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65-10,407
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SEMI-MONTHLY ABSTRACTS

Section C-II

File Chemistry and General Chemistry

Period From January 1 to 15, 1947

INV.
9-47

HIGH TEMPERATURE FILE PROGRAM

(C. A. Boyd)

Reaction Between Steam and BeO (M. G. Berkman)

Experiments are being continued in the investigation of the reaction between steam and beryllia at reduced water vapor pressure. The following experiments were carried out at 1400°C. The values are calculated for 2½ - hour runs.

Run	Temp. of BeO Pellet (°C)	Rate of Steam Condensation (ml/min)	Water Vapor Pressure (mm Hg)	Weight of BeO Lost (%)
71	1400	0.04	15	0.25
72	1400	1.4	90	0.64
73*	1400	3.1	90	0.70
74*	1400	3.3	200	0.79

* Recorded values are extrapolated from 2-hour runs.

Graphite Impregnation (M. A. Kanter, R. W. Phillips, A. L. King)

Studies on the effect of pretreatment of the graphite samples were made. In all previous work the samples were boiled in water for 30 minutes to remove loose graphite particles and then fired in a helium atmosphere prior to impregnation. However, in these experiments the samples were boiled in concentrated nitric acid and fired in helium at 800°C. An increase in the volume of water absorbed (measured as in ANL-OCS-97) was noted, larger than would correspond to the graphite lost, presumably by oxidation. The following table shows the increase in penetration by water with this treatment. The data are for three fuel rod sections of AGR graphite.

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	Apparent Density *		
Initial	1.96	1.97	1.97
After one nitric acid treatment	2.12	2.14	2.12
After two nitric acid treatments	2.15	2.13	2.16
After three nitric acid treatments	2.15	2.14	2.17

* Density as computed from the weight of the sample in air and the weight immersed in water.

When this work was repeated half the samples were boiled in distilled water as a control. Here the controls also showed increasing water absorption but not quite as much as nitric acid treated samples. Upon impregnation with aqueous solutions of uranyl nitrate (45 gms UNH/100 cc of solution), these treated samples showed gains in weight after firing averaging 4.00% as compared to 3.25% for samples treated as in previous experiments.

Samples treated in this way show no measurable improvement in reproducibility of results (see ANL-OCS-97) or in distribution of U_3O_8 in the final rod. Calculation shows that the volume of the impregnating solution corresponding to weight of U_3O_8 in the final fuel tube was from 45 - 60% of the volume of water the same sample absorbed prior to impregnation.

Dimension changes of +0.25 percent were noted as a result of the first nitric acid treatment with no change on subsequent treatments. Then impregnation resulted in a further increase of 0.25 percent in linear dimensions. Boiling in water and subsequent firing gave no dimensional change.

* * * * *

An evacuation technique for impregnating with aqueous solutions of uranyl nitrate was tried. Earlier work (ANL-OCS-53) with ethereal solutions had shown no marked improvement of vacuum impregnation over the refluxing technique.

The graphite samples were placed in a vessel which was then evacuated. The aqueous solution of uranyl nitrate was then admitted slowly. Data is presented below for samples impregnated by the vacuum technique and by refluxing. Pretreatment and firing of the samples were identical in both cases.

Percent Weight Gain	
Evacuated Samples	Refluxed Samples
3.13	2.50
2.17	2.61
3.10	2.74

AGR graphite is now being investigated.

Measurement of the absorption by AGR graphite fuel tube sections of boiling water and boiling uranyl nitrate showed that, after fifteen minutes, the absorption rate had fallen essentially to zero. The refluxing time of thirty minutes now used in impregnation should not introduce errors.

The Diffusion of Fission Products (J. E. Wilson)

Three runs on diffusion of 5 da. Xenon from 1 cc graphite cubes have been made at 1000°C. The cubes, impregnated with about 5% UO₂ (lean-riched), were furnished by C. A. Boyd. Two of the cubes were of density 1.55 g/cc and the third was 1.68 g/cc. The two runs on low density graphite showed 2.7% and 2.5% Xenon diffused in 3 hours, averaging 2.5%. The high density sample lost 1.9% in the same length of time. The corresponding diffusion constants were calculated to be 6×10^{-8} and 8×10^{-8} cm²/min. for low and high density, respectively. This would indicate roughly 2 or 3 times as much activity in the coolant stream when graphite rods are used as when beryllia is used.

