature was raised to 1200°F, and the bomb was allowed to fire. The bombs contained various amounts of Mg in the form of strips or turnings. The bombs, according to the Mg used, were:

(1) 100 per cent normal granulated Mg,

(2) 97 per cent normal Mg + 3 per cent Mg in the form of strips (1" × 5" × 0.014") placed radially through the charge,

(3) 90 per cent normal Mg + 10 per cent Dow Mg in the form of turnings (8" to 10" × ½" × 0.010") blended together,

(4) 70 per cent normal Mg + 30 per cent Dow Mg in the form of turnings blended together,

(5) 70 per cent normal Mg + 30 per cent Metal Sellings Mg in the form of strips (2.5" × 0.5" × 0.014") blended together, and

(6) 40 per cent normal Mg + 60 per cent Metal Sellings Mg in the form of strips (2.5" × 0.5" × 0.014") blended together.

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[1] Neumann, N. F., *et al.*, *Process Development Quarterly Progress Report, Part I*, Mallinckrodt Chemical Works, *MCW-1403* (July 1, 1957), p 99-118

[2] Leifield, R. F., *et al.*, *Process Development Quarterly Progress Report, Part I*, Mallinckrodt Chemical Works, *MCW-1425* (January 3, 1959), p 37-88

[3] Neumann, N. F., *et al.*, *Process Development Quarterly Progress Report, Part I*, Mallinckrodt Chemical Works, *MCW-1410* (January 2, 1958), p 63

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D. Results and Discussion

Charge center heating curves are shown for each bomb in Figure 5.

The data indicate that addition of Mg strips or turnings to the charge can increase the heating rate of the charge. As expected, the charge heating rate generally increased with increases in the Mg turnings-to-chips (normal Mg) ratio. However, the apparent equivalence of 30 and 60 per cent Metal Sellings Mg could indicate that there is a limit to the beneficial effect of Mg strips and turnings. Since these bombs were not fired in the normal manner, no conclusions can be drawn regarding the effect of the large Mg pieces on the metal yield. However, experience in the past has shown that Mg turnings above 10 per cent decrease crude yields. Bombs fired with less than 10 per cent Mg as strips have given good yields. In addition, the bomb charge weight must be decreased when using Mg turnings because of the large volume-to-weight ratio of the Mg.

V. Reduction of Green Salt Containing Added Water

A. Summary

Bombs have been fired with liquid water added directly to the charge. The amounts of added water were 10.1, 20.2, and 40.4 grams (equivalent to 280, 560, and 1120 ppm H_2 on a uranium basis). These bombs were fired at various center temperatures ranging from 230°F to 830°F. Water added in this manner is effective in raising the hydrogen content of the uranium produced above that of a "normal" bomb to which no water was added, but which was fired under otherwise identical conditions. The effect of additional water on increasing hydrogen in uranium is greatly depressed when the bombs are allowed to "soak" at about 650°F for sixteen hours.

B. Introduction

It has been suspected that there is a tendency for the hydrogen content of uranium metal produced in the plant to increase during the summer months and decrease during the winter months. Though this fluctuation has not been thoroughly substantiated, a compilation of analytical data indicates that the H_2O content of green salt does increase during the period April to September and falls to lower values in the period October to March. The graph in Figure 6 shows this data. It has been found that the amount of water sorbed by green salt is proportional to the UO_2F_2 content of the material (in the range 0.8 - 6.0% UO_2F_2).[4]

[4] Finch, W. F., and Kennelley, J. A., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, *MCW-1428* (April 1, 1959), p 23-27

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Figure 5

CENTER HEATING CURVES IN A 900°F FURNACE FOR 4-KG DINGOT BOMB CHARGES
IN WHICH MAGNESIUM SHAVINGS AND STRIPS WERE SUBSTITUTED FOR A PART OF THE MAGNESIUM CHIPS OF THE NORMAL CHARGE

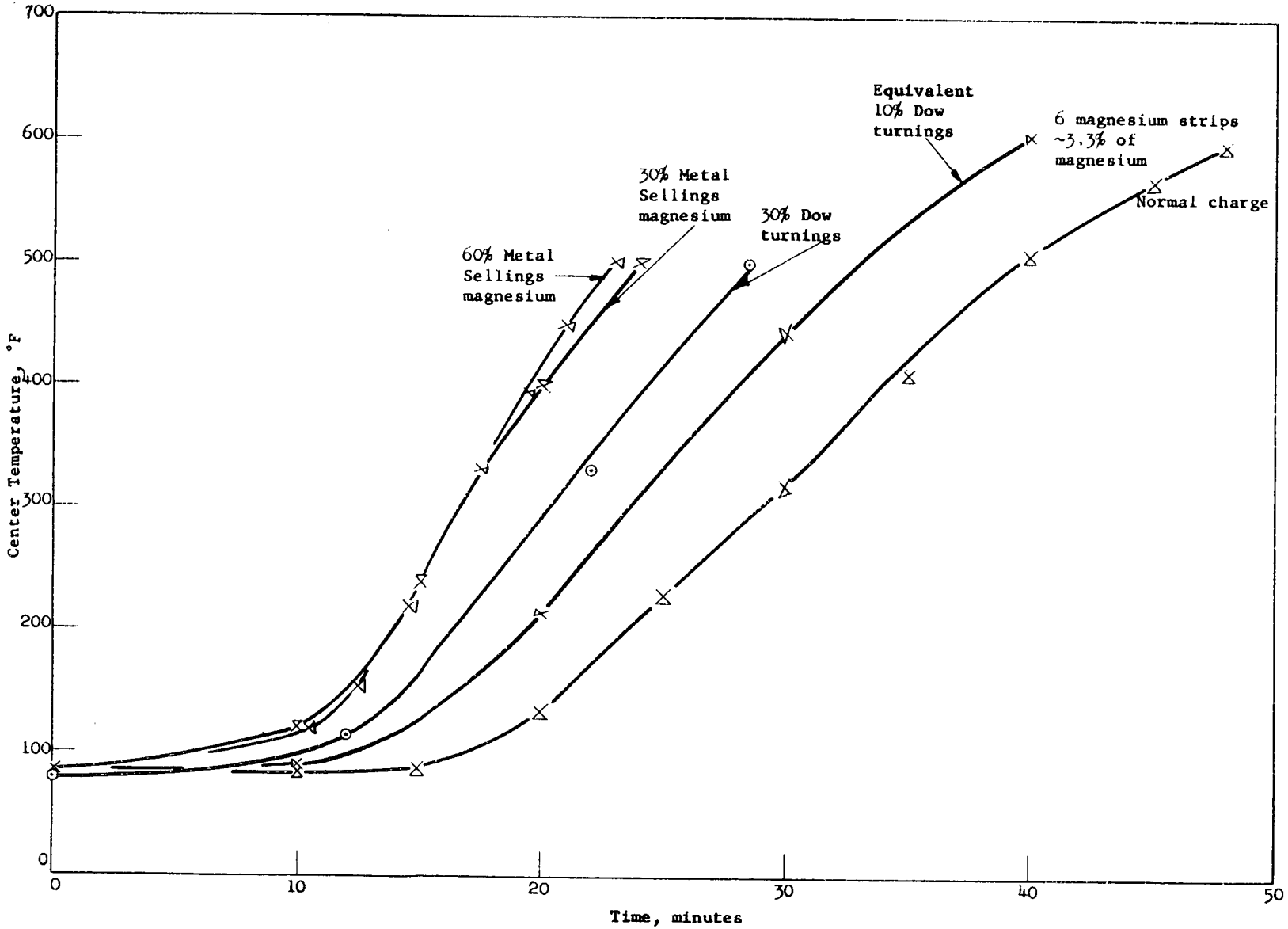
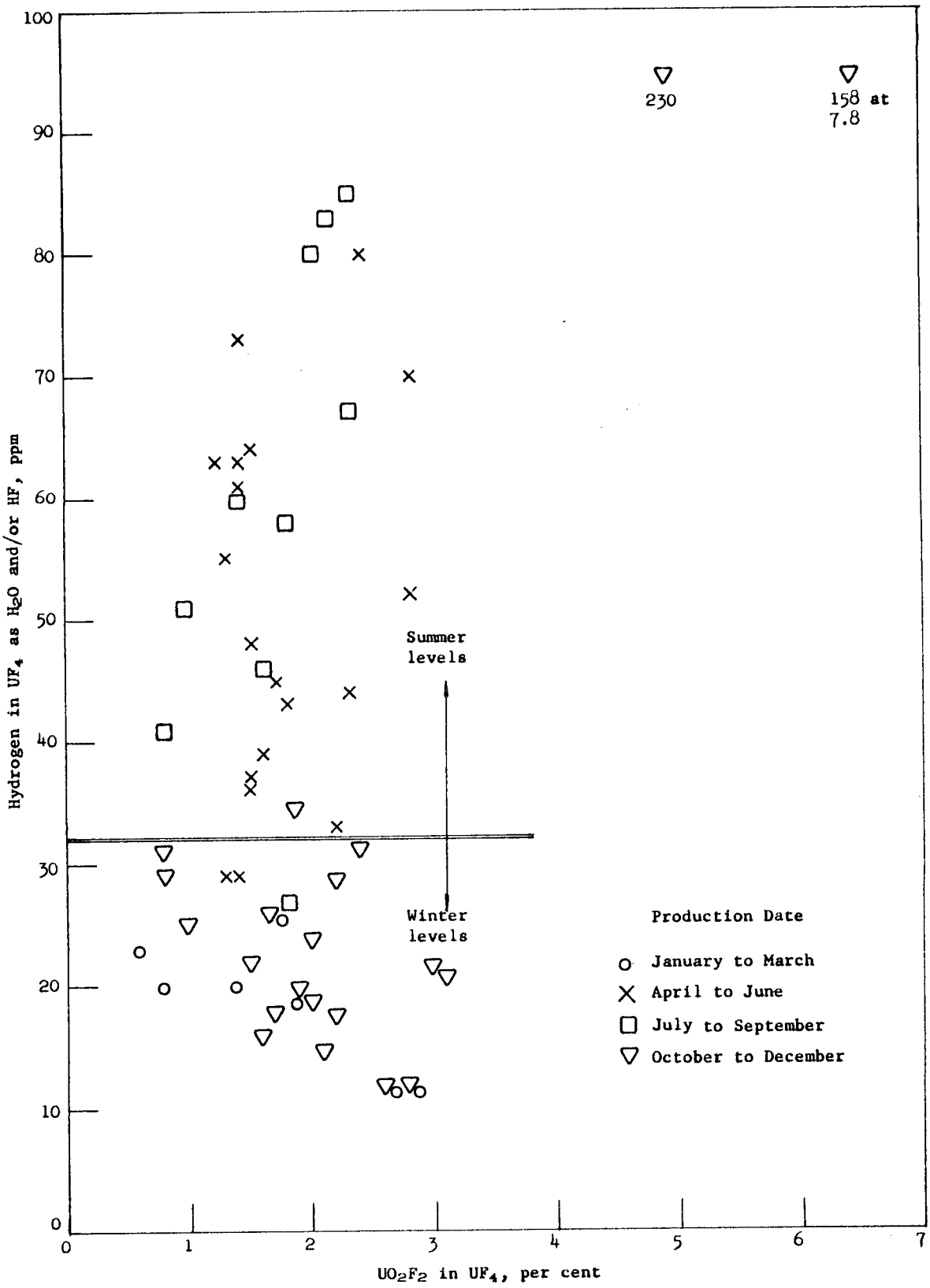


Figure 6

HYDROGEN CONTENT OF UF_4 PRODUCED AT VARIOUS TIMES OF THE YEAR



It is necessary to compare the water content of green salt lots containing the same quantities of UO_2F_2 in order to evaluate the importance of seasonal effects on the water content. The data in Figure 6 show a generally higher water content in green salt lots made in the period April-to-September than in lots made during the winter months. This seasonal difference is largely independent of the UO_2F_2 content of the material.

A laboratory investigation was therefore begun to determine if the summer-winter effect could be directly related to the H_2O absorption by green salt. The most obvious relation between H_2O content and seasonal change is the variation in absolute humidity of the atmosphere. A given volume of air often contains (in the Weldon Spring vicinity) as much as six times the amount of water in the summer as it does in the winter. As bomb charge components (especially green salt) are exposed to these varied conditions for approximately equivalent times both summer and winter, they will absorb water from the atmosphere in amounts proportional to the absolute humidity.

C. Experimental

An attempt was made to simulate a charge which had reached equilibrium with water vapor at 20°C by purging the bomb with water-saturated air at this temperature. At the end of ten days, however, equilibrium had not been attained and this approach was abandoned. It was decided instead to make water additions directly to the charge in the amounts of 10.1, 20.2, and 40.4 grams (equivalent to 280, 560, and 1120 ppm H_2 on a uranium basis). These quantities of water were chosen because they represent approximately one-half, one, and two times the theoretical amount of water that can be absorbed from air at 100 per cent relative humidity (20°C) by the UF_4 charge.[5] The water was added as the Mg-green salt charge was prepared, and the mixture was blended for 30 minutes.

The 4-kg bombs were heated by the "hot plate" technique (hot plate furnace, 650°C set temperature, 90 per cent power). A thermocouple was placed in the center of each bomb charge to measure the center temperature at ignition (abscissa on the graph). The increase of charge center temperature with time was interrupted in every case at a temperature of ~215°F, at which point the water boiled off at constant temperature. After removal of the water, the rate of temperature increase continued as before. The length of time during which the charge center remained in this isothermal condition was directly proportional to the water content.

Some water additions were also made to bomb charges which were subsequently stored for 7 and 14 days. The purpose of this experiment was to determine if this "hold period" was

[5] Finch and Kennelley, *MCW-1428*

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influential on the bonding of H_2O and the charge components to the extent that varying hold periods would alter the ease with which the charge was dehydrated during the preignition heating period.

D. Results

The data compiled in Table I show the effect of increasing amounts of water added to the bomb charge on the resultant hydrogen content of uranium. Individual data for each bomb are available in Table II and the graph in Figure 7. It is readily seen that bombs containing added water, but fired under otherwise normal conditions, are almost without exception higher in hydrogen content in uranium than "normal," *i.e.*, bombs to which no water has been added. No direct or simple quantitative relationship between the amount of water added and the amount of hydrogen in uranium above the "normal" range was found; however, it would be expected that such a relationship would be relatively obscure, due to the effect of water content on heating rate and the temperature profile of the bomb charge.

