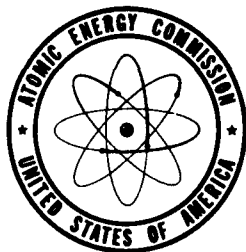METALLURGY AND CERAMICS

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ZONE MELTING OF URANIUM

By
C. I. Whitman
V. Compton
R. B. Holden

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ABSTRACT

A study was made of the possible
application of the zone melting
technique to the separation of
uranium from fission products and
other impurities. Bar specimens
of uranium having various alloy-
ing elements were zone purified in
thoria-coated alumina boats. Uran-
ium bars previously irradiated in
the Brookhaven pile were also zone
melted.

Although zone melting did not ap-
pear promising as a method of pro-
cessing irradiated uranium because
of slagging of fission products into
the surface of the bar, this tech-
nique has potential application to
removing such fission products as
zirconium, niobium, and ruthenium,
and to purifying ordinary uranium
from such impurities as boron, iron,
silicon, nickel, and cobalt.

I. INTRODUCTION

Zone melting is a purification technique which has been used to prepare very pure germanium metal in which the quantity of impurities present is of the order of parts per billion. The success of this technique with germanium suggested an investigation of its possible application to the purification of uranium from fission products and other impurities. This report presents the results of such an investigation.

In the zone melting process a narrow molten zone, produced by induction or resistance heating, is made to traverse the solid metal by movement either of the heater or of the metal, as shown in Fig. 1. Since the solubility of an impurity will generally be different for solid and liquid (see Fig. 1), segregation will occur as the solid refreezes at the rear solid-liquid interface. Impurities which are more soluble in the liquid phase tend to concentrate in the molten zone and are carried to one end of the bar. Impurities which are more soluble in the solid phase tend to move to the opposite end, and thus the center portion of the bar is purified. Additional passes in the same direction produce further purification, although eventually an "ultimate distribution" is reached after which additional passes have no effect.

A measure of the tendency of the impurity to migrate is given by the distribution coefficient $\underline{k}$, which is defined as the ratio of the solute concentration in the solid to that in the liquid at equilibrium. The greater the factor by which $\underline{k}$ differs from unity, the more readily will impurities migrate.

A simple theory of zone melting has been developed by Pfann[1], in which it is assumed that solute diffusion in the liquid is sufficiently rapid that the impurity concentration is uniform in the molten zone while diffusion in the solid phase is negligible. From this theory it is possible to calculate the effect of repeated zone passes if the distribution coefficient is known. In practice one expects less migration than that calculated, because the assumptions of complete equilibrium on which the calculation is based will not be strictly true. In any case, the purification which is attained will depend on the number of passes, the ratio of molten zone length to bar length, the equilibrium distribution coefficient $\underline{k}$ and the rate of zone travel.

In Table I are given $\underline{k}$ values for some metals in uranium, estimated from the particular uranium-metal phase diagrams. The theoretical ratio of impurity concentration between the ends of the bar after seven zone passes (zone-length to bar-length ratio of 1:10) is also given.

TABLE I

DISTRIBUTION COEFFICIENTS FOR SOME METALS IN URANIUM

Element	k*	Theoretical concentration ratio+ between ends of bar after seven zone passes
Iron	~0.1	~10^6
Molybdenum	~1.0	1
Nickel	~0.03	>10^6
Niobium	~5.0	>10^6
Silicon	~0.2	~10^5
Tin	~1.0	1
Zirconium	~2.0	10^4
Plutonium	~0.5	10^3

* Estimated from available phase diagrams.

+ Taken from calculations by I. G. Dillon, kindly
   furnished by L. Burris and I. G. Dillon of Argonne
   National Laboratory.

II. EXPERIMENTATION

A. Apparatus

Two types of apparatus were employed in the study; one,
used for the most part, in which the coil moved relative to
the bar, and one in which the bar was moved.

In the single-coil arrangement shown in Fig. 2, the induction
coil was mounted on the travelling carriage of a small lathe
bed. The coil was advanced by means of a low-velocity motor
connected to a "Zero-Max", adjustable ratio torque converter,
which in turn was used to drive the lead screw of the lathe.
In this way, rates of molten zone travel of 0 to 12"/hr could
be obtained. The uranium was contained in a boat placed with-
in a Vycor tube, approximately 2" in diameter, which was
closed at one end. The other end of the tube was connected
by means of a 75/50 semi-ball connection to a high vacuum
system consisting of a three-stage oil diffusion pump and a
mechanical pump. If desired, the zone melting could also be
carried out in an inert atmosphere.

The multi-coil apparatus shown in Fig. 3 utilized stationary coils surrounding a Vycor tube. The boat containing the sample was pulled through the coils by means of a zirconium wire attached to the rod of a National Research Corp. rotary, push-pull vacuum seal at one end of the Vycor tube. The wire was wound on the rod at an adjustable rate controlled by a variable ratio "Zero-Max" torque converter in a manner similar to the simple coil arrangement discussed previously. The vacuum seal was connected to the glass vacuum system through a metal male ground joint. The other end of the tube was attached by a means of a 75/50 semi-ball connection to a high vacuum system similar to the one described previously. This arrangement operated satisfactorily and demonstrated the practicality of a production line setup for continuous zone melting.