The Effect of Neutron Irradiation on the Thermal Resistivity of BeO-UO₂ Samples (J. L. Weeks)

The change in thermal resistivity of the BeO-UO₂ prisms subjected to 131 days irradiation at HSW has been determined using a new "heat wave" apparatus. This apparatus is essentially similar to the one used in previous determinations. However, instead of placing a wax drop on top of the prism and observing the length of time required to melt the drop, the apparatus has been so designed that the moment the prism drops into the mercury pool a thermocouple makes contact with the top of the prism, and the length of time required to reach a given temperature is observed and compared with the time required for the top of an unirradiated sample to reach the same temperature. The temperature rise is plotted against time for both exposed and standard prisms and values for comparison are taken only from linear portions of the curves. By dividing the value for the exposed sample by the value for the unexposed standard the ratio of the thermal resistivity of irradiated and unirradiated BeO-UO₂ is obtained.

A sufficient time (c. 3 hours) is allowed between runs for the prisms to return to room temperature. Using a Capacitrol with an external resistance in parallel with the apparatus, a small current is always passing into the heating coil, thus reducing temperature fluctuations of the mercury heating bath to $100^{\circ} \pm 2^{\circ}\text{C}$. It is, however, possible to introduce an error of perhaps 5% in timing since no automatic mechanism is employed.

Data is presented in Tables 1 and 2 for prisms of the third (131 day) irradiation. It is believed that better precision is attainable by this thermocouple method than by the wax drop method. These data indicate a slightly greater increase in thermal resistivity for prisms containing 2% UO₂ as compared with prisms containing 10% UO₂. There also seems to be a somewhat greater increase for "high" density prisms as compared with "low" density prisms. The greatest increase in thermal resistivity was found for the 2% UO₂ high density samples, the ratio of the thermal resistivities of the exposed

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TABLE I
Effect of 131 Days Irradiation at HEW on Thermal Resistivity of
BeO-UO₂ Prisms
(Thermocouple Method)

Sample Number and Material	Time Required to Reach 40°C (sec)*	Resistivity Ratio $\frac{R \text{ irradiated}}{R \text{ unirradiated}}$	Time Required to Reach 46°C (sec)*	Resistivity Ratio $\frac{R \text{ irradiated}}{R \text{ unirradiated}}$	Remarks
Low Density; 10% UO ₂					
C-8 Unirradiated Standard	9.9 11.2 <u>9.6</u> Avg. 10.2		15.0 17.6 <u>13.7</u> Avg. 15.4		
C-3 Irradiated	58.5 57.2 <u>56.7</u> Avg. 57.5	5.64	88.2 84.6 <u>88.7</u> Avg. 87.2	5.66	
C-4 Irradiated	56.6 58.4 <u>57.0</u> Avg. 57.3	5.62	87.7 89.3 <u>87.6</u> Avg. 88.2	5.72	Avg. Ratio = 5.66
Low Density; 2% UO ₂					
C-23 Unirradiated Standard	8.1 8.5 7.0		11.7 11.0		
C-24 Unirradiated Standard	8.6 8.1 8.1 Avg. 7.9		12.7 11.3 12.1 Avg. 11.8		
C-19 Irradiated	46.2 47.0 <u>47.1</u> Avg. 46.8	5.95	72.0 74.2 <u>72.0</u> Avg. 72.7	6.15	
C-20 Irradiated	46.8 45.8 <u>45.8</u> Avg. 44.8	5.68	74.5 67.5 <u>67.8</u> Avg. 69.9	5.92	Avg. Ratio = 5.92

* Temperature of mercury heating bath = 100 ± 2°C.
Temperature of samples at start = 25-26°C.