Table I

Effect of Water Additions to Four-Kilogram Bomb Charges on Hydrogen in Uranium

	Standard Firing Procedure				Bombs Soaked	
Water Added, g	0.0	10.1	20.2	40.4	20.2	40.4
Hydrogen Added, ppm	0	280	560	1120	560	1120
Range of Values of H_2 in Uranium, ppm	2.0-2.2	2.2-3.5	3.0-8.4	4.5-6.5	1.1 (16 hr) 1.3 (1.2 hr) 3.0 (1.5 hr) 5.7 (3.0 hr)	1.3 (1.2 hr)
Average Hydrogen, ppm	2.1	2.9	4.5	5.6	3.3	1.3
Range of Center Temperatures at Firing, °F	320-400	480-500	230-800	380-400	640-680	820
Number of Bombs Fired	2	2	10	3	3	1

Table II

Effects of Water Addition to Four-Kilogram Bomb Charges[a]

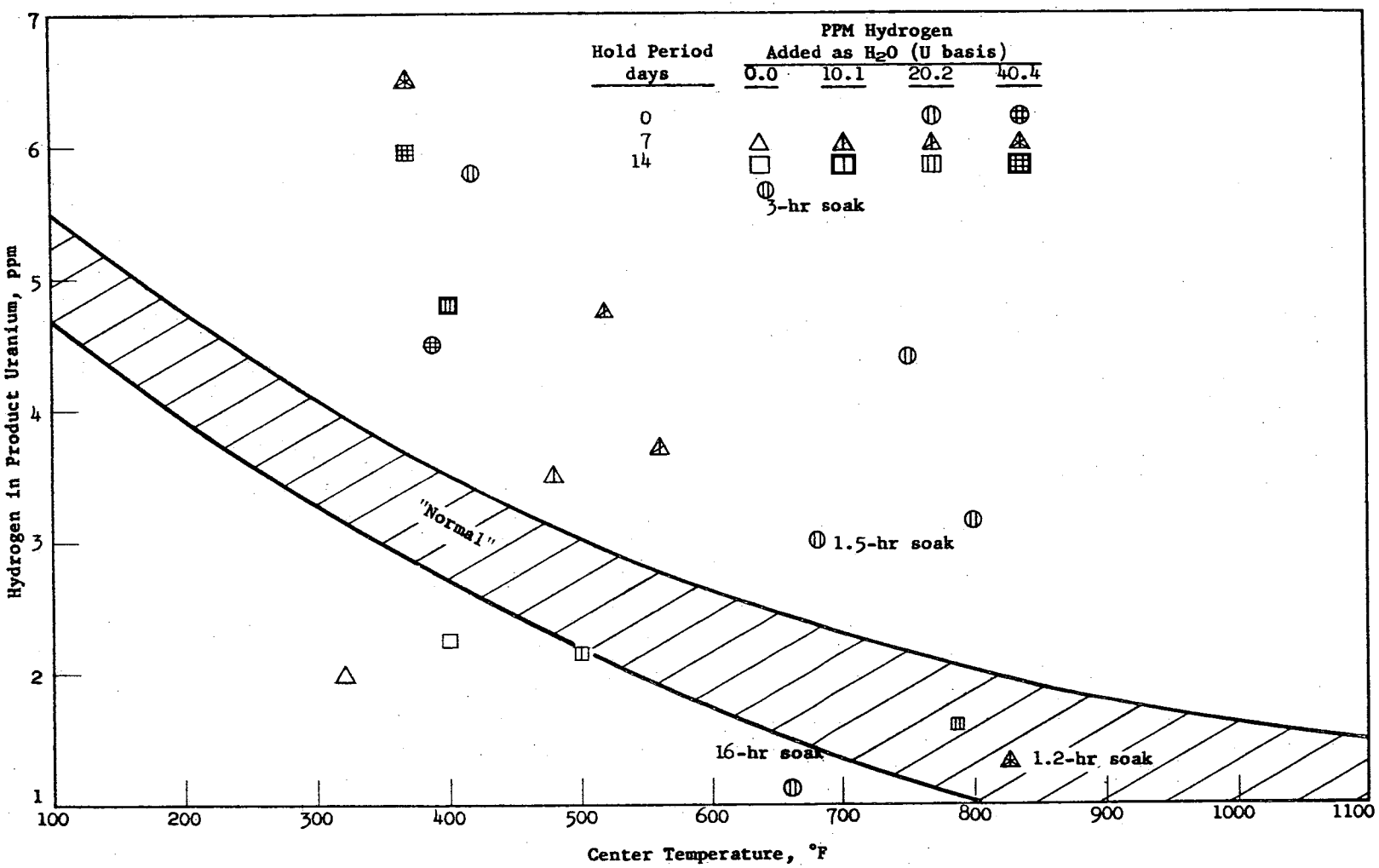
Hold Period, days	7	7	14	14	7	14	7	14	7	14	7	0	0	0
Charge Number	B-627	B-634	B-628	B-635	B-636	B-637	B-638	B-639	B-640	B-641	B-645	B-661	B-667	B-668
H_2O Content, grams	20.2	40.4	20.2	40.4	10.1	10.1	00.0	00.0	20.2	20.2	40.4	20.2	20.2	20.2
Center Thermocouple	yes											yes	yes	yes
Charge Analysis														
UF_4	24 ±1 ppm H_2; 96.70% UF_4; 1.84% W.S.[b], 1.40% AOI													
Mg	32 ±4 ppm H_2													
MFL	38 ±2 ppm H_2													
Soak Time												3 hr	99 min	16 hr
Soak Temperature, °F												650	680	660
H_2 in UF_4, ppm														
Before hold	140	270	150	160	75	76	25	24	100	120				
After hold	210	270	220	350	110	120	29		210					
H_2 in Mg, ppm														
Before hold	100	120	160	130	42 ±5	37 ±4	35 ±4	33 ±4	79 ±9	82 ±10				
After hold	180	470	220	360	62 ±7	63 ±8	30 ±4	36 ±4	210	220				
Preignition Time, min	43	77	51	38	37	39	26	31	40	37	36	3-hr soak	99-min soak	16-hr soak
Center Temperature at Firing, °F	520	825	785	370	480	500	320	400	560	400	370	640	680	660
H_2 in Metal, ppm	4.8 4.7	1.3 1.3	1.4 1.8	5.6 6.5	3.4 3.6	2.1 2.2	2.0 2.0	2.3 2.2	3.7 3.7	4.8 4.9	6.8 6.0	5.6 5.7	3.0 3.0	1.1 1.2
Time for Plant Bomb to Reach this Center Temperature, hours	25	-	-	19	23	24.5	17	20	27	20	19			
Normal Hydrogen Content of Comparable Plant Bomb, ppm	2.0- 3.0	0.9- 1.9	1.1- 2.1	2.9- 3.7	2.3- 3.2	2.2- 3.1	3.2- 4.0	2.7- 3.5	1.9- 2.8	2.7- 3.5	2.9- 3.7	1.6- 2.5	1.4- 2.3	1.5- 2.4

[a] Bombs fired by hot plate heating; 650°C set temperature, 90% power.

[b] W.S. (or "Water Soluble") is UO_2F_2.

Figure 7

EFFECT OF WATER CONTENT OF THE BOMB CHARGE ON THE HYDROGEN CONTENT OF URANIUM PRODUCED IN 4-KG DINGOT BOMBS



Comparison of bombs containing added water and subjected to "hold periods" with those fired immediately after blending shows no significant difference in the hydrogen content of the metal produced. It appears that the effect of contact time on the binding occurring between water and bomb charge components, if there is an effect, is not influential on the rate at which dehydration occurs during the preignition period at the water levels of this set of experiments.

One important effect observed is that despite the presence of large amounts of hydrogen (contained as water), a sufficiently long preignition period will expel the water and produce metal having a hydrogen content within the "normal" range. Sixteen-hour "soak" bombs, initially containing 20.2 grams water (equivalent to 580 ppm H_2), produced uranium containing normal and less then normal quantities of hydrogen. (Table II and Figure 7) Therefore, soaking at high temperatures can be utilized in offsetting the relatively high water contents of green salts produced during summer months.

VI. Ignition Temperatures of Stirred Magnesium and Green Salt Mixtures

A. Summary

Mixtures of green salt and Mg were subjected to temperatures up to 565°C while being mechanically stirred in a steel "500-gram" bomb shell. Ignition of these charges occurred between temperatures of 393°C and 565°C, depending on the physical and chemical condition of the Mg used. These experiments were conducted to define safety limitations for operating conditions in the pilot plant where a procedure of preheating bomb charges was anticipated.

B. Introduction

Lower values for hydrogen in metal can be obtained by attaining a relatively high center temperature in the bomb charge just prior to ignition. An increase in center temperature can result from increasing the preignition heating period per bomb. An obvious method of obtaining high center temperatures at ignition without excessively long preignition periods is to preheat the charge components before the bomb shell is filled. Though this proposal has merit, there is considerable danger involved in handling large quantities of hot charge, for which precise ignition temperatures at these conditions are undetermined. It was with the aim of determining safety limits for preheating a magnesium - green salt charge that the laboratory undertook the following work.

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C. Experimental and Results

An apparatus was prepared for agitating a green salt-magnesium blend in a steel 500-gram bomb shell which was placed in a Kanthal furnace. A thermocouple was placed in the charge bed to record the charge temperature accurately. A variety of heating and mixing procedures was used. Table III gives the experimental results of all runs with remarks describing specific procedures. These data show that preheating a green salt-Mg mixture is without hazard from rapid chemical reaction at temperatures below 300°C for any mesh size Mg. Use of the normal mesh size or filmed Mg would raise this to approximately 400°C. No significant departure from these limits occurred when the Mg component was added to the hot green salt. The temperature limits to which green salt alone can be heated are considerably above those applied to the blended charge, because the cold Mg lowers the green salt temperature by a considerable amount (see CAP-11). This relaxation in safety temperature limit, however, was not recommended because unusual or unanticipated conditions which might occur in plant operation could conceivably lower ignition temperatures considerably.

Table III

Ignition Temperatures of Stirred and Heated Green Salt and Magnesium Mixtures[a]

Run No.	Time min	Mg Mesh	Ignition Temperature °C	Remarks
CAP-1	95	-50	355	The ignition temperature may be in error by as much as ±40° due to error in thermocouple placement.
CAP-2	15 hr	-50	none	The external shell temperature of this run was recorded at a peak of 420°C.
CAP-3	99	-50	433	
CAP-4	69	-50	447	
CAP-5	93	-50	393	
CAP-6	166	normal	505	
CAP-7	172	normal	485	
CAP-8	80	-50	448	A Tesla coil discharged at 50° intervals showed no effect on ignition.
CAP-9	16 hr 90 min	-50	none at 330 ignition at 550	The blend was heated for 16 hours at 330° and no ignition occurred; the temperature was raised until ignition did occur at 550°. Tesla discharge had no effect at any temperature.
CAP-10	70 9	none -50	none at 375 487	Green salt only (-50) Mg was added to hot green salt, but a Mg spill into the furnace caused rapid heating and was probably responsible for ignition.
CAP-11	85 38 50	none +12 +12	none at 365 none at 260 ignition at 558	Green salt heated to 365°, (+12) Mg added caused temperature to drop over 38 minutes to 260°; continued heating caused ignition at 558°.
CAP-12	80	none filmed Mg	none at 370 none at 350	Same procedure as CAP-11, except that heating was not resumed after Mg addition due to stirrer failure.
CAP-13	68	filmed Mg	565	The reaction mixture from CAP-12 was recharged into functioning apparatus and fired.

[a] All runs were made in an air atmosphere and with constant stirring except when Mg additions were made to hot green salt, in which cases the stirring was stopped only during the time of addition.

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It is interesting to compare the ignition temperatures of runs CAP-2, CAP-9, CAP-11, and CAP-13 with the other ignition temperatures. In run CAP-11, +12 mesh Mg was used in the charge, and in run CAP-13 filmed Mg with a normal particle size distribution was used. The similarity in ignition temperatures (558°C and 565°C, respectively) might be indicative of the similarity of the reactivity of the Mg in these two states. In run CAP-9, -50 mesh Mg was used, but it was stirred and heated with green salt for 16 hours to permit filming the Mg by any residual HF in the UF_4. In view of the ignition temperature of 550°C, there is a very good possibility that this *did* occur.

During the experimental run CAP-4, a beaker of the charge mixture was placed about 3 feet from the reactor apparatus. When the experimental charge (CAP-4) ignited from furnace heat, a spark from the ignited charge flew into the adjacent open beaker causing its contents to ignite and react completely. This unexpected occurrence prompted additional experimentation relating to possible accidental ignition of a hot charge by an electrical spark; this might arise from an accumulation of static charges during hopper discharge in the plant or a power line spark caused by faulty electrical connection. These conditions of "cold" and "hot" sparks were simulated by means of discharges from a Tesla coil and a high-voltage transformer, respectively. The energy outputs from these sources were estimated to be 30 watts and 900 watts, respectively. The spark from the Tesla coil did not ignite the charges under any conditions (see Table III). The spark from the 900-watt high-voltage transformer, ignited charge mixtures containing -50 mesh Mg, cold or hot, but did not ignite cold mixtures containing +12 mesh Mg or fluoride filmed Mg. Apparently, under most circumstances, electrical discharges (excluding high voltage) have no hazardous effect on igniting hot blended charges.

VII. Porous-Top Bombs

A. Summary

"Stovepipe," *i.e.*, porous-top bombs, were fired using graphite or firebrick disks as a replacement of the MFL cap and steel bomb lid. Metal resulting from these bombs contained lower amounts of hydrogen in the 200-600°F-center temperature range than that from normal 4-kg bombs ignited at equivalent center temperatures. In the 600 to 900°F-center temperature range, the hydrogen results were the same as normal bombs. Metal yields were lower in some cases and preignition times were shorter than normal 4-kg bombs. Graphite and firebrick appeared to be equivalent in lowering the hydrogen in the metal, but firebrick had the disadvantage of reacting with Mg vapor, leading to increased blowouts.

B. Introduction

Previous laboratory work on sealed bombs has shown that hydrogen-in-uranium values are strongly dependent on the pressure within the bomb during the thermite reaction.[6] Pressures at firing need only rise approximately 20 psi to increase the hydrogen in uranium 100 per cent, *i.e.*, from 2 to 4 ppm.

Pressure during ignition might be decreased by replacement of the normal MFL cap and the steel bomb lid with a more porous material, thus allowing the bomb to "vent" itself during ignition. Porosity measurements have shown that graphite and firebrick are four to five times more porous than packed MFL. Therefore, a number of 4-kg bombs have been fired in the laboratory, using a ¼-inch-thick graphite disk in place of the MFL cap. A few bombs have been fired using 1- to 2-inch-thick firebrick disks. In addition, the steel lid normally used was replaced by a 4-inch steel pipe. The 4-inch pipe served as a bomb vent directly to the atmosphere in the furnace. A retainer ring was welded to the pipe to keep the disks from being blown from the bomb. A slight argon flow minimized oxidation of both the carbon and UF_4.

C. Experimental

Three laboratory heating techniques were employed in firing porous-top bombs:

1. Normal heating: Furnace - 650°C; power - 4600 watts

2. Accelerated heating: Furnace - 900°C; power - 6500 watts

3. Hot plate heating: Furnace - 650°C; power - 6500 watts plus 900-watt hot plate in bottom of furnace.

The graphite used for bomb tops was electrode grade. The plates were usually recovered intact and were cleaned by scraping and soaking in HCl solution, and dried in an oven before reuse. This treatment restored most of the plate's original porosity. Since the porosity of the plates was reduced almost to zero after the firing act by condensed Mg and fused slag, the degree to which the plates maintained their porosity during the firing act was unknown. It was found that a ¼-inch thickness was needed to withstand both the thermal shock and Mg vapor attack during ignition.

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[6] Leifield, R. F., *et al.*, *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, *MCW-1425* (January 2, 1959), p 37-88

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Firebrick used for caps was SiO_2-Al_2O_3 (G-26 grade) manufactured by A. P. Green. A one-to-two-inch thickness was required to prevent a total blowout. However, even with this thickness, partial blowouts occurred. These blowouts were caused by the reaction of SiO_2 with Mg vapor during ignition. Consequently, firebrick tops were not recovered intact.