A double pancake-type coil (2-1/4" I. D.) with a total of ten turns (five for each pancake) of 3/8" diameter copper tubing was used in these studies. Power for the single-coil apparatus was supplied from a Sylvania Bombarder with an operating frequency of 400 kc and an output rating of 10 KW. The multi-coil apparatus used a Ther-Monic Generator with a 10 KW output and an operating frequency of 400 kc. Both induction heating units were of the vacuum tube type.

B. Container Materials for Uranium

The development of a suitable container material for the uranium proved to be the principal experimental problem encountered. Graphite boats, which were used early in the program, reacted excessively with the uranium. Although stabilized zirconia was sufficiently inert with respect to uranium attack, it had extremely poor thermal shock resistance under the conditions of zone melting, continually causing the boats to crack. Alumina (Norton Co. mixture RA 98) was found to be more resistant to thermal shock and was used subsequently in preference to zirconia.

Alumina boats used to contain the uranium were obtained by cutting furnace tubes (12" long, 3/4" bore) in half lengthwise and plugging the ends with alumina discs. A thoria wash, consisting of thorium oxide powder suspended in a nitro-cellulose lacquer (Raffi and Swanson No. 2695) diluted 5-to-1 with n-butyl acetate, was applied to the inner surface of the boat and to the end plugs. This served to reduce any attack of alumina by uranium. Three such coats were usually applied, with drying under an infra-red lamp between coats. The boats were then fired at 900° to 1000°C to form a loosely adhering protective coating of thoria. The use of higher firing temperatures resulted in a decrease in the

thermal shock resistance of the alumina. Boats made in this manner have been used for as many as twenty zone passes without breakage. If this treatment were omitted,the principal effect would be aluminum pickup by the uranium.

Prior to use, the alumina boats were outgassed to a vacuum of $\leq 0.02\mu$ by heating a bar of zirconium within the boat to approximately 1300°C. The boat containing the uranium was placed in an outer boat which would prevent uranium from flowing onto the Vycor tube in case of failure of the inner boat.

C. <u>Atmosphere</u>

The uranium alloys used in the study were prepared by powder metallurgy hot-pressing techniques. This material contained far more residual gas than the usual vacuum-cast uranium. Upon melting of the alloys under vacuum, considerable outgassing occurred, which was sometimes violent enough to spatter uranium over the interior surface of the Vycor tube. This was avoided by melting under a static atmosphere of 200 to 300 mm of argon.

Zone melting of vacuum-cast uranium was conducted under a continuous vacuum of $\leq 0.01\mu$. The resulting bar had a smooth, steel-grey surface (presumably UO) which remained virtually unchanged for weeks.

D. <u>Zone Length</u>

The boats used varied in length from 6 to 12 inches and in width from 3/4 to 1-1/2 inches. The boundaries of the molten zone were distinguished by a slight jarring of the apparatus. Generally, the desired zone length was 1/10 the bar length but experimentally this was difficult to maintain. At constant power input, the zone length for 10" bars varied from 3/4" in the center portion to 2" at the ends of the bar. The increase in zone length at the ends is attributed to heat transfer from the molten zone through the uranium bar in only one direction; whereas in the center portion heat transfer occurs in two directions. Variation in zone length could be corrected by appropriate adjustment of the power input, resulting in a uniform zone length of 3/4 to 1 inch.

III. RESULTS

Zone melting was applied to:
      a) binary uranium alloys
      b) vacuum-cast uranium
      c) irradiated uranium
in that order. Suitable experimental procedures were developed
simultaneously as the investigation progressed. A rate of zone
travel of 1 to 2 inches per hour was eventually adopted as the
best for these reasons:

   a. At faster zone travel rates, separation was poorer.
   b. While slower rates may have increased separation be-
      cause of a closer approach to equilibrium conditions,
      any practical application of zone melting would require
      a reasonable rate of zone travel for economic reasons; and
   c. With this rate it was not necessary to allow experiments
      to run unattended overnight.

A. Uranium Alloys

The experimental results on zone melting of uranium alloys
are summarized in Table II. The alloys were prepared by
powder metallurgy, and the zone melting was conducted generally
in a static atmosphere of argon. The single-coil apparatus
was used in all experiments except ZM-37 in which the multi-
coil arrangement was employed. Segregation was noted in the
zone melting of binary alloys of uranium with zirconium,
niobium, ruthenium, iron, nickel and silicon. The indicated
migration of tin in melt No. ZM-10 may possibly be attributed
to experimental error in the analytical procedure, since
according to the phase diagram tin should not segregate. No
migration of tin was observed in a later experiment (ZM-34).
The indicated direction of migration of zirconium (ZM-7) is
opposite to that expected from the phase diagram. The ends
of the bar were probably inadvertently switched after zone
melting.

However, where comparison is possible with Table I, it is
seen that the actually observed differences are at best only
factors of two or three whereas factors of 10 to 100 and
more would be expected from theory. If these experiments were
repeated, better results would be expected because of sub-
sequent improvements in technique, but it is unlikely that
anything resembling theoretical concentration differences
would be attained except with impractically slow rates of
zone travel.