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TABLE II
Effect of 131 Days Irradiation at HEW on Thermal Resistivity of
BeO-UO₂ Prisms
(Thermocouple Method)

Sample Number and Material	Time Re-quired to Reach 40°C (sec)*	Resistivity Ratio $\frac{R \text{ irradi.}}{R \text{ unirrad.}}$	Time Re-quired to Reach 46°C (sec)*	Resistivity Ratio $\frac{R \text{ irradi.}}{R \text{ unirrad.}}$	Remarks
High Density; 10% UO ₂					
C-15 Unirradiated Standard	8.2 8.2 <u>7.9</u> Avg. 8.1		11.3 12.2 <u>11.1</u> Avg. 11.5		
C-13 Irradiated	50.1 49.0 <u>50.6</u> Avg. 49.9	6.16	74.6 69.9 <u>71.9</u> Avg. 70.9	6.16	
C-14 Irradiated	52.7 48.0 <u>51.6</u> Avg. 50.1	6.18	67.8 73.0 <u>70.4</u> Avg. 70.4	6.12	Avg. Ratio = 6.16
High Density; 2% UO ₂					
C-31 Unirradiated Standard	7.9 7.9 <u>6.8</u> Avg. 7.5		10.3 10.9 <u>9.3</u> Avg. 10.2		
C-29 Irradiated	50.5 49.8 <u>47.4</u> Avg. 49.2	6.56	73.6 70.5 <u>64.0</u> Avg. 69.4	6.60	
C-30 Irradiated	49.3 47.2 <u>45.3</u> Avg. 47.3	6.31	69.6 68.3 <u>63.6</u> Avg. 67.2	6.59	Avg. Ratio = 6.57

* Temperature of mercury heating bath = 100° ± 2°C.
Temperature of sample at start = 25-26°C.

and unexposed samples being 6.57. Thus the irradiated samples have a thermal conductivity which is only 15% of the original.

Heat of Solution of Beryllia (S. R. Gaarder)

A possible method of determining the stored energy of irradiated beryllia lies in a comparison of its heat of solution with that of unirradiated beryllia. In order to establish the magnitude of the temperature change which accompanies the dissolution of beryllia, these crude scouting experiments have been carried out wherein powdered beryllia (Brush high-fired 200 mesh) was dissolved in HF at 21°C and 62°C, and in $H_4P_2O_7$ at 260°C. In all cases a rise in temperature was noted. The pertinent data are summarized in Table I. As mentioned the experimental method was crude - in those experiments above room temperature a sand bath was used with variations in bath temperature being followed as well as variations in solution temperature. The room temperature experiment was carried out using glass wool as an insulating material around the reaction vessel.

TABLE I. Dissolution of 200 mesh Brush High Fired Beryllia
(0.5 g BeO powder in 10-15 ml solvent)

Solvent & Temp.	Maximum Temp. Rise (°C)	Minutes to Reach Maximum	Amount BeO Dissolved in 30 min.	Remarks
HF (21°C)	7.5	11.5	< 1/2	manual agitation
HF (62°C)	10	0.5	> 3/4	manual agitation
$H_4P_2O_7$ (260°C)	21	2.0	> 3/4	no agitation

ANALYTICAL CHEMISTRY

(F. S. Tomkins)

Spectrographic Laboratory (F. Tomkins, J. K. Brody, I. S. Bubes, J. Paris, M. Walsh, J. Goleb)

A. Service Analysis: The following analyses have been completed since January 1, 1947.

1. Thirty-three samples of BeO were analyzed quantitatively for B and other impurities.
2. Two samples of BeSO₄ were analyzed quantitatively for B and other impurities.
3. The Be in 14 samples was quantitatively determined for health physics.
4. Thirteen qualitative analyses were carried out on a variety of materials.