D. Results

A convenient method of comparing the hydrogen results of porous-top bombs with that of normal bombs is plotting the hydrogen results from both types of bombs versus the charge center temperature at ignition. A plot of normal laboratory and the average of 900 plant bombs is shown in Figure 8. It is seen that there is a relationship between hydrogen and center temperature, and that the two lines drawn on the figure encompass the weighted majority of data. Thus, any point within the "band" represents a normal value.

Since thermocouples were not placed in the charge center of the porous-top bombs, a center temperature at ignition was not obtained. However, it is possible to estimate the center temperature of these bombs fairly accurately by using Figure 9, which shows center temperature versus time for the three laboratory heating techniques. Thus, preignition time can be used to estimate the center temperature at ignition. The hydrogen in uranium versus center temperature at firing for porous-top bombs is plotted in Figure 10. The "normal band" for plant and laboratory bombs is included for comparison.

E. Discussion

The data in Figure 10 show that porous tops are more effective in lowering hydrogen in metal at center temperatures below 600°F than at higher temperatures. From 200°F to 600°F there was only one bomb out of 12 which fell in the normal band, while above 600°F, 6 out of 11 bombs fell in the normal band. This is to be expected since the charge gas content at lower temperatures is greater than at higher temperatures. Hence, the more gas left in the charge, the higher the possible pressure surge during ignition.

Preignition times were shorter, and crude yields were slightly lower for porous-top bombs. A partial cause of the lower yields was probably heat loss through the bomb top. The main reason for using firebrick as a lid was the insulating property of this material. However, reaction of Mg with SiO_2 in the firebrick caused blowouts and made yields worse instead of better. Shorter preignition times probably were caused by the escape of gases from the bomb which are normally involved in Mg filming reactions.

Figure 8

RELATIONSHIP BETWEEN CHARGE CENTER TEMPERATURE AT FIRING AND HYDROGEN CONTENT OF URANIUM PRODUCED IN DINGOT BOMBS UNDER VARIOUS HEATING CONDITIONS[a]

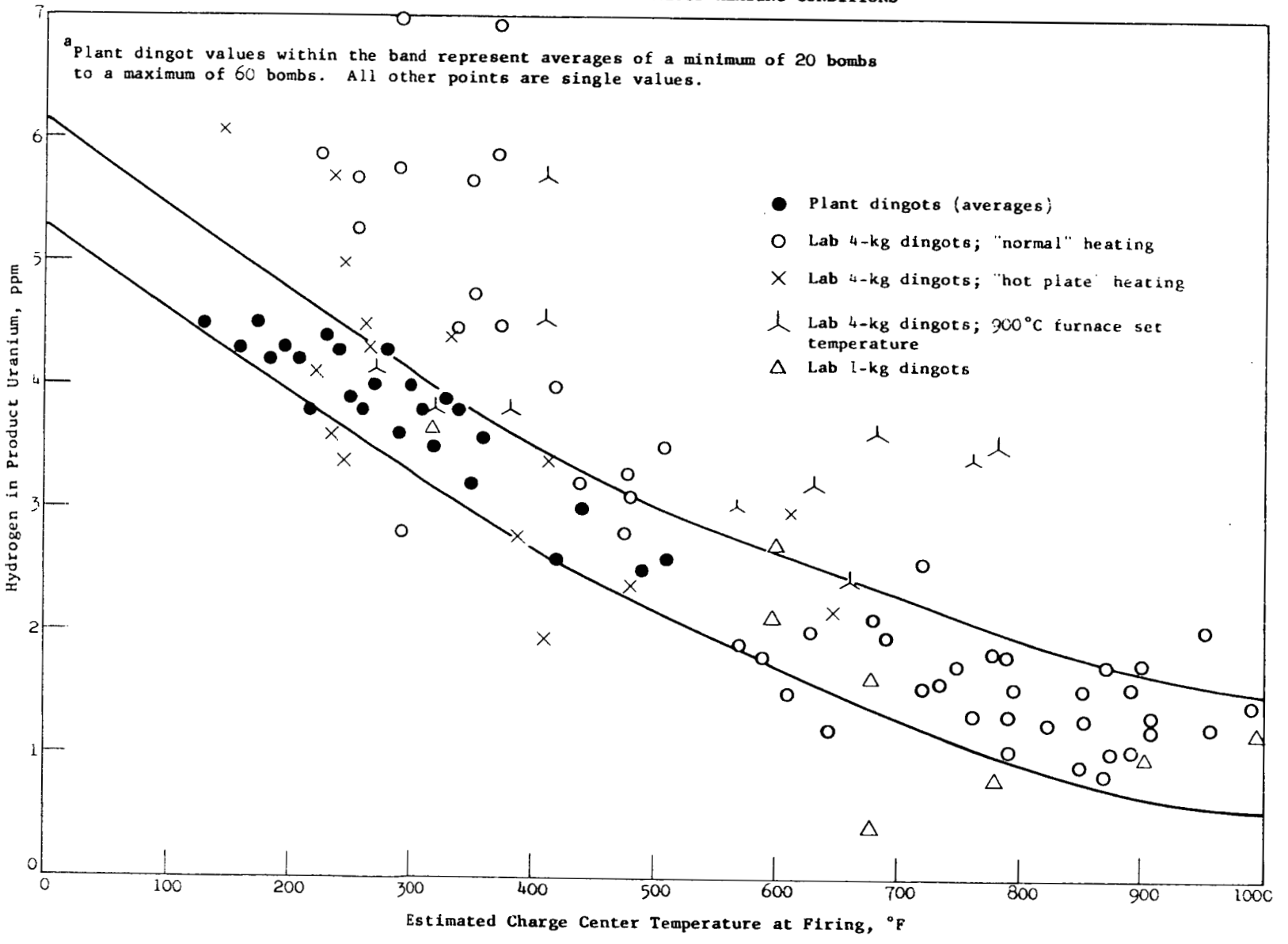


Figure 9

HEATING CURVES FOR 4-KG DINGOT BOMBS

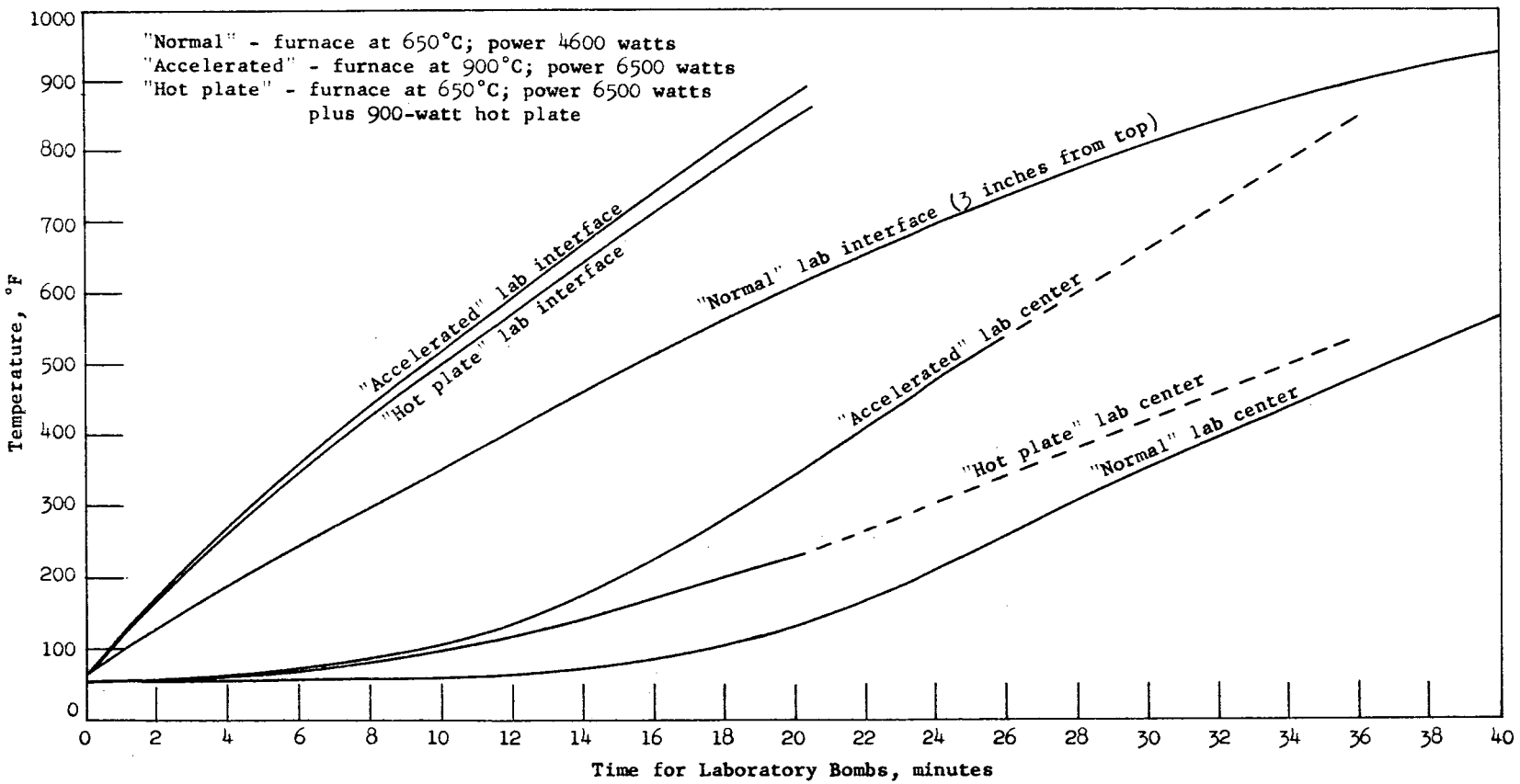
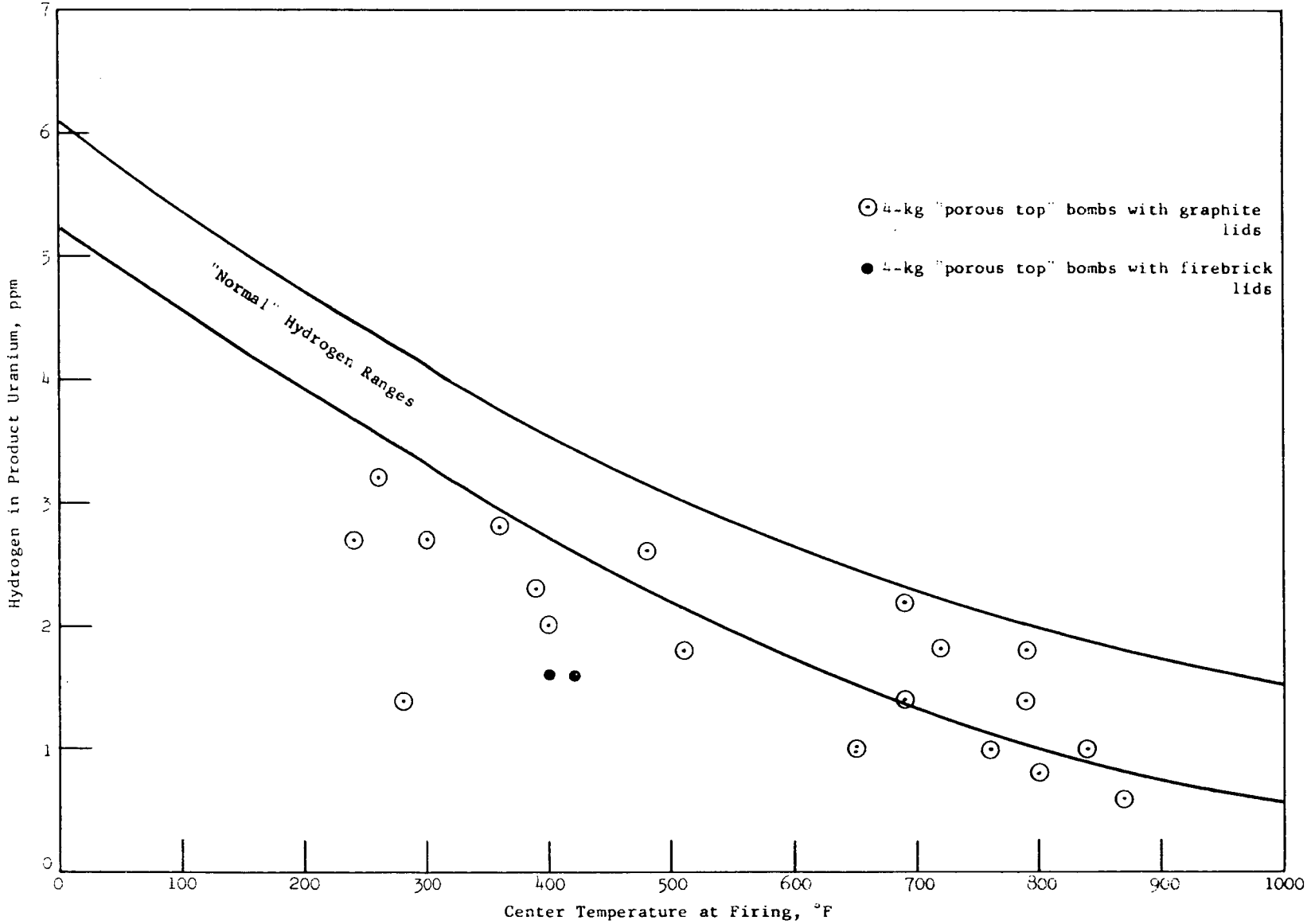


Figure 10

THE DECREASE IN HYDROGEN CONTENT OF URANIUM BY PRODUCTION IN WELL-VENTED DINGOT BOMBS



On the whole, the hydrogen results were encouraging and the technique offers a means of producing low-hydrogen metal at increased production rates.

VIII. Pickup of Hydrogen Gas by Molten Uranium During Free Fall Through Hydrogen, Water Vapor, and Hydrogen Fluoride Atmospheres

A. Summary

Molten uranium was poured through hydrogen, water vapor, and hydrogen fluoride to study the effect of these gases on the sorption of hydrogen by liquid uranium.

Hydrogen sorption was very rapid, and no large differences between gases were observed. All three gases could be important sources of hydrogen in uranium in the dingot process.

B. Introduction

Previous work in this laboratory has indicated the presence of hydrogen, water vapor, and hydrogen fluoride in the thermite bomb during the preheat period. Rates of sorption of hydrogen by liquid uranium from hydrogen and water vapor atmospheres have been determined.[7,8] It was the basic purpose of this work to extend this information to hydrogen fluoride atmospheres.

C. Experimental

The all-graphite apparatus used for this work is pictured in Figure 11, and a schematic diagram of the system is shown in Figure 12. A coating of magnesium oxide was sprayed on the outside of the graphite to prevent excessive oxidation. The graphite assembly was enclosed and insulated by heavy ceramic cylinders filled with small alumina bubbles.