TABLE II

ZONE MELTING OF URANIUM ALLOYS PREPARED BY POWDER METALLURGY

Material	Alloy[1] %	Melt No.	Boat[2]	Vac. μ	Passes	Speed in./hr	Zone Length in.	Theoretical Concentration Ratio Between Ends of Bar	Sample No.[5]	Fe	Ni	Nb	Ru	Si	Sn	Zr
Iron	0.01	ZM-5	Graphite	0.03	10	6	~1 (4)	~10^8	0	0.01						
									1	0.01						
									2	0.01						
									3	0.01						
	0.2	ZM-11	ZrO_2	A (8)	3	2	~2 (3)	~10^3	1	0.13						
									2	0.26						
Nickel	0.1	ZM-16	ZrO_2	A (8)	4	1	~1 (3)	>10^4	1		0.06					
									2		0.16					
									3		0.19					
Niobium	0.5	ZM-8	ZrO_2	0.05	10	6	~1 (3)	>10^6	1			0.49				
									2			0.43				
									3			0.45				
	0.5	ZM-8A	ZrO_2	A (8)	7	1	~3/4 (3)	>10^6	1	0.01		0.59				
									2			0.44				
									3	0.01		0.30				
Ruthenium	0.5	ZM-17	ZrO_2	A (8)	8	1	1 (3)		0				0.52			
									1				0.50			
									2				0.49			
									3				0.79⎫			
													1.07⎭			
	0.6	ZM-37	Al_2O_3 (9)	<0.01	6	1	1 (3)		1				0.37			
									2				1.54			
									3				1.50			
Silicon	0.01	ZM-1	Graphite	≤1	7	8	~1 (4)	~10^5	1					0.002		
									2					0.012		
									3					0.011		
	0.5	ZM-4	ZrO_2	0.05	8	6	~1 (4)	~10^5	1					0.41		
									2					0.43		
									3					0.44		
	0.2	ZM-6	Graphite	0.05	10	8	~3/4 (4)	~10^6	0					0.18		
									1					0.17		
									2					0.18		
									3					0.21		
	0.2	ZM-12	ZrO_2	A (8)	2	3	~1 (3)	~10^2	1					0.17		
									2					0.19		
									3					0.24		
Tin	0.5	ZM-10	ZrO_2	A (8)	6	1	1 (3)	~1	1						0.54	
									2						0.55	
									3						0.63	
Zirconium	0.5	ZM-7	ZrO_2	A (8)	5	4	2 (3)	>10^3	1							0.16
									2							0.60
									3							0.44
																(7)

For Notes See Succeeding Page

TABLE II
(cont'd)

(1) Alloys prepared by powder metallurgy. Powders pressed at 600°C and 12 tsi.

(2) Dimensions of boats: Graphite - 10" x 1"
                          Stabilized Zirconia - 6" x 1-1/2"
                          Alundum - 12" x 3/4".

(3) Zone length at ends of bar was approximately twice the length in the center of the bar. Value given is for zone length in center portion.

(4) Zone length kept constant by varying the power input.

(5) Sample 0 - pre-zone melting.
     Sample 1 - first portion of the bar to freeze.
     Sample 2 - center portion.
     Sample 3 - last portion of the bar to freeze.

(6) Analyses for alloys prepared by powder metallurgy expressed in w/o.

(7) Ends of bar were probably inadvertently switched after zone melting since the observed migration is opposite to that expected from the phase diagram.

(8) Zone refined in a static atmosphere of argon (250 mm of argon). No attempt was made to purify the argon.

(9) Boat had a thoria wash.

B. Vacuum-Cast Uranium

The experimental results on zone melting of vacuum-cast uranium are summarized in Table III. Vacuum cast uranium was zone refined in thoria-coated alumina boats under a continuous vacuum of $\leq 0.01\mu$ (ZM-27 and ZM-28). All runs were made in the single-coil apparatus. Migration of boron, iron, nickel, cobalt and silicon was noted, although it was not very extensive at a molten zone travel rate of 2"/hr. The behavior of copper was anomalous. Within the accuracy limits of analysis no carbon migration was found.

Considerable purification of uranium (containing small amounts of added metals) was effected from boron, cobalt, iron, nickel and silicon by zone melting in thoria-coated alumina boats at a molten zone travel rate of 1"/hr (ZM-34). Some migration was noted for copper and vanadium. Aluminum, magnesium, manganese, molybdenum and tin did not segregate. The increased migration in this melt, as compared to ZM-27 and ZM-28, probably resulted from a closer approach to equilibrium conditions between the liquid and solid phase at the slower zone travel rate. While still far less than that expected theoretically, the migration is sufficiently extensive to suggest the possibility of using zone melting as a method of producing high-purity uranium.

C. Irradiated Uranium

A bar of uranium metal, irradiated in the Brookhaven pile at a flux of 10^{11}nv for 55 minutes followed by approximately 60 days cooling, was given a total of twenty zone passes (ZM-36); 10 in one direction and then 10 in the reverse direction. The single-coil arrangement was used in these experiments. Autoradiographs were taken at various stages and the total radiation level along the length of the bar was measured.