B. Research:

1. Due to a respite from the Be metal samples, it has been possible to devote some time to the problem of densitometric procedures for the analyses of BeO. Working curves which are far superior to preceding ones have been obtained. The improvement has resulted from the use of a band line near the B lines as an internal standard. A small correction was also applied to compensate for the intensity of a cyanogen band which is coincident with the strong B line at 2497.7. The lower limit for B will be .2 ppm. New standard solutions were made and will be used to impregnate pure BeO to provide standards. In order to eliminate entirely any possibility of B contamination in the standards, these were made up in quartz laboratory ware using acids distilled in quartz.
2. For the copper spark restandardization 89 standard plates have been made. Some 63 elements have been restandardized over a wavelength range of 2000 - 6000 Å.
3. In the densitometric copper spark method for the accurate determination of small amounts of Be, the question arose as to the effect of acid concentration on the ratio of Be/Mo line intensities. Previous copper spark investigators state that line ratios remain constant if the acid concentration is around 1% HCl. An experiment was conducted to investigate this further and it was found that the ratio of Be/Mo lines in a 0.05% HCl solution dropped sharply from that in a neutral solution to 3/4 the value in the neutral solution. The ratio continued dropping to a low of 1/3 the value at 0.5% HCl, and then rose to slightly more than 1/2 the value at 1.5%, and remained fairly constant from 1.5% through 3% HCl. Standards having constant amounts of Be and Mo, but containing varying acid concentrations, were used. Thus the variation of line intensity ratios with acid concentration makes accurate detection of Be possible only with a closely controlled acid value.

Curves drawn from data on neutral solutions of Be, using Mo as the internal standard, showed precision of better than 10%. However, since Mo slowly precipitates in a hydrochloric acid solution, a different internal standard must be chosen for determinations in acid solutions.

Wet Chemical Analysis (R. W. Bane, B. Holt, R. Hospelhorn, K. Jensen, R. Telford)**A. Services:**

1. Two zirconium silicate samples were analyzed for zirconium and silicon.
2. One solution of a thorium boron compound was analyzed for thorium and boron.
3. Two waste solutions were analyzed for their uranium content.
4. Two NaK alloys were analyzed for their sodium and potassium content.
5. Two beryllium uranium alloys were analyzed for uranium.
6. Three water samples were analyzed for chloride and chlorine.

B. Research:

1. The determination of micro amounts of fluorine in beryllium is still unsuccessful. Five runs were made distilling 600 ml instead of the usual 200 ml in the hope that a longer distillation would yield better fluorine recoveries. However, the results were still inconsistent and recoveries poor. Work on this problem has been discontinued for the present.
2. Three runs were made with the beryllium chloride volatilization apparatus for the determination of beryllium oxide in beryllium metal. Inconsistent values were obtained and all results were high compared with those obtained on the same material by the Brush Beryllium Corporation.
3. An all-glass still has been fabricated for the analysis of micro amounts of chloride. The chloride standard solution was standardized by gravimetric analysis. When beryllium metal is dissolved in the small distilling flask by adding concentrated H_2SO_4 , free sulfur and hydrogen sulfide are found in the condenser and receiving flask. The presence of the hydrogen sulfide cannot be tolerated. If a small amount of water is present with the beryllium metal in the distilling flask when the H_2SO_4 is added, violent frothing occurs which often results in overflowing through the condenser. Beryllium was successfully dissolved by adding (1:9) H_2SO_4 to the metal in the cooled distilling flask and then slowly adding (9:1) H_2SO_4 .

Nephelometric readings were at first very inconsistent and changed rapidly with time. It was suspected that this was due to changes in the physical properties of the suspension of silver chloride. But experiments involving the use of a fresh standard with each chloride solution, and the control of the time from the formation of the suspension to the reading of the sample, did not improve the results. Then it was noticed that micro bubbles of carbon dioxide collect on the bottom surface of the plunger of the nephelometer. These bubbles, which cause erratic results, must be removed before a reading is taken. Experiments indicate that the silver chloride suspensions are sufficiently stable for accurate readings within a half hour after removal from the water bath. More accurate results are obtained when a standard curve is prepared for each series of chlorides to be determined.

A study of the optimum conditions for distillation indicate that the sulfuric acid should be fumed strongly in the still for at least five minutes to remove the last traces of chloride. Controls prepared by adding known amounts of chloride to beryllium solutions gave results in the order of 10% high. The beryllium solution was prepared by dissolving beryllium metal with sulfuric acid and fuming. However, perhaps a small amount of chloride remained in the solution, or the still may have been contaminated. Beryllium oxide believed to be free of chloride will be used to check the recovery of chloride from beryllium solutions.