The uranium was melted in the induction-heated graphite crucible under an argon atmosphere. A removable plug in the crucible bottom made it possible to pour the molten uranium into the funnel immediately below. From the funnel a stream of uranium dropped through a 1½-inch-diameter by 7-inch-long reaction tube. A second funnel at the bottom of the reaction tube channelled the uranium into the induction-heated receiving crucible, which was purged with argon to protect the collected metal from the reaction gas. After

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[7] Myers, H. W., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, *MCW-1410* (January 2, 1958), p 59-69

[8] Myers, H. W., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, *MCW-1412* (April 1, 1958), p 97-104

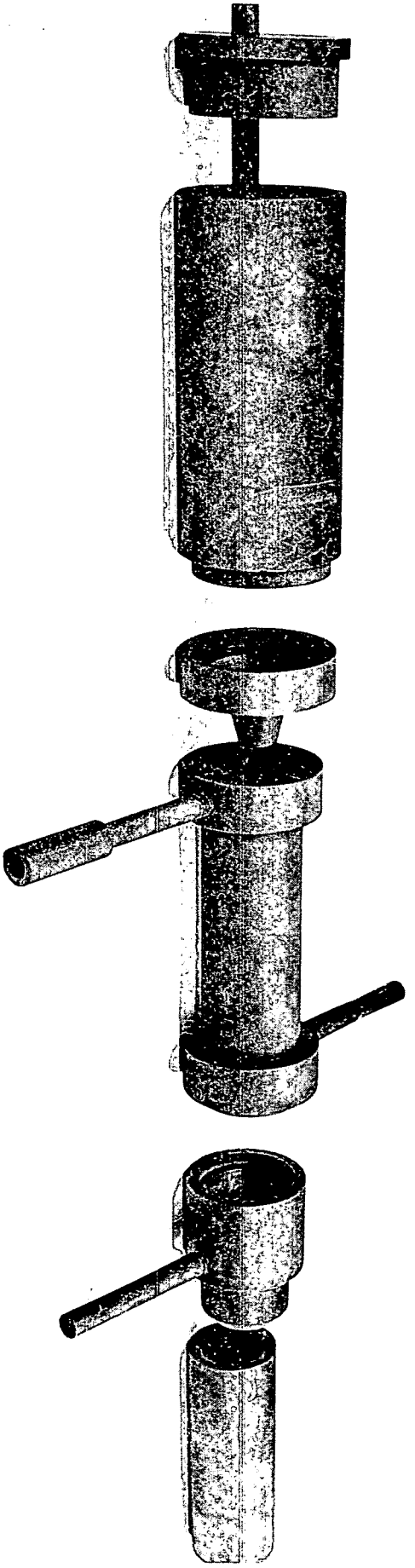

Figure 11

GRAPHITE APPARATUS FOR POURING URANIUM THROUGH REACTING GASES

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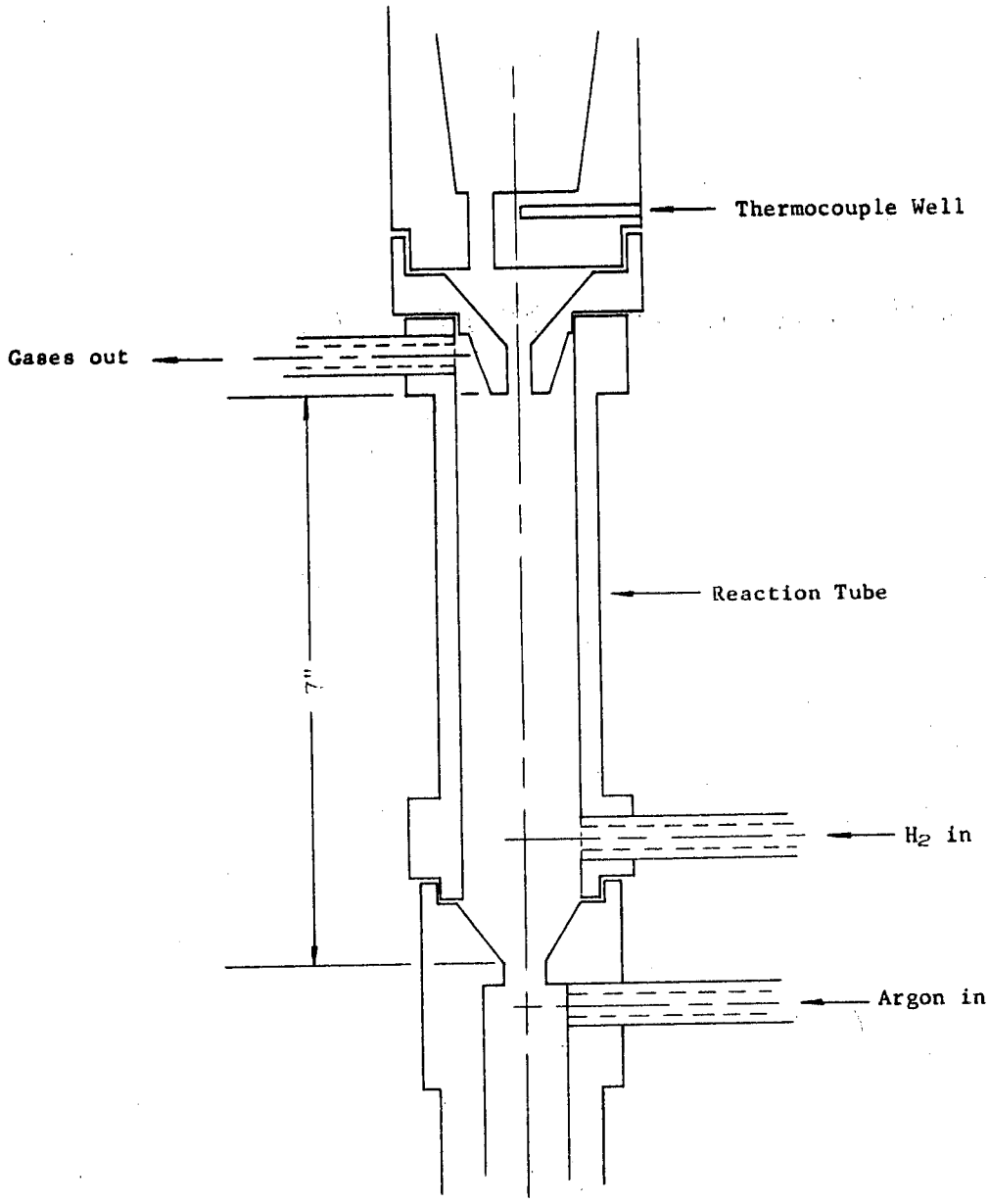
Figure 12

REACTION TUBE CROSS SECTION



initial exploratory runs, an attempt was made to maintain the following experimental conditions:

Melting crucible temperature	1250°C
Reaction tube temperature	700°C
Receiving crucible temperature	1000°C
Hold time before pouring	18 minutes
Pour funnel stem diameter	$^{3}/_{16}$ inch
Inert gas (argon)	
Top crucible purge	635 ml/min
Receiving crucible purge	156 ml/min

Immediately upon pouring, the receiving crucible was allowed to cool rapidly.

D. Results and Discussion

Forty-three pours through argon, hydrogen, water vapor, and hydrogen fluoride were attempted. Some melts were unpoured due to difficulties with the pour plug. Analysis of these unpoured melts indicated no contamination of the metal by the reaction tube gases prior to the pour. Pours through argon established blank corrections. The exposure time of a given area segment of the surface of the falling uranium was estimated to be between 0.1 and 0.2 seconds.

A summary of results is given in Table IV, and the blank pours through argon are listed in Table V. Although the results were too random to permit any correlation between the hydrogen increase in the metal and the hydrogen concentration in the reaction chamber the fact that an increase in hydrogen occurred in every run but one evidenced a very fast reaction and/or sorption rate for all three gases. Also, the data do not indicate any gross differences in behavior between the gases.

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Table IV

Summary of Pours

Principal Gas in Reaction Tube	Run No.	Hydrogen Content: Initial PPM	Hydrogen Content: Final PPM	Hydrogen Content: Corrected Increase PPM [a]	Reaction Tube Hydrogen Concentration per cent[b]	Calculated Surface Hydrogen Sorption γ/cm^2 [c]
Hydrogen	5	0.5	2.4	-	20.0	-
	10	2.9	4.6	1.7	60.6	3.84
	11	0.5	3.3	0.4	60.6	0.90
	13	2.9	5.4	2.5	89.1	5.65
	14	3.0	9.2	6.2	96.3	14.00
	15	3.2	5.7	2.5	96.3	5.64
	16	3.0	7.7	4.7	96.3	10.63
Water Vapor	17	3.1	3.8	0.7	89.6	1.58
	20	3.0	6.5	3.5	97.4	7.92
Hydrogen Fluoride	27	3.0	5.2	2.2	95.6	4.96
	28	0.2	5.1	2.2	95.6	4.97
	29	0.2	5.0	2.1	95.6	4.74
	31	0.2	5.1	2.2	88.2	4.97
	32	0.2	5.4	2.5	88.2	5.64
	33	3.0	4.6	1.6	88.2	3.62
	35	2.9	3.8	0.9	89.2	2.30
	37	3.2	6.8	3.6	93.4	8.12
	40	2.9	7.2	4.3	93.4	9.68
	43	3.2	5.2	2.0	95.6	4.52

[a] Corrected for argon blank.

[b] Based on hydrogen equivalent of reacting gas and one atmosphere pressure.

[c] Total micrograms (γ) of hydrogen increase divided by total exposed surface of metal.

Table V

Melts Poured Through Argon

Run No.	Hydrogen Content: Initial PPM	Hydrogen Content: Final PPM	Hydrogen Content: Increase PPM	
3	0.5	2.7	2.2	Av. 2.5
4	0.5	3.6	3.1	
6	0.5	2.1	1.6	
24[a]	0.2	2.2	2.0	
25	0.2	4.1	3.9	
7	3.0	3.7	0.7	Av. 0.0
22	3.0	2.3	-0.7	

[a] After Run No. 20 all argon was purified by passing it over hot uranium turnings.

It is evident from these data that the rate of contamination of liquid uranium is rapid from all three atmospheres. The reproducibility of the results is insufficient to permit correlation of the amount of hydrogen pickup by the uranium with the concentration of hydrogen compounds in the gas phase, but at least qualitatively, molecular hydrogen, water vapor, and hydrogen fluoride all behaved the same. (No preferential source of the hydrogen entering the metal from the gas phase can be indentified from these experiments.)

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THERMAL DIFFUSIVITY OF LINER MATERIALS

by

Richard W. Gaver
James A. Kennelley

Summary

Thermal diffusivity measurements on MFL were made at 650°C to determine whether differences in dingot heating rates were caused by variations in the diffusivity of daily batches of MFL.

The thermal diffusivity of most MFL samples (regular, roasted, or leached) at 650°C was found to be approximately 2.0×10^{-5} cm²/sec. However, an initially high diffusivity (3×10^{-3} cm²/sec) was always found in measurements on regular MFL. This high diffusivity may be due to the copious quantities of ammonia and then hydrogen gas (above 300°C) which are usually evolved when regular MFL is heated.

No significant variation in thermal diffusivity was found in the seven samples of regular MFL tested to-date. However, some differences in the initial heating rate of the dingot could be caused by differing rates of hydrogen gas evolution.

Introduction

In connection with the problem of high hydrogen levels in dingot metal, much attention has been focused on the bomb liner material (MFL) as a possible cause of non-reproducible dingot preignition times. To date, no significant variations in the chemical or general physical properties of regular MFL samples have been found which can account for these variations. Measurement of the thermal diffusivity of MFL is a method for directly testing daily batches of plant MFL to detect differences in thermal properties.

Some low temperature (below 300°C) studies were made on the thermal diffusivities of bomb components by Beatty,[1] but this data did not include the 650°C furnace temperature employed in the plant.

Experimental

The method involved measuring the rate of increase in temperature of the center of a long cylinder of MFL when the outside temperature of the cylinder was suddenly increased from room temperature

[1] Beatty, K. O., Jr., *Thermal Diffusivities and Conductivities of Green Salt, Green Salt-Magnesium Blends, Dolomite, and Slag*, National Lead Company of Ohio, *FMPC-471* (July 1, 1954)

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to 650°C. The diffusivity constant was calculated from the equation $\frac{T - T_1}{T_0 - T_1} = 1.60\ e^{-1.02\ kt}$ where T = center temperature at time t, T_0 = ambient temperature, T_1 = new surface temperature, and k = diffusivity constant.

Details of the method of calculation are given in appendix I. The sample tube was constructed from a thin-wall nickel tube 2 inches in diameter by 26 inches long. A 28-gauge chromel-alumel thermocouple was placed inside the tube so that the thermocouple bead was in the exact center. A second chromel-alumel thermocouple (Inconel-sheathed) was attached to the outside of the tube with its bead in the same horizontal plane as that of the center thermocouple. Both center and outside temperatures were recorded on the same graph by the use of a timing device which periodically (every 30 seconds) switched thermocouple leads to a single pen Brown recorder.

In order to bring the sample tube surface to the desired new surface temperature instantaneously and hold it there during the entire run, a large, well-insulated tube furnace was constructed employing a 4-inch-diameter by 20-inch-long Kanthal resistance element. The element was mounted vertically. The annular space between the furnace element and sample tube was filled with a stainless-steel heat-sink. A slot or key-way down the inside of the heat-sink provided room for the outside thermocouple and allowed a very close fit between the tube and heat-sink.

The MFL to be studied was packed in the sample tube by jolting with laboratory equipment until the maximum packing density was achieved. Usually about 5 pounds of MFL were required. Pack densities were determined for each run and were found to be quite reproducible. Good agreement between pack densities and previously determined tap densities was also obtained. The center thermocouple position was checked several times during the jolting operation to make sure it remained correctly centered. The loaded tube was closed with a Monel cap.

The initial furnace set temperature was 60 - 70°C above the control temperature (650°C) to allow for the heat capacity of the nickel sample tube.

Measurements were made by plunging the sample tube into the furnace and simultaneously starting the recorder and timer. The furnace controls were then re-set, and the temperature surrounding the sample tube was carefully controlled at the desired level. In about 40 minutes the difference between center and outside temperatures was usually only 5 to 10 degrees, and the run was then terminated. After cooling, the sample tube was unloaded and the center thermocouple checked; then, the sample tube was reloaded with a new sample.

A precision study was made with samples of roasted MFL and leached MFL. Their diffusivities varied somewhat during the measurements, so calculations were made for various times for each run. A comparison of several runs for both types of MFL is given in Table I, appendix II, where the maximum deviations are summarized. A mean deviation of about 4% is indicated. This

is reasonably low considering that a calculation error of up to 2% is possible below 600 seconds, and that above 1500 seconds a small variation in center temperature has a large effect on the calculated diffusivity constant (see Table II, appendix II). Less precision was obtained with regular MFL samples, but the deviation rarely exceeded 6%.

Results and Discussion

Nine samples of liner material, including roasted and leached MFL, have been studied. (See appendix III, Table I, for representative chemical analyses.) The thermal diffusivities of roasted MFL and leached MFL were found to be about the same ($\sim 2 \times 10^{-3}$ cm^2/sec). It was also found that their diffusivities varied only slightly during the entire run. Regular MFL samples behaved quite differently. The diffusivity of regular MFL was initially near 3×10^{-3} cm^2/sec but it dropped as the run progressed (see Figure 1). In Table I are listed the diffusivities of regular, roasted, and leached MFL, which were calculated for a number of points during each run.