An autoradiograph (4 hr. exposure) taken after the initial melting of the bar and after pickling in 1:1 HNO_3 showed a highly irregular distribution of activity (Fig. 4a). After completion of the first ten passes with the highest activity at the upstream end (first portion of the bar to freeze), a 15 min. exposure was sufficient to show displacement of activity toward each end of the bar (Fig. 4b). In addition there was an unmoved region of activity in the middle of the bar. The extent of migration is more apparent after pickling in dilute nitric acid. (Fig. 4c). These autoradiographs and the high activity of the pickling solutions indicated considerable concentration of the fission products at the surface of the uranium.

TABLE III

ZONE MELTING OF VACUUM-CAST URANIUM

Melt No.	Boat[1]	Vac.[3] μ	Passes	Speed in/hr	Zone Length in.	Sample[6] No.	B	Analysis[7]					
								Co	Cu	Fe	Ni	Si	V
ZM-22	Al$_2$O$_3$	<0.02	3	2	3/4	0	<0.2			115	~30		
					(4)	1	<0.2			39	~30		
						2	0.23			17	~40		
						3	0.43			57	~60		
ZM-27	Al$_2$O$_3$ (2)	<0.02	9	2	3/4	0	<0.2	~5	~10	35	~40	20	
					(4)	1	<0.2	-	<1	28	~20	~20	
						2	<0.2	~5	~1	48	~30	~30	
						3	0.22	~7	<1	68	~60	~30	
ZM-28	Al$_2$O$_3$ (2)	<0.02	7	2	5/8	0	<0.2	~5	~10	35	~40	20	
					(5)	1	<0.2	-	<1	27	~20	~20	
						2	<0.2	~5	~3	45	~40	~20	
						3	0.20	~5	~5	67	~60	~30	
ZM-34 (8,9)	Al$_2$O$_3$ (2)	<0.02	9	1	1	1	-	10	1	15	20	20	30
					(4)	2	-	30	5	30	30	50	30
						3	0.41	150	5	200	200	200	50

(1) Dimensions of alumina boat - 12" x 3/4".
(2) Boat had a thoria wash.
(3) Vacuum reading off scale; measured with a Philips Gauge (lowest scale reading 0.02μ).
(4) Zone length at ends of bar was approximately twice the length in the center of the bar. Value given is for zone length in center portion.
(5) Zone length kept constant by varying the power input.
(6) Sample 0 - pre-zone melting
Sample 1 - first portion of the bar to freeze
Sample 2 - center portion
Sample 3 - last portion of the bar to freeze.
(7) Spectrographic analysis for vacuum-cast uranium expressed in parts per million.
(8) No migration was observed for Al, Mg, Mn, Mo and Sn.
(9) Vacuum-cast uranium (app. 500 g.) melted onto the following powders:
14 mg Ag; 70 mg Al; 14 mg Co; 21 mg Cr; 14 mg Cu; 70 mg Mn;
21 mg Mo; 35 mg Ni; 21 mg Pb; 35 mg Si; 21 mg Sn; 35 mg V.

Beta and gamma radiation levels, before and after pickling, were measured along the length of the bar with a radiation survey meter through a 1/2" lead slit and with the meter 4" away from the bar. Results of beta activity measurements are plotted in Fig. 5. From these measurements it is clear that some migration, although not too extensive, had occurred since there is a concentration of activity at each end of the bar (beta activity to a greater extent than gamma).

The bar was then given 10 additional zone passes in the reverse direction with highest activity at the downstream end (last portion to freeze) to determine whether the activity could be moved. This resulted in a peak in the beta activity at the upstream end and a general leveling of gamma activity along the bar.

At the end of 20 passes the boat itself was found to possess beta activity comparable to that of the bar itself while the gamma activity was essentially background.

These observations were not made in such a manner as to provide quantitative data but it is obvious that:

1) Migration in each direction was observed, but it was not extensive.
2) Considerable amounts of activity concentrated in the surface layer of uranium, where it could be removed by pickling, and also diffused into the alumina boat.

While no direct identification was made, the activity concentration noted at the upstream end was probably due to zirconium and niobium, and ruthenium at the downstream end. The conditions under which the zone melting was carried out are exactly those for a combined oxide slagging and volatilization. As has been determined experimentally,[2] the major portion of the fission products, comprising the rare earths, alkali and alkaline earth metals should either enter a slag layer, volatilize or diffuse into the oxide container. Thus there would be little if any migration of these elements. The remaining important fission products zirconium, niobium, ruthenium and molybdenum are incompletely removed by this oxide slagging and volatilization. Of this group only molybdenum does not migrate.

IV. SUMMARY AND CONCLUSIONS

1. Suitable apparatus for the zone melting of uranium has been developed. An alumina boat, coated with a loosely adhering layer of thoria, is a satisfactory container for uranium from the standpoint of inertness and resistance to thermal shock. Motion of the coil relative to the bar and motion of the bar relative to fixed multiple coils has been used successfully.

2. Migration of boron, iron, nickel, cobalt, silicon, copper, zirconium, niobium, and ruthenium was observed. No migration was detected for aluminum, magnesium, manganese, molybdenum and tin. It was found that slow zone travel rates ($\sim 1"$/hr.) improved the extent of migration appreciably, presumably because of a closer approach to equilibrium conditions.