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SPECIAL PROBLEMS

(O. C. Simpson)

Remote Control and Hot Lab Development (F. L. Belletire, R. Millor, R. W. Holmes,
R. Blomgren, H. Andrews, M. Rebenak)

B-2 Hot Lab. The initial construction order has been nearly completed which included:

1. Complete paint job.
2. Fluorescent lighting in hood and room.
3. Raising of overhead utilities to get them out of the road of cranes, etc.
4. Installation of hoist and rail.
5. Installation of two lead doors in cave and the addition of 6" of lead to the top of the existing wall.
6. Repair of all electrical and ventilation equipment.

Additional orders were written to do the following:

7. Build a partition to separate B-1 from B-2.
8. Lay linoleum on floor.
9. Install stainless steel bench top and sink.
10. Install trap tank between drains and sewer main.
11. Install double reflection mirrors.
12. Install shields which can be adjusted to reduce hood opening size.

All but items 8, 9, 10, 11, and 12 are nearly completed.

As soon as the painters have finished, installation of the tracks will be started. The cranes, etc., are being built and should be ready shortly after the tracks have been installed.

Equipment is being planned and built to handle the one gram sample of Hanford irradiated radium.

Rough sketches have been made and some material has been ordered for the conversion of an analytical balance to remote control.

Van de Graaff Generator (F. L. Belletire, H. C. Andrews, M. Rebenak)

A great amount of time is being spent on the generator in hopes that a formerly efficient piece of apparatus can be again put into operation and that a 100% output may be attained. To reach this goal, the generator has been thoroughly cleaned. All rust at connection points has been removed, belts and gaskets have been replaced, wiring that showed signs of deterioration has been replaced or repaired, and other miscellaneous cleaning and repairing has been done.

It is hoped that the generator will be in operation by the end of the week ending January 24.

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8.

Ionization Potential of Plutonium (E. G. Rauh)

Further measurements on the indirectly heated cathode indicate that while the necessary temperature could probably be reached, the life of the tungsten filament will become too short for practical use. The heating currents are high which means a loss of a unipotential emitting source, the application of empirical correction factors, or a redesign involving insulating the filament which is mechanically impractical. An intermittently heated filament will be tried, where measurements on ion currents will be made on that part of the cycle in which the heating current is off. By this arrangement a unipotential source (to .001 volt) and an unvarying filament are expected.

Heat of Sublimation and Vapor Pressure of Graphite (R. J. Thorn)

The perforated graphite cylinder referred to in the last abstract has been baked out for 9 hours at 2204°C. Since Mr. Hodur has started to repair the quartz condenser a new series of runs using this cylinder should be started soon.

The electrical resistivity of graphite has been calculated from the reflectivity of the deposit previously reported. This calculation has been carried out with the equation

$$\textcircled{c} \quad R = 1 - \frac{4\alpha}{2\alpha^2 + 2\alpha + 1} \quad (1)$$

in which R is the reflectivity measured with light of frequency ν , and $\alpha = (\nu \rho)^{\frac{1}{2}}$ where ρ is the electrical resistivity. For $R = 0.255$, and $\nu = 0.665$, one obtains for the resistivity of the deposit a value of 1178 microhm-cm. compared with an experimental value of 800 microhm-cm. This agreement is about what one would expect since equation (1) is not generally applicable for high values of the frequency ν .

It is interesting to observe that for graphite, silver, aluminum, gold, platinum, nickel, cobalt, and zinc an empirical relation between the resistivity and reflectivity can be obtained which describes the data better than equation (1). This relation is

$$R = 1.07 \rho - 0.214 \quad (2)$$

The values calculated by equations (1) and (2) are compared with the experimental values in Table I.