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Table I

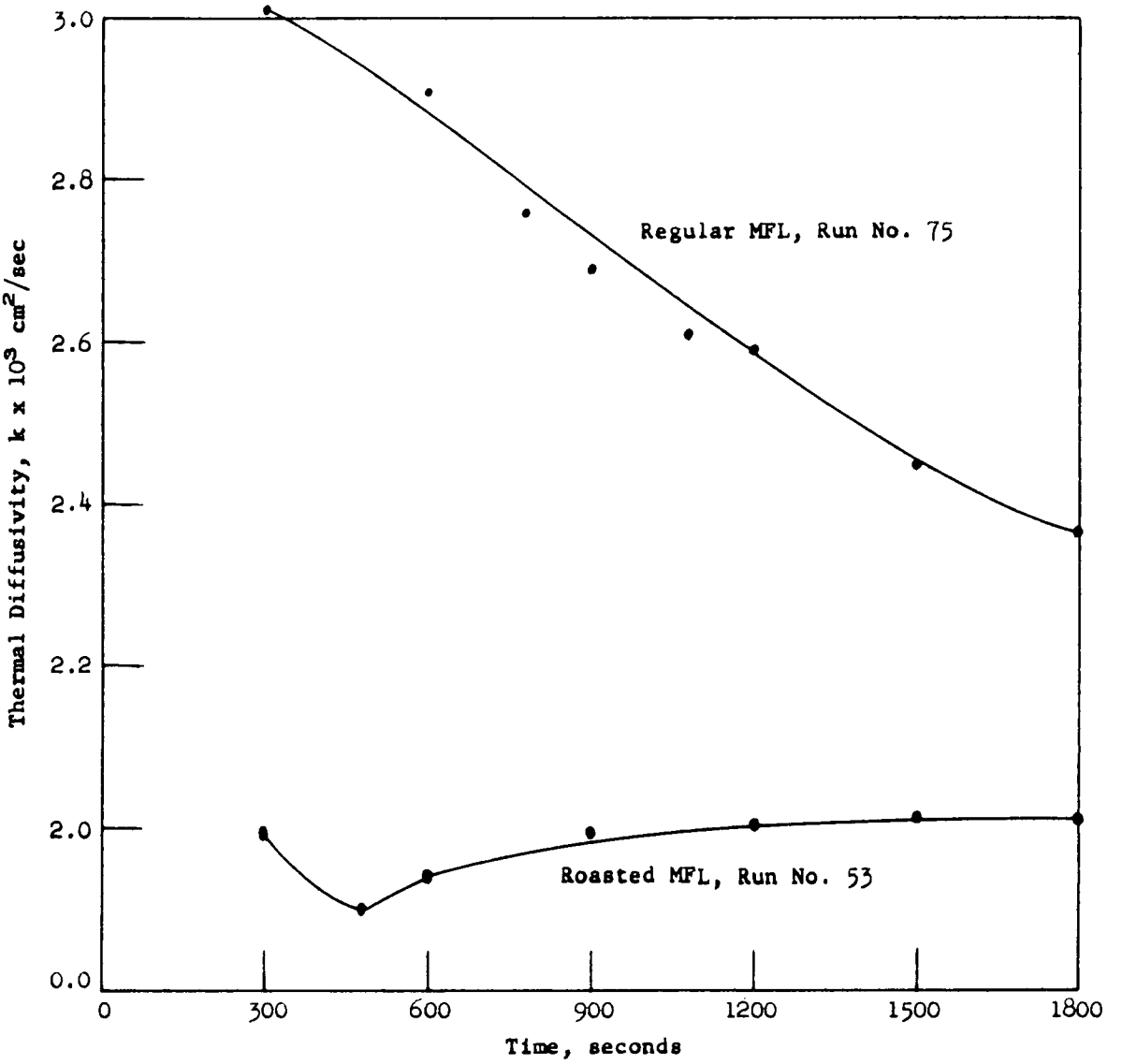
Thermal Diffusivity of Liner Materials
$k \times 10^3$ cm²/sec at 650°C

Time seconds	Roasted MFL (average)	Leached MFL (average)	W.S.MFL A[a]	W.S.MFL B[b]	W.S.MFL C[c]	W.S.MFL D[d]	W.S.MFL E[e]	W.S.MFL F[f]	Plant 6E MFL[g]
300	1.96	2.00	3.24	3.04	3.24	2.92	2.81	2.84	3.19
480	1.87	1.74	3.18	2.94	3.07	2.93	2.65	2.87	3.16
600	1.90	1.76	3.10	2.91	3.02	2.85	2.56	2.81	3.08
780	1.96	1.81	2.91	2.76	2.91	2.77	2.46	2.70	2.94
900	2.00	1.86	2.76	2.69	2.83	2.71	2.42	2.64	2.84
1080	2.04	1.91	2.58	2.61	2.69	2.64	2.35	2.54	2.70
1200	2.04	1.94	2.48	2.59	2.62	2.62	2.31	2.48	2.65
1500	2.04	2.00	2.42	2.45	2.46	2.52	2.25	2.36	2.51
1800	2.04	2.00	2.30	2.37	2.41	2.32	2.24	2.25	2.34

[a] Weldon Spring lot of 5/6/58 Hopper 23.
[b] Weldon Spring lot of 5/8/58 Hopper 1.
[c] Weldon Spring lot of 664-11018-007 Batch 8.
[d] Weldon Spring lot of 664-11018-404 Hopper 12.
[e] Weldon Spring lot of 664-11018-410 Hopper 8.
[f] Weldon Spring lot of 664-11018-416 Hopper 36.
[g] Plant 6E lot 163-01148-010 Drum 2 (Destrehan site).

Figure 1

THE RELATIONSHIP BETWEEN THERMAL DIFFUSIVITY AND TIME FOR REGULAR AND ROASTED MFL



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Evolution of hydrogen gas may have caused the irregular diffusivity of normal MFL. Thermal diffusivity of powders is known to vary with the composition of the gas in the void spaces.[2] The composition of the interstitial gas is altered during the course of a run with normal MFL by (1) the evolution of ammonia and desorption of water vapor, and (2) by the copious evolution of hydrogen as the MFL is heated.[3] However, the evolved hydrogen appears to have a greater initial effect on the diffusivity constant than could be attributed to gas composition changes alone. "Turbulence" in the gas phase, caused by a high rate of gas evolution, provided favorable heat transfer characteristics and hence, high initial values of k. As the temperature increased, the rate of gas evolution gradually decreased and led to less favorable heat transfer. The observed decrease in k corresponded to the decrease in the rate of gas evolution. An indication of this effect was obtained in a study of the thermal gradients in laboratory reduction bombs.[4] It was found that higher charge heating rates with normal-MFL-lined bombs (compared to roasted-MFL-lined bombs) were directly related to the copious evolution of hydrogen.

To determine the effect of gas evolution, two samples of MFL were run several times without removing them from the sample tube. The results are compared to a similarly treated sample of roasted MFL in Table II. After the first run, where most of the hydrogen and ammonia were expelled, the diffusivity of regular MFL approached that of roasted MFL and became quite constant.

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[2] Schumann, T. E. W., and Voss, V., "Heat Flow Through Granular Materials," *Fuel* 13, 249 (1934)

[3] Neumann, N. F., *et al.*, *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, *MCW-1399* (January 1, 1957), p 98

[4] Gaver, R. W., and Neumann, N. F., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, *MCW-1407* (October 1, 1957), p 85

Table II

Effect of Repeated Measurements[a] on the Thermal Diffusivity of MFL
$k \times 10^{5}$ cm^2/sec at 650°C

Time seconds	Roasted MFL		W.S. MFL of 5/8/58 Hopper 1				W.S. MFL -416 Hopper 36			
	1st.	5th.	1st.	2nd.	3rd.	4th.	1st	2nd.	3rd.	4th.
300	1.99	2.25	3.04	2.29	2.27	2.29	2.84	2.32	2.24	2.24
480	1.84	2.06	2.94	2.02	2.00	2.03	2.87	2.10	1.98	1.98
600	1.88	2.01	2.91	1.98	1.91	1.96	2.81	2.06	1.92	1.93
780	1.95	1.98	2.76	1.98	1.92	1.93	2.70	2.01	1.89	1.90
900	1.99	1.97	2.69	1.98	1.91	1.93	2.64	1.99	1.88	1.90
1080	2.05	1.95	2.61	1.99	1.90	1.92	2.54	1.98	1.88	1.89
1200	2.07	1.94	2.59	1.99	1.90	1.91	2.48	1.96	1.88	1.90
1500	2.15	1.96	2.45	1.96	1.87	1.90	2.36	1.93	1.86	1.83
1800	2.21	1.91	2.37	1.91	1.84	1.86	2.25	1.91	1.84	1.82

[a] MFL sample left in sample tube after each run, cooled, then run again.

Another change, which could have an effect on the diffusivity constant, takes place in the MFL during the heating cycle. Regular MFL contains several per cent of elemental uranium and magnesium. These metals oxidize during a run, as indicated in Table II, appendix III, and they could be contributing to the observed decrease in the diffusivity constant.

Conclusions

It seems apparent from these results that after a bomb liner stops evolving gases such as ammonia and hydrogen its thermal diffusivity approaches the value 2×10^{-3} cm^2/sec. (or 7.8×10^{-2} ft^2/hr.). The results in Table II further indicate that the final values for the diffusivity constants of most batches of regular, roasted, or leached MFL are similar. Differences in intial diffusivities, as given in Table I, however, may indicate differing amounts of hydrogen released by these liner materials. Since this hydrogen probably diffuses through the charge, and hence increases its thermal diffusivity, the initial heating rate of the charge could be affected by liner materials of different initial diffusivities.

Appendix I - Calculations

Solutions to the differential equation for heat transfer, were discussed at length by Williamson and Adams[1] to provide a means of calculating heating and cooling curves for various solid shapes. For the temperature change in the center of an infinite cylinder whose surface is suddenly heated or cooled, they derived the equation

$$\frac{T - T_1}{T_0 - T_1} = 2 \sum_{m=1}^{m=\infty} \left[\frac{1}{Rm\, J_1(R_m)} \right] \cdot e^{-\frac{kR_m^2 t}{x^2}}$$

T – center temperature at time t in °C.

T_0 – original uniform temperature in °C.

T_1 – new surface temperature in °C at time zero

k – diffusivity constant in cm^2/sec

t – time in seconds

x – distance (radius) in cm

m – any integer

Rm – and – J_1 (Rm) are Bessel Functions whose values can be obtained from a standard table of Bessel Functions.

Solving this equation for the first two terms, where the cylinder radius is 0.936 inches, gives $\frac{T - T_1}{T_0 - T_1} = 1.60\, e^{-1.02\, kt} - 1.06\, e^{-5.43\, kt}$. However, only the first term is significant. The final equation, $\frac{T - T_1}{T_0 - T_1} = 1.60\, e^{-1.02\, kt}$ is quite simple, and k can be obtained using a table of exponential functions.

To consider this equation valid for calculating the diffusivity constants of MFL samples, two assumptions were necessary: that the coefficient of heat transfer to the sample was unity (e.g., no barrier to heat flow), and the diffusivity of the sample container was large enough compared to that of the sample to cause no significant error in the measurements.

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[1] Williamson, E. D., and Adams, L. H., Phys. Rev. *14*, 99-114 (1919)

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The thermal conductivity and diffusivity of a solid are related by the equation

$$k = \frac{K}{e\,C_p}, \quad \text{where } k = \text{diffusivity constant } (cm^2/sec)$$

K = conductivity constant ($cal \cdot cm/sec \cdot cm^2 \cdot {}^\circ C$)

e = density of the solid ($grams/cm^3$)

C_p = heat capacity of the solid (cal/g)

Another term must be added to the equation when the material is in powder form to account for the composition of the gas or gases in the void spaces. Some calculations were made by Schumann and Voss,[2] but the term is complicated by changes in gas composition, and it is best determined experimentally.

[2] Schumann, T. E. W., and Voss, V., "Heat Flow Through Granular Materials," *Fuel* 13, 249 (1934)

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Appendix II

Table I

Thermal Diffusivity of Treated MFL
$k \times 10^5$ cm²/sec at 650°C

	Roasted MFL					Leached MFL				
Time seconds	53 Tube 1	55 Tube 1	65 Tube 1	Average	Deviation ±%	59 Tube 1	62 Tube 2	64 Tube 2	Average	Deviation ±%
300	1.99	1.88	2.02	1.96	3.5	1.89	2.14	1.96	2.00	6.3
480	1.90	1.74	1.98	1.87	6.4	1.72	1.83	1.68	1.74	4.3
600	1.94	1.79	1.97	1.90	4.7	1.77	1.79	1.71	1.76	2.3
780	1.97	1.88	2.04	1.96	4.1	1.85	1.79	1.80	1.81	1.7
900	1.99	1.93	2.08	2.00	3.8	1.89	1.83	1.87	1.86	1.6
1080	2.02	2.00	2.09	2.04	2.2	1.96	1.85	1.93	1.91	2.9
1200	2.00	2.04	2.08	2.04	2.0	1.98	1.86	1.98	1.94	3.1
1500	2.07	2.10	1.96	2.04	3.4	2.02	1.90	2.07	2.00	4.3
1800	2.03	2.05	2.05	2.04	0.5	2.00	1.90	2.10	2.00	5.0

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Appendix II

Table II

The Calculated Effect of a 5°C Deviation in Center Temperature on the Thermal Diffusivity Constant

Assume value of k: 2×10^{-3} cm²/sec.

Time seconds	Calculated[a] Center Temp. °C	Calculated Effect on k of 5°C Deviation in Center Temperature ± %
0	x	x
100	x	x
300	100	1.5
600	349	1.5
900	485	1.5
1200	559	2
1500	600	3.5
1800	623	6
2100	635	9.5
2400	642	21

[a] Calculations based on a long sample tube of 1-inch radius.

Appendix III

Table I

Chemical Analysis of MFL Used in Thermal Diffusivity Measurements

Analysis	Roasted MFL	Leached MFL	W.S.MFL A[a]	W.S.MFL B[b]	W.S.MFL C[c]	Plant 6E MFL[d]
MgO, %	2.1	0.92	2.4	2.5	2.4	3.3
Total Uranium, %	2.0	0.17	2.1	2.1	2.0	2.0
Elemental Uranium, %	0.31	0.03	1.3	1.2	1.2	1.3
Elemental Magnesium, %	0.01	0.004	0.07	0.05	0.08	0.14
Hydrogen, ppm (present as H_2O or HF)	8.6	19.	44.	47.	48.	77.
Sieve Analysis						
% +20	0.1	0.4	0.2	0.4	0.3	0.2
-20 +40	0.7	1.0	1.4	2.0	2.1	1.3
-40 +60	4.6	1.7	6.9	6.8	5.3	5.5
-60 +100	12.4	4.5	13.0	12.7	11.1	9.5
-100 +200	21.8	20.8	26.9	27.0	30.0	21.4
-200 +325	13.7	18.2	14.3	15.2	17.0	13.8
-325	46.6	53.0	36.5	35.1	33.7	47.7

[a] Weldon Spring lot of 5/6/58 Hopper 23.

[b] Weldon Spring lot of 5/8/58 Hopper 1.

[c] Weldon Spring lot 664-11018-007 Batch 8.

[d] Plant 6E lot 163-01148-010 Drum 2 (Destrehan site).