3. An autoradiograph of irradiated uranium subjected to zone melting showed that migration had occurred to each end of the bar. This was attributed to zirconium, niobium and ruthenium. A considerable amount of activity was found to concentrate in the surface of the bar.

4. Zone melting shows promise as a means of purification of uranium from traces of such elements as boron, iron, nickel, cobalt, silicon, and copper although in no case is the extent of migration as extensive as would be expected on the basis of simple zone melting theory.

5. Zone melting shows no promise as a general method for removing fission products from uranium. A possible specialized application would be for removal of such elements as zirconium, niobium, and ruthenium. Other fission products either do not migrate or are slagged into the oxide skin always present.

6. The behavior of plutonium on zone melting was not investigated. It is conceivable that zone melting would be useful as a plutonium concentrating technique.

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REFERENCES

1. W. G. Pfann, "Principles of Zone Melting", Trans. AIME, 194, pp. 747-753 (1952).

2. H. M. Feder, N. R. Chellew and M. Ader, "Interim Report - Purification of Nuclear Fuels by Melting in Refractory Oxide Crucibles", ANL-5255, March 15, 1954 (Secret).
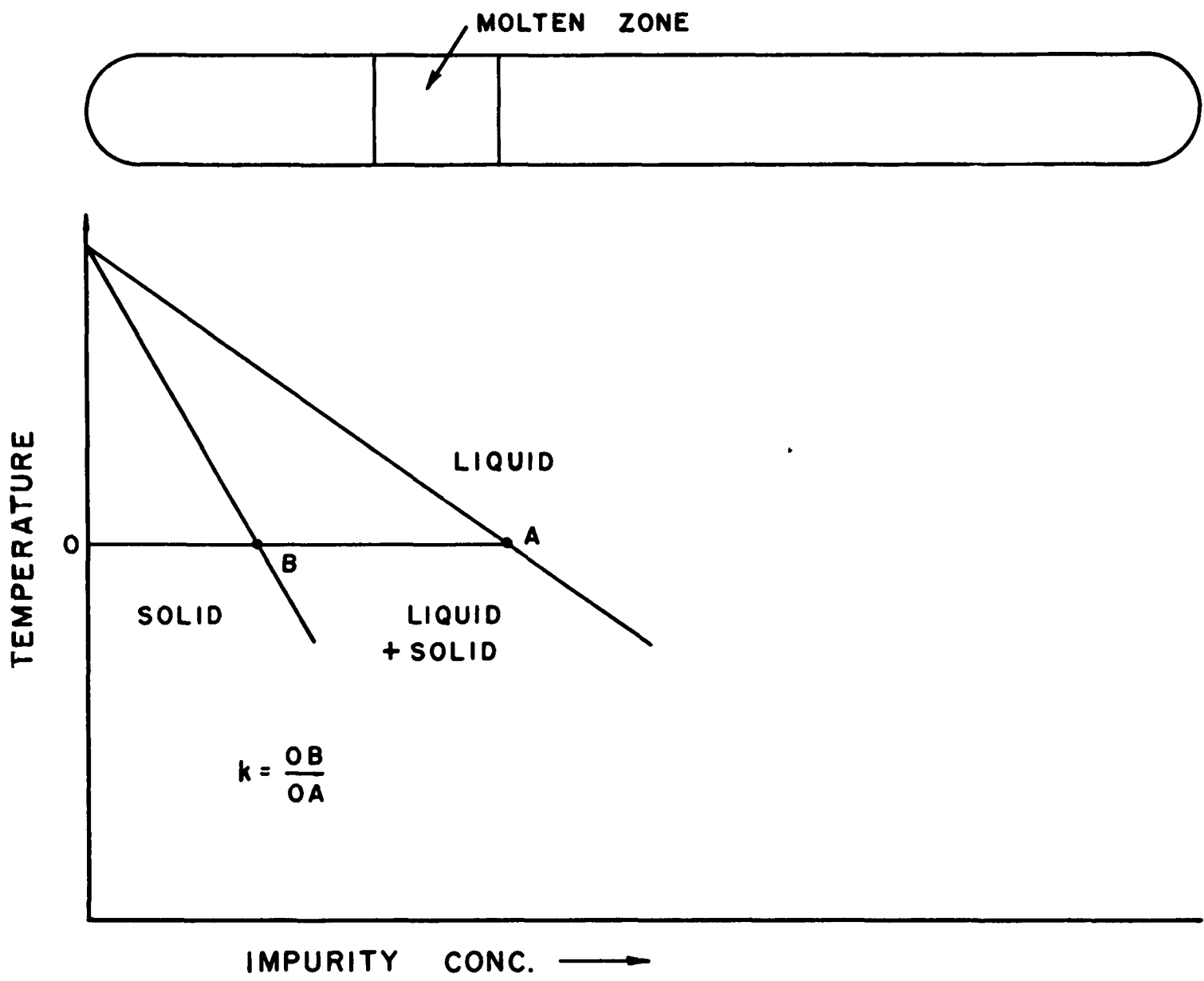
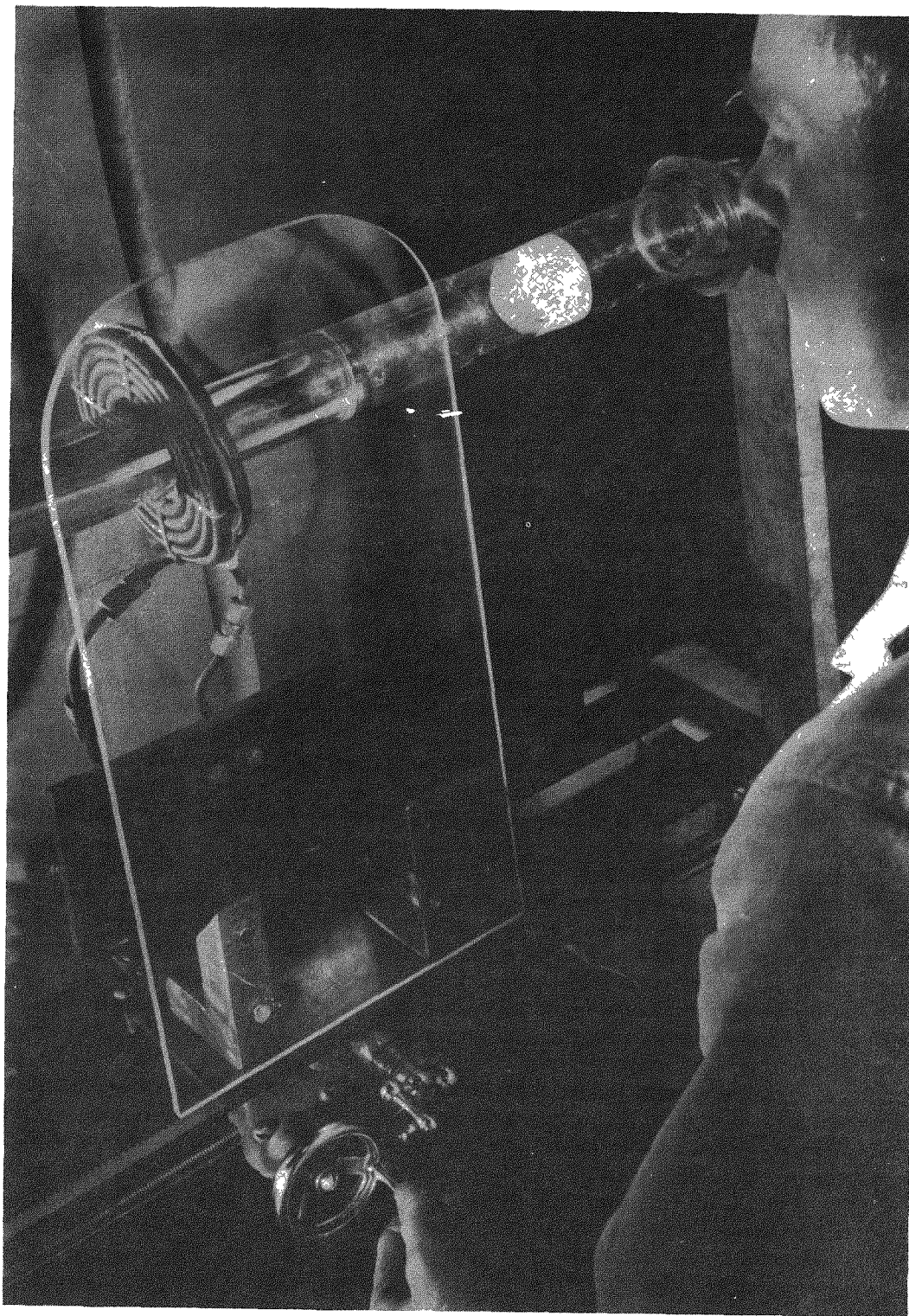Fig. 1 – General phase diagram showing nature of distribution coefficient in zone melting.
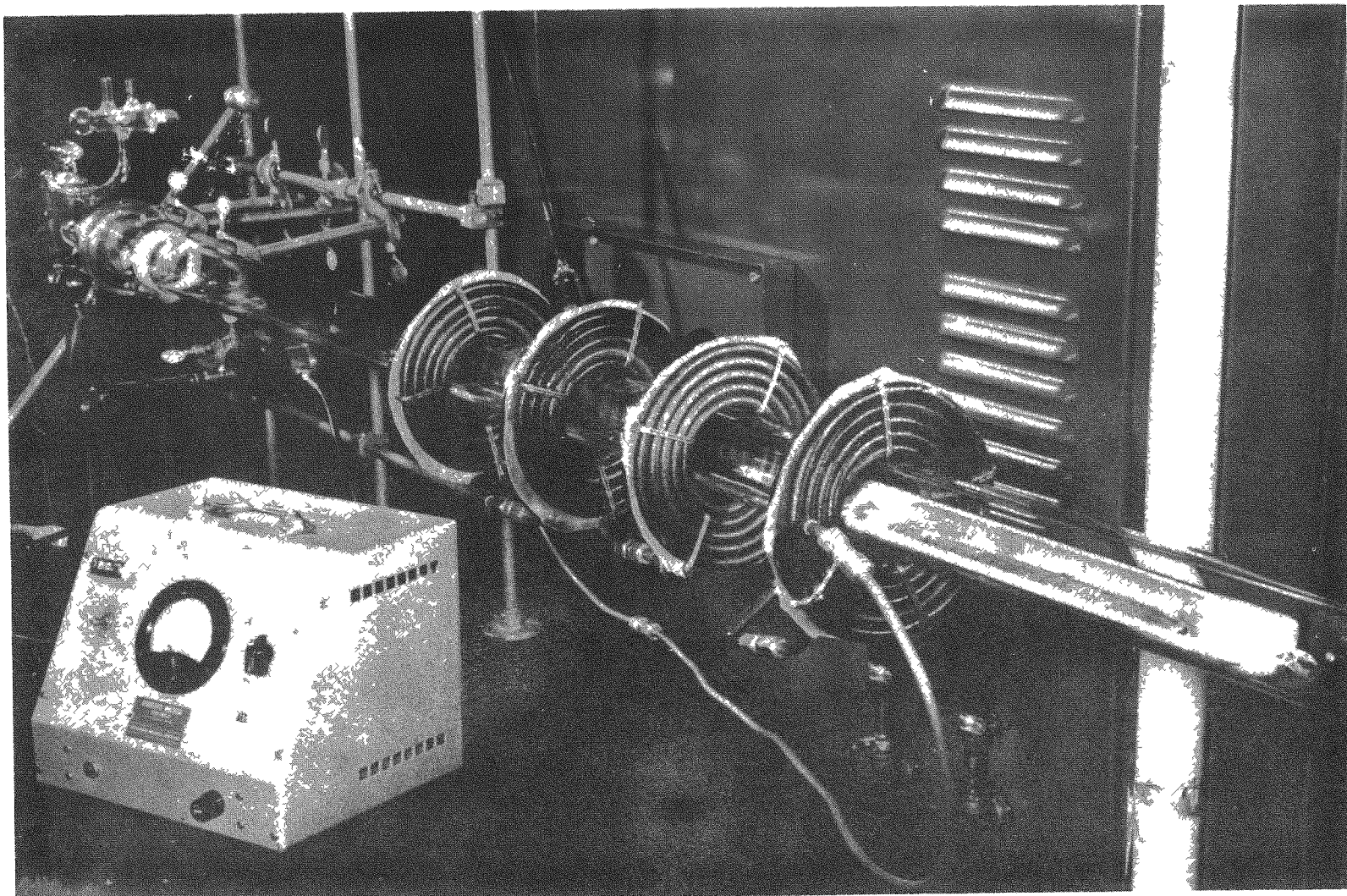