* Abraham and Becker, The Classical Theory of Electricity and Magnetism, p. 192

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TABLE I

Material	Reflectivity (R)	Resistivity (microhm-cm)		
		Exptl. (20°C)	Calculated	
			Eqn. (1)	Eqn. (2)
Silver	0.96	1.62	0.81	1.69
Gold	0.89	2.39	6.66	2.40
Aluminum	0.87	2.69	9.67	2.65
Zinc	0.73	6.31	49.5	6.06
Nickel	0.67	7.97	31.2	9.03
Platinum	0.66	11.96	87.4	9.62
Cobalt	0.65	9.70	95.5	10.38
Plutonium	0.55*	109.	96.*	31.
Graphite	0.25 ₅	800.	1178.	816.

* Measured at a glass-metal interface; modified form of Eqn. (1) used.

It is also interesting to note that Long and Morrish {Proc. Roy. Soc. (Lond.) A 187, 337 (1946)} very recently surveyed the available information regarding the heat of sublimation of graphite and have concluded that the monatomic heat of sublimation (to the β state) is 190 ± 10 kcal. The value obtained in the present study is (as reported previously) 190 ± 4 kcal at 25°C. The agreement may be purely coincidental.

GRAPHITE PROGRAM

(T. J. Neubert)

Stored Energy by the Sykes Method (R. B. Lees, H. A. Kierstead)

Several new runs have been made on samples from the water-cooled test holes of the B and D piles at HEW. From these runs and the runs on T-bar, the activation-energy spectrum for heating of stored energy, $F_0(E)$, has been calculated by the method of V. Vand (Proc. Phys. Soc., 55, 222 (1943)). Corrections were made to take account of the non-uniform heating rate.

In Figure 1 the activation energy spectra of three sidehole samples are plotted.

Bombardment of Uranium-Impregnated Graphite (M. J. Nagy, H. A. Kierstead)

Weight and resistance measurements have been made on graphite and uranium-impregnated graphite samples which were irradiated in CP-3 at Argonne. The samples were given a bombardment of 2829 Kw-hr. (0.1411 units). Table 1 gives the fractional changes in weight and resistance which occurred due to impregnation and due to bombardment, the latter being referred to the values measured after impregnation.

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ACTIVATION ENERGY SPECTRA FOR RELEASE OF STORED ENERGY IN IRRADIATED GRAPHITE