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Appendix III

Table II

Chemical Analysis of MFL Samples after Diffusivity Measurements
Effect of Heating on Chemical Composition

Analysis	W.S.MFL A[a]	W.S.MFL B[b]	W.S.MFL C[c]	Plant 6E MFL[d]
Elemental Uranium, %	0.31	0.45	0.35	0.33
Elemental Magnesium, %	0.06	0.03	0.06	0.12
Sieve Analysis				
% +20	0.1	0.1	0.3	0.2
-20 +40	1.4	1.5	2.4	1.5
-40 +60	7.3	6.0	5.5	6.3
-60 +100	13.2	12.2	11.4	11.8
-100 +200	22.4	26.7	28.0	19.5
-200 +325	19.2	17.4	18.3	15.4
-325	36.1	36.1	33.9	45.2

[a] Weldon Spring lot of 5/6/58 Hopper 23.
[b] Weldon Spring lot of 5/8/58 Hopper 1.
[c] Weldon Spring lot 664-11018-007 Batch 8.
[d] Plant 6E lot 163-01148-010 Drum 2 (Destrehan site).

THE DISSOLUTION OF URANIUM METAL IN NITRIC ACID. PART III

by

W. J. Robertson
G. P. Lang

Summary

Work has begun on an experimental study of the mechanism of uranium dissolution in nitric acid. The results of some early experiments are presented.

Introduction

A brief speculative discussion of a possible mechanism for the dissolution of uranium metal in nitric acid has appeared in a previous report.[1] An experimental program to determine the rate law for the dissolution has been started.

Experimental and Results

The uranium metal sample now under study is a small rod, approximately 50 mm in length and 7 mm in diameter, which was machined from a "normal" β-treated dingot slug. The rod is affixed to the end of a stainless steel shaft by a threaded end on the shaft and a drilled and tapped hole in the uranium sample. A teflon gasket is put between the steel and the uranium to seal the uranium surface on top and prevent attack at the crevice. The steel shaft is chucked in a stirrer, and the sample rotated in nitric acid. The cylindrical vessel containing the nitric acid is held in a constant-temperature bath. Conditions arrived at for the experiments were a temperature of 50°C and a rotation rate of 1000 rpm. The uranium sample had a surface area of 11.5 sq cm and the solution volume used was 150 ml. These factors were chosen on the basis of convenience. The reaction was followed by withdrawing 2.0-ml samples for analysis. Two such samples were withdrawn at one time, one was analyzed for uranium and the other for nitrous acid. This data permits the calculation of the milligrams of uranium dissolved as a function of time, and gives directly the nitrous acid concentration as a function of time. A typical experiment is shown in Figure 1. The actual rate of dissolution of uranium is obtained by determining slopes from the plot of milligrams dissolved *versus* time. The functional dependence of the rate on the concentration of nitrous acid is shown in Figure 2. It will be necessary in future experiments to employ different nitric acid concentrations, different rates of sample rotation and different sample sizes to determine the effects of these variables.

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[1] Robertson, W. J., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, *MCW-1425* (January 2, 1959), p

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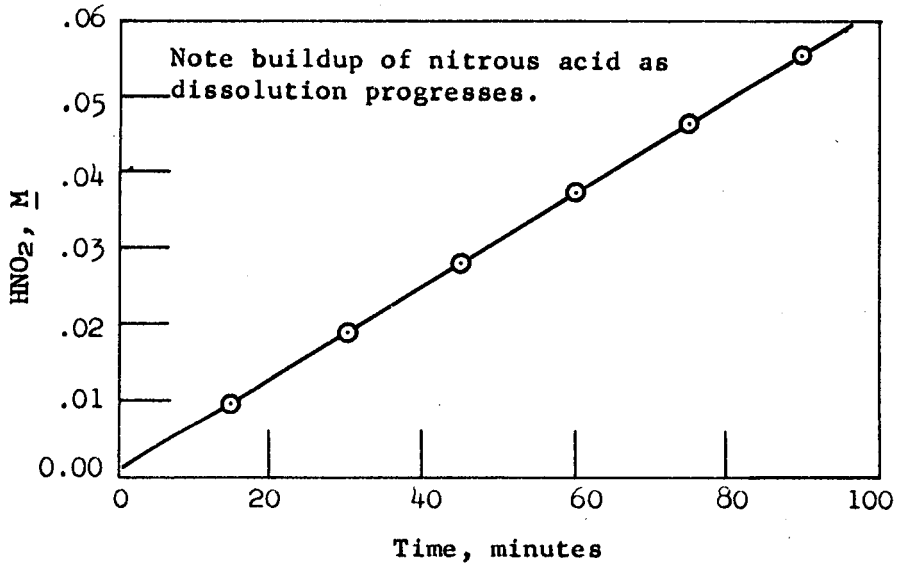
Figure 1

THE DISSOLUTION OF DINGOT URANIUM IN 13.1M HNO_3
AT 50°C; ROTATION RATE OF SAMPLE = 1000 RPM



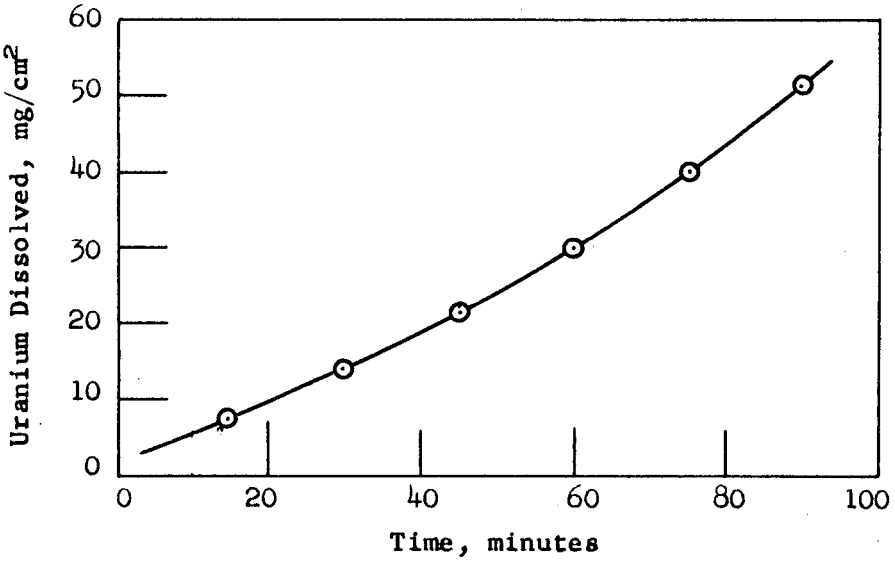
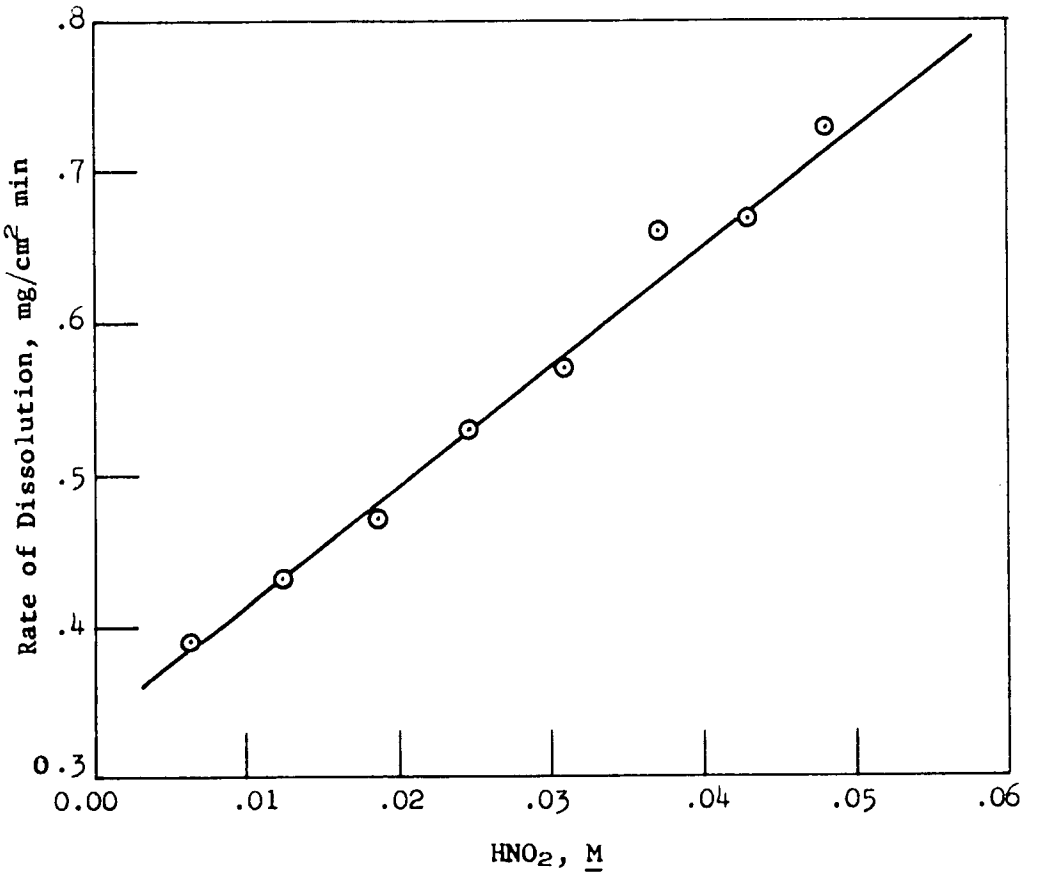


Figure 2

DEPENDENCE OF THE RATE OF DISSOLUTION OF DINGOT URANIUM IN 13.1M HNO_3 ON THE CONCENTRATION OF HNO_2



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Conclusions

Preliminary experiments show that the rate of dissolution of uranium in nitric acid depends on the nitrous acid concentration. Other variables, including the nitric acid concentration, sample rotation rate, sample size, and temperature, remain to be investigated.

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HAZARDS ASSOCIATED WITH THE OPERATION OF A METAL DISSOLVER

by

W. J. Robertson
G. P. Lang

Summary

The plant metal dissolver experienced difficulties on startup on several occasions as manifested by an extremely vigorous and potentially hazardous reaction. Attempts have been made to trace the cause of this behavior.

Introduction

The plant metal dissolver is a stainless steel tank equipped with a recycle system for the dissolver liquor, and with the necessary fume disposal system. When the dissolver is shut down the uranyl nitrate-nitric acid liquor is drained off and the metal remaining in the tank is covered with water. On startup the covering water is drained and nitric acid is introduced into the tank. The recycle is started as the tank is filling with acid. The concentration of refinery acid has been increased from 40 w/o to 45 w/o as a result of a change in plant operating procedure. Shortly after this change, a more violent reaction occurred in the dissolver on startup than was expected from past experience. The operator present heard a dull report and saw evidence of nitrogen dioxide evolution at a greater rate than that expected for the dissolver. The tank was immediately flooded to stop the reaction. The startup was repeated and no further incident occurred. This pattern was followed several times on subsequent startups, always after the dissolver was shut down for a weekend. Because of the potential hazard of uranium fires the use of the dissolver was suspended while an investigation was made.

Investigation and Results

The investigation disclosed that the increased violence of the reaction was due to the reaction of corrosion products from localized areas on the metal surface with the nitric acid. X-ray diffraction analysis of these corrosion products indicated uranium dioxide and finely divided uranium metal. The presence of finely divided metal has been noted in the corrosion product from the reaction of uranium with boiling water.[1] The presence of uranium in finely divided

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[1] Stewart, O. M., Berry, W. E., Miller, P. D., Vaughan, D. A., Schroeder, J. B., Fink, F. W., and Schwartz, C. M., *An Investigation of Uranium Corrosion in 100°C Water and 200°C Steam at Atmospheric Pressure*, Battelle Memorial Institute, *BMI-1271* (June 19, 1958)

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state accounts for the enhanced activity of the metal. The increase in the concentration of the plant nitric acid from 40 w/o to 45 w/o was sufficient to increase the violence of the reaction and actually cause ignition at times. It is probable that this condition existed before the acid concentration was changed and that the reaction was never violent enough for ignition to occur. Observations have shown the inconsistent nature of the corrosion process, that is, that the corrosion does not occur over every shutdown period. It was noted in laboratory experiments with corroded metal that ignition could occur with 50 w/o nitric acid. The ignition was actually a small explosion which threw pieces of glowing metal (or oxide) out of the corrosion spot.

In the effort to find out why the uranium corrodes in this manner, interest has centered on the water used to flood the tank when the dissolver is shut down. This water is treated with a commercial compound consisting of sodium dichromate and sodium triphosphate, and, in addition, the pH is adjusted with sulfuric acid. It has been found that a dilute solution of nitric acid prepared with this treated water will corrode uranium metal; however, dilute nitric acid prepared with distilled water will not. Furthermore, when a piece of metal that is undergoing corrosion is placed in pure dilute nitric acid, the corrosion stops. Attempts to determine which substance, or combination of substances, is responsible for the corrosive action of the treated water-nitric acid have not been successful as yet. This type of hazard in working with uranium metal dissolvers was not reported in a recent monograph on the subject of uranium fires,[2] and as far as is known was observed here for the first time.

The metal dissolver is now operating with a procedure that builds up the acid concentration slowly on startup. No difficulties have been experienced. The source of water for the tank flooding system is scheduled to be changed to untreated water.

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[2] Smith, R. B., *The Fire Properties of Metallic Uranium*, Technical Information Service, United States Atomic Energy Commission, *TID-8011* (April 12, 1956)

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X-RAY SPECTROGRAPHIC DETERMINATION OF URANIUM IN SOLUTION

by

W. C. Stoecker

I. Summary

X-ray fluorescence spectrographic methods have been developed for the determination of uranium in solution.

One method, for aqueous solutions of uranium, utilizes strontium as an internal standard in much the same way as the procedures previously reported for uranium in raffinate[1] and slag[2]. Direct determination can be made for uranium concentrations in the range of 0.1 to 1.5 g/l, and at 1 g/l or more a relative precision of ±1.3 per cent at a 95 per cent confidence level was found. Since solutions with high uranium concentrations can be suitably diluted, the method is believed to be applicable to virtually any aqueous solution with a uranium concentration above 0.1 g/l (at this point the relative precision at a 95 per cent confidence level is about ±7 per cent).

The method for aqueous solutions was modified to provide for the determination of uranium in the TBP-hexane mixture used as refinery solvent. Techniques were developed for introducing the strontium internal standard, and for handling volatile organic liquids in the X-ray machine. The uranium concentration range is 0.2 to 4.4 g/l, and the relative precision at a 95 per cent confidence level was found to be ±1.0 per cent at concentrations of 2 g/l or more. As in the case of aqueous solutions, there is no upper concentration limit.

While an interference study is yet to be made, it is expected that very few elements will interfere seriously, since this has been the result in other cases where strontium was used as an internal standard.

II. Introduction

Many workers have used the X-ray spectrograph to determine various elements in aqueous and other solutions. Several studies of uranium solutions have been made. Flikkema, Larsen, and Schablaske[3] determined uranium in nitric acid solutions of nuclear reactor fuels using only the

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[1] Stoecker, W. C., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, *MCW-1410* (January 2, 1958), p 107-14

[2] Stoecker, W. C., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, *MCW-1415* (July 1, 1958), p 155-158

[3] Flikkema, D. S., Larsen, R. P., and Schablaske, R. V., *The X-Ray Spectrometric Determination of Uranium in Solution*, Argonne National Laboratory, *ANL-5641* (November, 1956).