Fig. 2 - Single-coil arrangement for zone melting.
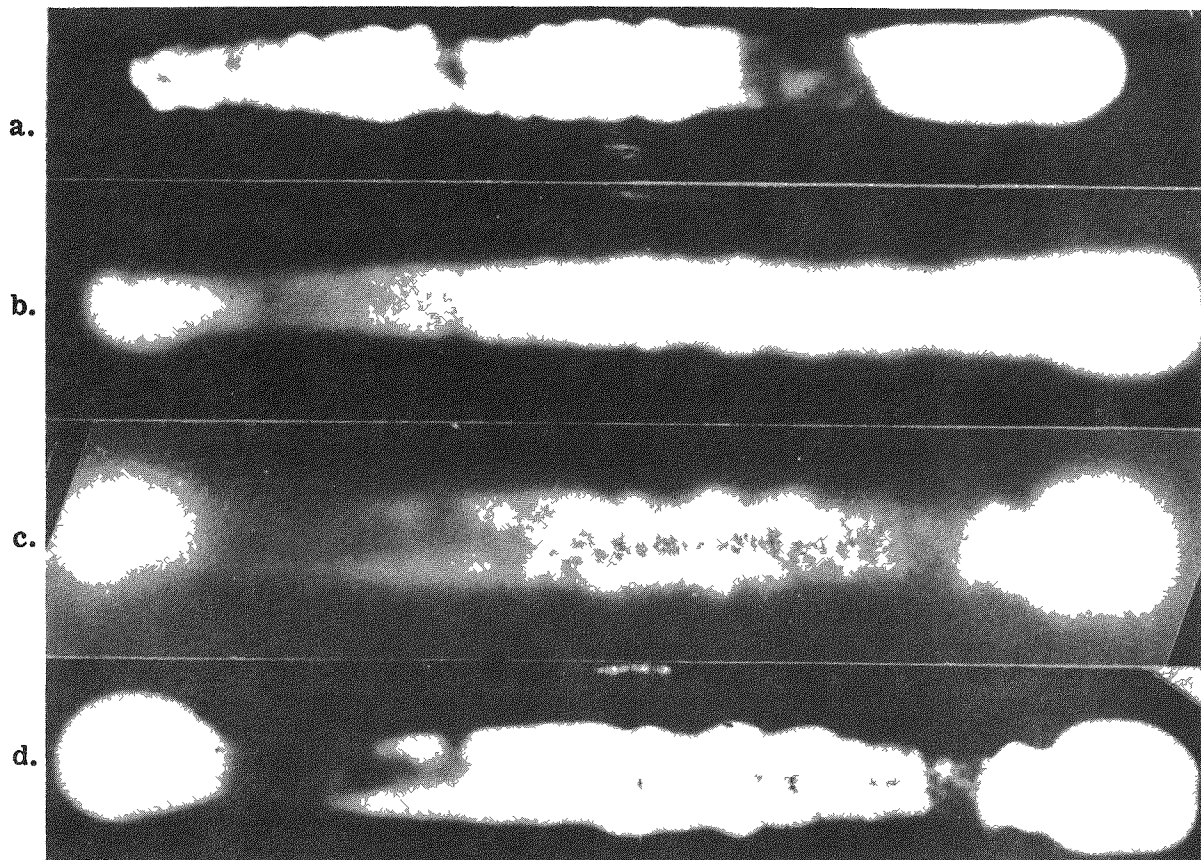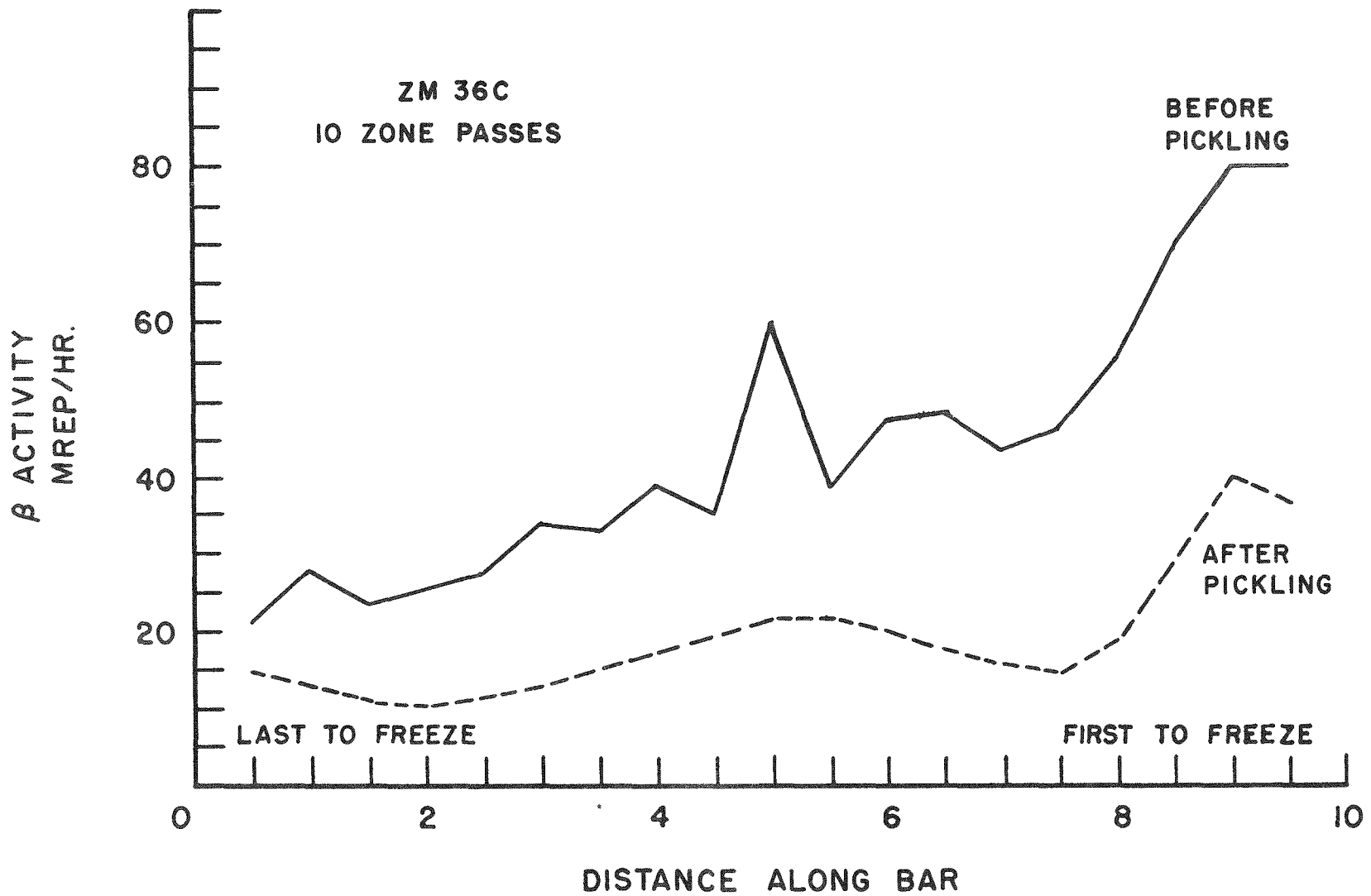
Fig. 3 - Multiple-coil arrangement for zone melting.

Fig. 4

a. Irradiated bar prior to zone melting.
   Zone melting was done from right to left.

b. Bar after 10 zone passes.

c. Same as b. but after pickling.

d. Same as c. but longer exposure to film.

Fig. 5 – Results of beta-activity measurements on zone melted uranium bar which had previously been irradiated.