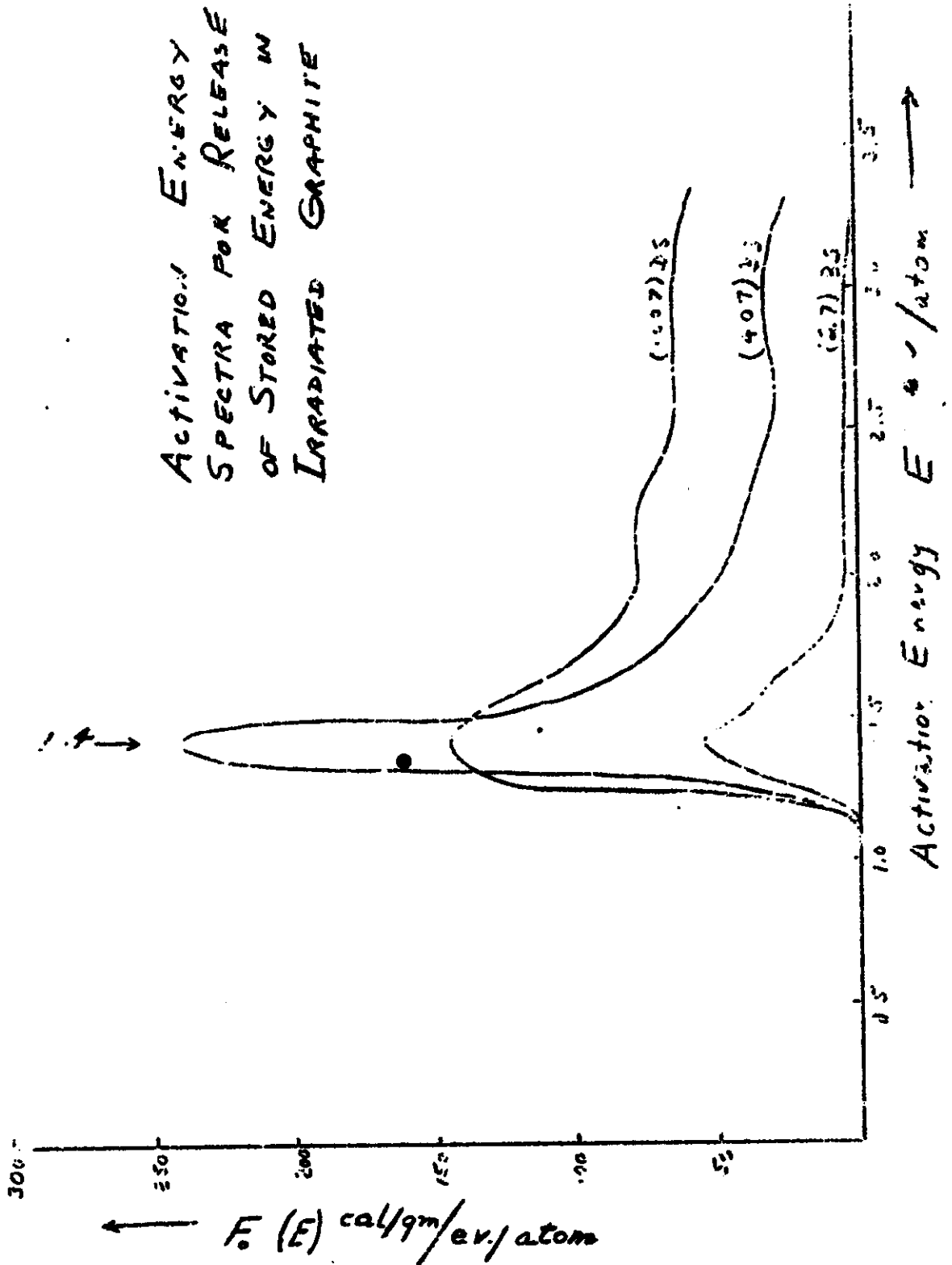


Figure I

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Impregnation with 7 percent of uranium appears to about triple the effect of bombardment on the resistance. However, the resistance changes can not be correlated very well with the weight changes due to impregnation. Perhaps this difficulty will be cleared up when analyses are obtained of the amount of uranium in the samples.

Table 1
Weight and Resistance Changes of Impregnated Graphite

Treatment	Sample #	% Weight Change		% Resistance Change	
		Impregnation	Bombardment	Impregnation	Bombardment
Kendall Blanks	KP-1027		-0.061		1.29
	KP-1029		-0.013		0.85
	KP-1037		0.230		2.78
	KP-1039		0.089		0.05
	KP-992		0.072		1.34
	KP-989		0.248		1.72
	KP-999		0.181		1.34
	Mean		0.108		1.34
AGR Blanks	AP-50		0.499		1.86
	AP-51		0.604		1.35
	AP-36		0.403		1.41
	AP-37		0.438		1.05
	AP-48		0.435		2.90
	AP-49		0.244		0.98
	Mean		0.437		1.59
1 Impreg- nation	AP-5	3.02	0.188	0.15	1.72
	AP-15	3.24	0.497	1.19	3.28
	AP-16	2.92	0.268	0.30	2.78
	AP-59	2.57	0.284	1.19	2.87
	AP-62	2.84	0.526	-0.04	3.08
	Mean	2.92	0.353	0.56	2.87
2 Impreg- nations	AP-17	5.90	0.418	1.96	2.21
	AP-18	5.54	0.346	1.93	2.87
	AP-19	5.87	0.583	2.89	2.31
	AP-55	3.90	0.240	1.58	2.42
	AP-58	4.75	0.278	0.19	4.88
	AP-60	4.36	0.411	2.22	3.13
	Mean	5.05	0.379	1.80	2.97
3 Impreg- nations	AP-14	5.81	0.130	3.54	4.09
	AP-20	7.00	0.234	2.71	3.87
	AP-21	7.43	0.125	1.25	4.75
	AP-56	6.42	0.276	1.74	5.50
	Mean	6.66	0.191	2.31	4.55