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uranium Lα peak count. They used an all-glass sample cell having a height of 1.0 cm and a window thickness of 0.007 cm designed for use in a Philips Electronics spectrograph similar to the instrument in operation here. Pish and Huffman[4] determined uranium and thorium in aqueous raffinate, and tributyl phosphate-"aliphatic diluent solvent" solutions. They used strontium as an internal standard for aqueous solutions and bromine (as bromobenzene) for the organic solutions. A glass sample cell with a mica window was assembled prior to each use and filled with a syringe. Their instrument was a General Electric XRD-3 fluorescence unit. Unfortunately, the experimental details of this important work were of limited use in the present investigation because of differences in the instruments. Another study of reactor fuel elements was made by Silverman, Houk, and Moudy.[5] They determined uranium in solutions resulting from perchloric acid dissolution of a uranium dioxide-iron mixture together with its stainless steel sheath. Strontium was used as an internal standard, and large amounts of iron, chromium, and nickel did not interfere.

The development of a way to handle liquids was the first problem to be met. No sample cell was available, and no reference was found which described a cell entirely suitable for the present instrument. Work on this problem resulted in different techniques for the two types of solutions.

A problem with the organic solutions was the introduction of strontium or other internal standard in a form miscible with the liquid.

Other features of the work followed established procedures.

III. Experimental

A. Apparatus

The Philips Electronics X-ray spectrograph, Type No. 52260, was used with a lithium fluoride analyzer crystal and a scintillation counter detector.

The aqueous solutions were analyzed in a Plexiglas sample cell of 7-ml capacity which had at one time been used for raffinate powders. The cell was filled level to the top with the aid of a dropper or stirring rod and then covered with a sheet of 0.001-inch Mylar cut to fit. The assembly was then clamped into the aluminum sample holder and inserted into the spectrograph. This arrangement was sufficiently leakproof for aqueous solutions. A new Mylar cover was used each time the cell was filled.

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[4] Pish, G., and Huffman, A. A., "Quantitative Determination of Thorium and Uranium in Solutions by Fluorescent X-Ray Spectrometry," *Anal. Chem.* 27, 1875-8 (1955)

[5] Silverman, L., Houk, W., and Moudy, L., " Determination of Uranium Dioxide in Stainless Steels by the X-Ray Fluorescence Solution Method," *Proceedings, 6th Annual Conference on Industrial Application of X-Ray Analysis*, Denver Research Institute, (August, 1957), p 271-281

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The cell for organic liquids consisted of a rectangular block of Teflon, 46 × 35 × 11 mm, into which a rectangular cavity was machined, 23 × 20 × 7 mm deep. The cavity was so located as to be under the most intensely irradiated area of the aluminum sample holder window. This area is approximately the rear half of the rectangular window. Two holes (approximately 4-mm diameter) were drilled into the cavity from the front edge of the block sloping upward from the bottom of the cavity at a small angle from the horizontal. The cell top consisted of a strip of 1-inch Scotch tape placed across the cavity and trimmed at the sides of the cell block with scissors. This was replaced with each use. The cell was filled through either access hole by use of a 10-ml Luer-type syringe. The holes were stoppered with small Teflon plugs. The cell was cleaned with acetone after removing and discarding the Scotch tape strip. The adhesive on the Scotch tape was attacked slowly by the solvent, but ample time was available for making readings before the cell started to leak. The tape and layer of adhesive resulted in a loss of only about one per cent of the net uranium peak intensity.

B. Reagents

The following standard solutions are used:

(1) Strontium Stock Solution (Sr concn. = 20 mg/ml). Prepare from reagent grade strontium carbonate by dissolution in sufficient nitric acid to give an excess of 3 ml of nitric acid per liter.

(2) Strontium Internal Standard Solution, Aqueous (Sr concn. = 3 mg/ml). Prepare by dilution of (1) with water.

(3) Strontium Internal Standard Solution in Methyl Cellosolve (Sr concn. = 3 mg/ml). Prepare by dilution of (1) with methyl Cellosolve.

(4) Uranium Stock Solution, Aqueous (U concn. = 20 mg/ml). Prepare by dissolution of standard black oxide in sufficient nitric acid to give an excess of 3 ml of nitric acid per liter.

(5) Uranium Stock Solution in Methyl Cellosolve (U concn. = 20 mg/ml). Dissolve 5.896 g of U_3O_8 in 4 ml of water and 3.7 ml of nitric acid (a 1-ml excess). Add 20 ml of water and dilute of 250 ml with methyl Cellosolve.

(6) Uranium Standard Solutions. Prepare various dilutions of (4) in water and (5) in methyl Cellosolve as required for calibration. Use good volumetric technique throughout.

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C. Analytical Procedures

1. Procedure for Aqueous Solutions

For direct determination in aqueous solutions, the uranium concentration should not be more than 1.5 g/l.

To a 100-ml glass-stoppered cylinder, pipette 5 ml of strontium standard solution (3 mg/ml), and then pipette 50 ml of the sample. Mix, and transfer to the sample cell. Place into the spectrograph and then count by means of the following strategy:

	2θ in Degrees	Number of Determinations	Number of Counts per Determination
Background	24.40	2	64,000
Sr Kα	25.13	2	256,000
U Lα	26.13	2	Adjust to obtain a count of 40-60 seconds
Background	27.00	2	64,000

The total counting time is about six minutes. Compute the uranium concentration as in the analysis of raffinate,[5] with the aid of a calibration curve or equation. In the event that a solution to be analyzed contains strontium, run a "residual strontium determination" by repeating the foregoing with 5 ml of water substituted for the strontium solution. Make the correction as for a sample of raffinate.

2. Calibration for Aqueous Solutions

Into 100-ml glass-stoppered cylinders pipette 5-ml portions of strontium standard solution. Add by pipette uranium standard solutions suitably diluted from the 20 mg/ml stock solution, to obtain 0, 15, 30, 45, 60, and 75 mg, respectively, of uranium. Add water to obtain a total volume of 55 ml in each cylinder, and mix. Count each solution, plot the results, and compute an equation.

3. Procedure for TBP-Hexane Solutions

To a 50-ml glass-stoppered cylinder pipette 5 ml of strontium standard solution in ethylene glycol monomethyl ether (hereinafter called methyl Cellosolve) having a strontium concentration of 3 mg/ml. Add 5 ml of methyl Cellosolve and 10 ml of acetone. Into the cylinder pipette 25 ml of TBP-hexane solution having a uranium concentration of not more than 4.4 g/l, dilute to the 50-ml mark with acetone, and

[5] Stoecker, *MCW-1410*

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mix. Fill the sample cell and obtain the X-ray counts as for aqueous solutions.

4. Calibration for TBP-Hexane Solutions

To 50-ml glass-stoppered cylinders add 5 ml of strontium standard solution, as above, and various volumes of uranium standard solutions in methyl Cellosolve containing up to 100 mg of uranium. The uranium standard solutions in methyl Cellosolve are dilutions of the stock uranium standard solution having a concentration of 20 g/l in methyl Cellosolve. Do not use pipettes smaller than 2 ml and do not add more than 5 ml of uranium solution or solutions. Add methyl Cellosolve so that the total of uranium solution and methyl Cellosolve is 5 ml. The total volume of methyl Cellosolve is therefore 10 ml. Add 10 ml of acetone and 25 ml of uranium-free TBP-hexane mixture containing 30 per cent TBP on a volume/volume per cent basis. Dilute to the 50-ml mark with acetone and proceed as in the case of an unknown. Plot, and compute an equation.

IV. Results and Discussion

A. Aqueous Solutions

1. Calibration

A series of standards was prepared by mixing accurately measured aliquots of uranium and strontium solutions to cover the uranium concentration range of 0 to 1.5 g/l. The procedure given in section III-B-2 was followed in the main. Although volumetric flasks were used, glass-stoppered cylinders are adequate since the uranium and strontium solutions are both pipetted. The results are shown in Figure 1, in which mg of uranium in 100 ml of solution is plotted against U/Sr count ratio. Each standard contained 30 mg of strontium per 100 ml of solution. (In the procedures given in sections III-C-1 and -2, the total volume of dilution is 110 ml for 30 mg strontium.) The slope of the curve is the product of two terms, the strontium concentration in mg per 100 ml, and an experimentally determined factor k, which depends on the relative net intensities of the uranium and strontium peaks. The factor k may be defined as mg uranium per mg strontium referred to unit U/Sr count ratio. In this case, k is observed to be 3.03 and the intercept on the concentration axis is negligible. Recent values of k were 3.07 for kaolin, 3.04 for raffinate, and 3.05 for slag (evaporation method for kaolin and raffinate). The uranium in 50 ml of an unknown solution is then given by

$$\text{Mg U} = 3.03 \times .15 \times \text{count ratio.}$$

Figure 2 shows how uranium and strontium count rates individually vary with increasing uranium concentration. Both plots are observed to be linear in the range studied.

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Figure 1

CALIBRATION CURVE FOR URANIUM IN AQUEOUS SOLUTIONS[a]

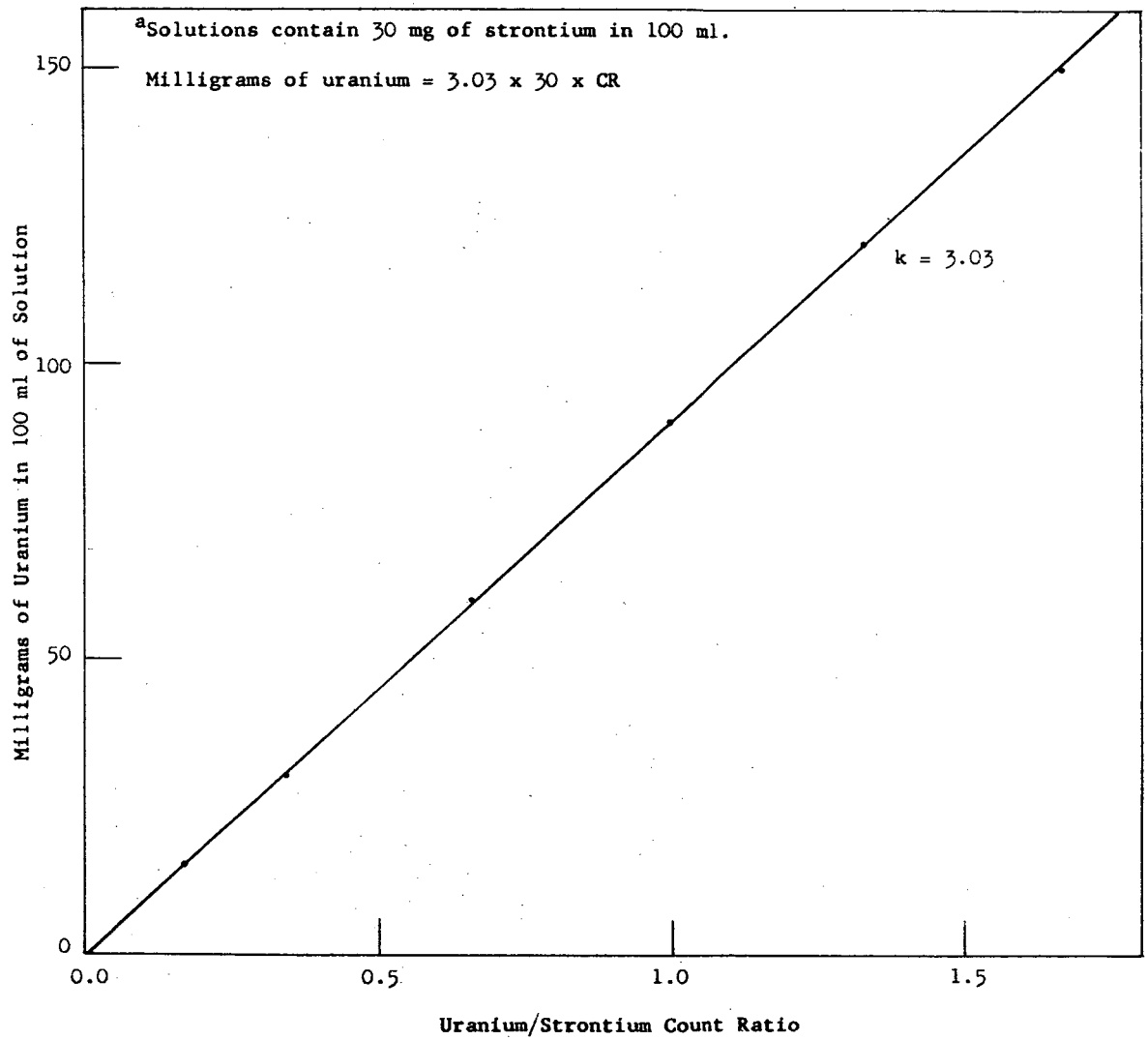
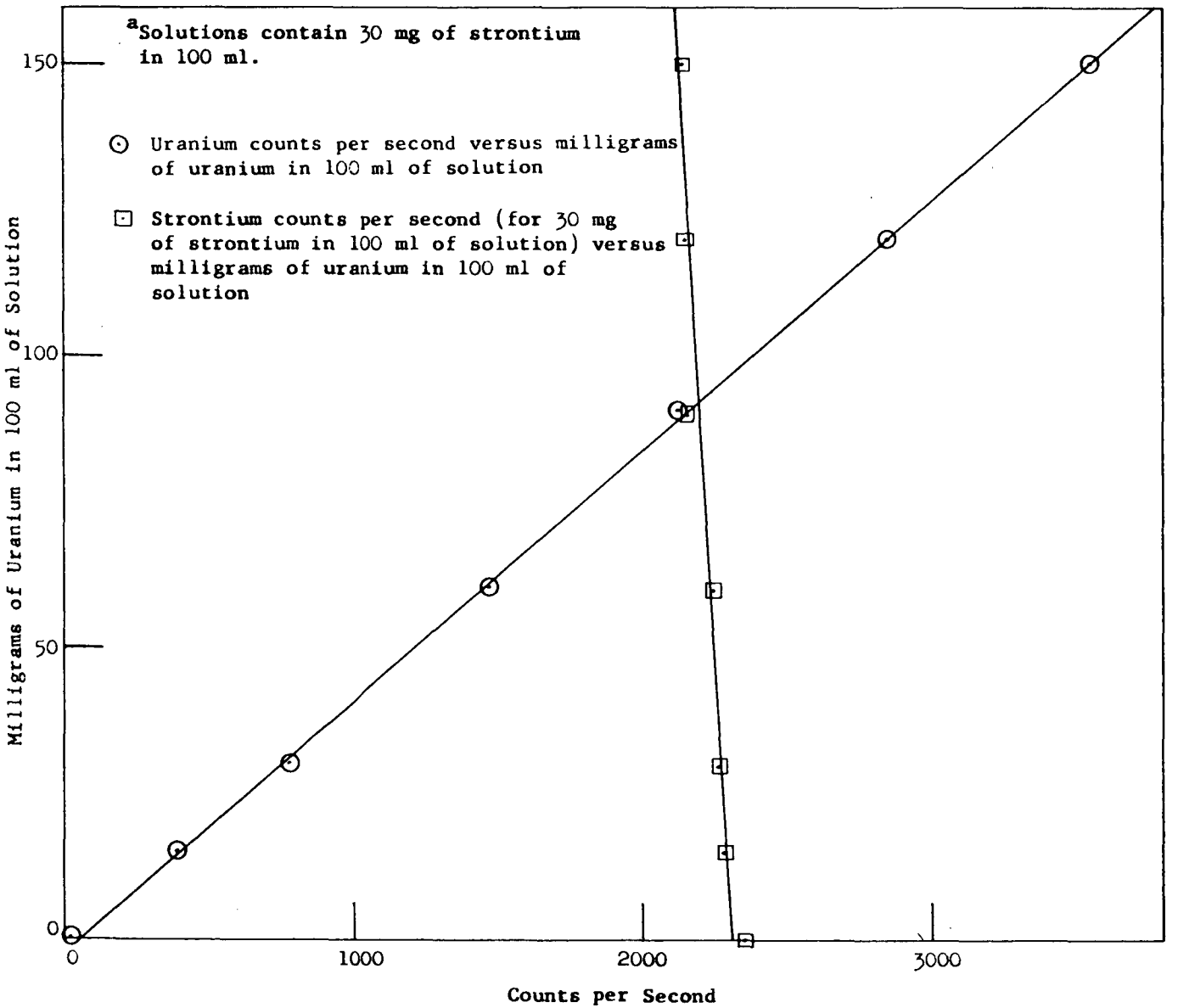


Figure 2

X-RAY COUNTS ON URANIUM AND STRONTIUM IN AQUEOUS SOLUTIONS[a]



2. Comparison of Methods

Two X-ray methods are now at hand for determining uranium in aqueous solution. A method has been previously described for determining total uranium in raffinate slurries[7] by evaporation with kaolin and a measured volume of strontium standard solution. This is obviously applicable in the case where all of the uranium is "soluble uranium." The usual way of determining uranium in aqueous solutions is colorimetrically by the alkaline peroxide method. The method is capable of good precision, particularly when the extraction steps are not required as is the case with NOK liquors and some high-uranium solutions. A series of 18 solutions of uranium originating in the refinery and pilot plant were analyzed by both X-ray methods. All except the soluble raffinates were checked by the colorimetric method as well. Recent calibration curves were prepared for the older X-ray method and the colorimetric method. All solutions with uranium concentrations of more than 1 g/l were diluted. The results are shown in Table I. Although the results are in reasonable agreement, small biases are indicated. For example, a 1.9 per cent relative bias exists between the two X-ray methods as computed from the 13 high-uranium solutions.

[7] Stoecker, W. C., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, *MCW-1407*, (October 1, 1957), p 101-105

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Table I

Analysis of Uranium in Aqueous Solutions

Solution	Identification (Lot, etc.)	Uranium g/l X-Ray, Solution	X-Ray, Evaporation	Colorimetric
Raffinate slurry, filtered	496	0.20	0.21	--
Raffinate slurry, filtered	July 20-27, 58	0.14	0.14	--
Raffinate slurry, filtered	Oct 6-12, 58	0.09[a]	0.11	--
UNH condensate	106	0.14	0.14	0.15
Sump tank liquor	11/19/58	< 0.01	< 0.01	< 0.01
NOK evaporator feed	716	105.	103.	107.
NOK evaporator feed	722	107.	104.	111.
NOK evaporator feed	724	114.	113.	117.
NOK evaporator feed	732	101.	99.	103.
NOK evaporator feed	733	111.	106.	114.
Pilot plant sump liquor, T-41	1279	7.5	7.3	7.6
Pilot plant sump liquor, T-41	1352	18.7	18.2	19.2
Pilot plant sump liquor, T-41	1733	26.8	26.8	27.4
Pilot plant fume scrubber	0100	89.	89.	90.
Pilot plant fume scrubber	1000	81.	82.	82.
Pilot plant fume scrubber	1330	19.8	19.7	19.1
Pilot plant fume scrubber	1630	19.3	18.5	19.3
UNH liquor	11/17/58	290.	283.	288.

[a] Recheck: 0.11.

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3. Precision

Precision was determined on a synthetic solution containing 0.900 g of uranium and 0.300 g of strontium per liter. This was the solution used for obtaining the 90-mg point in Figure 1. Twenty replicate determinations were made, and precision was computed on the basis of the constancy of the U/Sr count ratio. The observed precision was ±1.3 per cent relative at a 95 per cent confidence level.

An inherent limitation on precision lies in the nature of the X-ray detection process. Equations based on quantum counting statistics are given by Parrish[8] and others, and from these it is possible to calculate the approximate theoretical precision limit for various levels of uranium using actual count data. Calculations were made for both X-ray methods. In the evaporation method the calculation is based on the use of a 50-ml aliquot with 10 g of kaolin and 10 mg of strontium. Counting times are 6 to 8 minutes. Since the calculations are based on actual count data, not idealized, the result depends somewhat on minor experimental variations (exact counting time, sample position, *etc.*). The results, which are shown in Table II, are therefore reported to the number of places which are considered significant. Despite a poorer precision at the lower concentrations, the solution method should often be an advantage since sample preparation time is very much less. It is observed that the actual precision obtained for the 0.9-g-per-liter solution is very near the theoretical limit.

Table II

Theoretical Precision for the Analysis of Uranium in Aqueous Solutions

Uranium g/l	Relative Precision at the 95 Per Cent Confidence Level per cent	
	Solution Method	Evaporation Method
1.5	0.9	--
0.9	1.0	0.7
0.5	1.6	0.8
0.2	2.7	1.3
0.1	6.5	1.8

[8] Parrish, W., "X-Ray Intensity Measurements with Counter Tubes," *Philips Technical Review* 17 (7-8), 206-21, (1956)

B. TBP-Hexane Solutions

1. Techniques for Organic Solutions

The development of a cell for handling organic liquids presented some difficulty. A Teflon cell was made which was very similar to the Plexiglas cell for aqueous solutions. The assembled cell was found to leak badly when placed in the sample holder, however. Attempts were made to construct an all-glass cell similar to that described by Flikkema, *et al.*[9] However, in order to prevent excessive loss of X-ray intensity the cell top had to be 0.07 mm thick or less. Sealing such a top to the cell body proved impossible by the techniques available. The cell finally adopted permits handling the liquid without mess, and does not normally leak. There is some variation in convexity of the surface, however, and air bubbles often appear. It was found that variations due to such causes were compensated by the internal standard.

Some models of the X-ray spectrograph use "inverted optics," an arrangement in which the sample is located above the X-ray tube window. In instruments of this type the handling of liquid samples is somewhat simpler.

A further difficulty was the introduction of the strontium internal standard in a form miscible with the solvent. Strontium nitrate is insoluble in most organic liquids. Solutions in methyl Cellosolve and *n* propyl alcohol were easily prepared, but under most conditions strontium was precipitated when the solutions were added to refinery solvent, even though the pure liquids were miscible. Other internal standards were considered, but strontium has several important advantages. A compatible mixture was found, but it was necessary to use a 1:1 dilution of refinery solvent with the additives. This, of course, reduces the sensitivity of the test.

2. Calibration

The procedure given under section III-B-4 was used in the preparation of standards for the organic solutions. Figure 3 is the calibration curve resulting from X-ray counts on solutions containing up to 220 mg of uranium per 100 ml of test solution. As in the case of aqueous solutions, each solution contained 30 mg of strontium per 100 ml. The slope and value of k (3.03) for most of the curve are observed to be identical with those found for aqueous solutions. However, in this case, the intercept is not negligible. A negative intercept of 2.4 mg of uranium is indicated. The lower part of the curve (below 40 mg uranium) was investigated in some detail since it has a somewhat smaller slope and a numerically smaller intercept than the upper part. Equations for computing uranium in unknowns are shown on the figure.

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[9] Flikkema, *et al.*, *ANL-5641*

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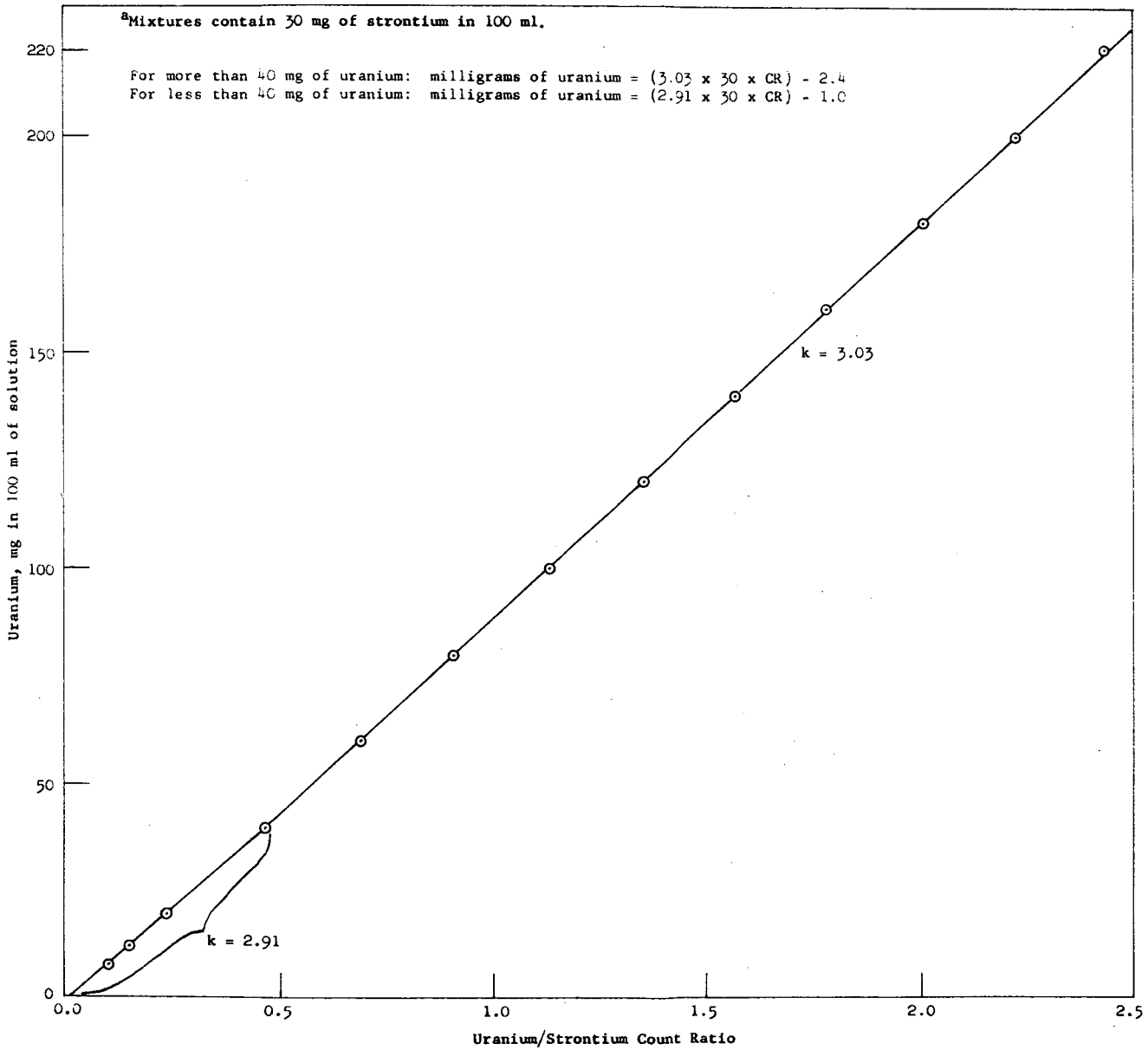
Figure 3

CALIBRATION CURVE FOR URANIUM IN TBP-HEXANE MIXTURES[a]



3. Precision

Precision was determined as for aqueous solutions, by making 20 replicate determinations on one of the solutions used for calibration. The 20 determinations included four separate preparations of a solution containing 100 mg of uranium and 30 mg of strontium in 100 ml of solution. Since one-half of the test solution is TBP-hexane mixture, the precision data corresponds to a refinery solvent solution with a uranium concentration of 2 g/l. As calculated from the constancy of the U/Sr ratio the precision was ±0.97 per cent relative at a 95 per cent confidence level, or about the same as for the equivalent aqueous solution. Theoretical precisions should be about the same as for equivalent aqueous solutions since net count rates and peak-to-background ratios are comparable (or slightly better).

By use of the same set of data a precision was calculated for the net rate (peak intensity) of the uranium peak. The precision was found to be ±5.7 per cent relative at the 95 per cent confidence level. This is the precision which would be expected without the use of an internal standard.

Another precision study was made on samples of "stripped solvent" originating in the refinery. The samples were obtained from the control laboratory after the control analysis had been completed. Duplicate determinations were made on 15 samples and the precision was computed based on the observed agreement between pairs. At the 95 per cent confidence level the relative precision was found to be ±1.9 per cent for the 15 samples, which had uranium concentrations from 0.69 to 1.08 g/l and averaged 0.81 g/l. This result agrees with theory since the precision of an equivalent aqueous solution (with a uranium concentration of 0.4 g/l) is about 1.9 per cent according to Table II. In most cases, good agreement was observed between X-ray and control laboratory results.

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Glossary of Specialized Terms

AOI	- ammonium oxalate insoluble (oxides of uranium)
billet	- a bar of forged dingot uranium suitable for subsequent rolling
black oxide	- U_3O_8
brown oxide	- UO_2
derby	- the uranium metal product of the nominal 300, 100 and 50-lb. reduction bombs which is subsequently recast.
dingot	- (direct ingot) the uranium metal product of 1400 and 3300-lb. reduction bombs. This metal not recast.
DMFL	- dingot magnesium fluoride liner
E_A^0	- distribution coefficient (organic to aqueous)
ESU	- easily soluble uranium
E-Z Hollow slug	- a hollow fuel element with approximately ¼-inch wall thickness, 8-inch nominal length, and nominal ODs of 2 and 3 inches.
green salt	- UF_4 containing small amounts of UO_2F_2 and uranium oxides
I & E slug	- (hollow) internally and externally cooled slug
ingot	- recast uranium metal
MFL	- magnesium fluoride liner
NOK	- a uranyl nitrate solution obtained by stripping uranyl nitrate from tributyl phosphate-hexane solvent with water
OK-liquor	- the uranyl nitrate liquor of highest purity used as a feed to the denitration pots
orange oxide	- UO_3
P - D	- pumper-decanter

(continued on next page)

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Glossary continued

preignition time - time interval between placing bomb in hot furnace and initiation of reduction reaction

raffinate - the aqueous residue remaining after tributyl phosphate extraction of a uranium concentrate previously digested with HNO_3

RMF - reject magnesium fluoride

rod - cylindrical length of uranium produced by rolling or extruding uranium billets and ingots

slag - magnesium fluoride formed in the thermite bomb reaction; it contains small quantities of uranium and magnesium

6-4 UF_4 - UF_4 produced by reduction of UF_6

slug - rods of uranium machined to specific diameter and lengths. Slugs, when canned, are used as fuel elements.

soda-salt - sodium diuranate; usually applied to raw materials of that composition

UNH - uranyl nitrate hexahydrate