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SEGREGATION IN URANIUM-ALUMINUM ALLOYS
AND ITS EFFECT ON THE FUEL LOADING
OF ALUMINUM-BASE FUEL ELEMENTS

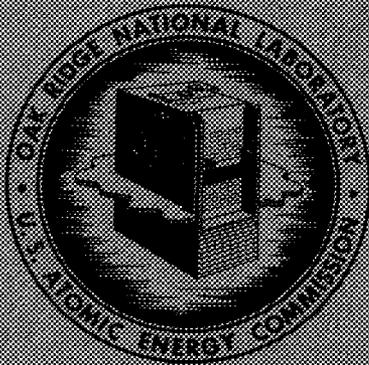
W. C. Thurber
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SEGREGATION IN URANIUM-ALUMINUM ALLOYS AND ITS EFFECT ON THE FUEL
LOADING OF ALUMINUM-BASE FUEL ELEMENTS

W. C. Thurber
R. J. Beaver

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SEGREGATION IN URANIUM-ALUMINUM ALLOYS AND ITS EFFECT ON THE FUEL LOADING OF ALUMINUM-BASE FUEL ELEMENTS

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SUMMARY

Techniques were devised for quantitatively determining the accuracy of potentiometric uranium analyses in uranium-aluminum alloys containing up to 55 wt % U and for evaluating the segregation existing in uranium-aluminum alloys containing as low as 7 wt % U and as high as 50 wt % U. A theory for predicting the mode of uranium segregation in these alloys was postulated. On the basis of the observed uranium segregation, the uranium content of a hypothetical fuel element was predicted by means of several sampling schemes. Dip sampling of the melt was demonstrated to be satisfactory for alloys containing 7 to 19 wt % U. However, this technique was not considered suitable for alloys containing 40 to 50 wt % U, because a significant number of samples is required from the casting or the wrought alloy to adequately represent the fuel content.

INTRODUCTION

Accurate knowledge of the uranium content of uranium-aluminum alloys is a prerequisite for control of fissionable material inventories and for predicting the uranium loading of reactor fuel elements. This knowledge depends on the effectiveness of analytical techniques for accurately determining the uranium content of alloy samples and of the selected sampling procedure for representing the uranium distribution in the alloy as a whole.

The purposes of the present investigation were threefold:

1. to determine the accuracy with which uranium assays could be made on uranium-aluminum alloys containing up to 55 wt % U,
2. to develop a consistent theory of macroscopic segregation in uranium-aluminum alloys substantiated by experimentation,
3. to illustrate the effect of various sampling methods on the predicted uranium content of fuel elements.

Standard assaying procedures for measuring the uranium content of selected samples were evaluated by analyzing small buttons of known uranium content. The developed segregation theory was

substantiated both with experimental alloys and with alloys selected from production heats. Finally, these data were interpreted in several ways to predict the uranium content of theoretical 16-plate fuel elements containing varying loadings of fissionable material.

CONCLUSIONS

Chemical assay of individual samples of uranium-aluminum alloys by potentiometric titration of the tetravalent uranium ion yields results which are on the average within 0.4% of the true uranium content. However, in terms of production accountability, the determination of U^{235} over a reasonable time period will be within 0.09% of the true uranium content.

Actual measured density values of arc-melted alloy buttons containing up to 35 wt % U show excellent correlation with the values calculated from theoretical data. Significant deviations occur in alloys more highly concentrated in uranium.

Segregation in uranium-aluminum alloys containing up to 55 wt % U and prepared by conventional casting techniques is inverse in nature because the eutectic liquid is fed, during solidification, to regions remote from the thermal center of the ingot. Inverse segregation persists in castings solidified over a wide range of cooling rates obtainable with graphite molds, and chilling the molds with liquid nitrogen does not increase the rate of cooling sufficiently to alter the mode of segregation.

Because of the good homogeneity in alloys containing 13 to 19 wt % U, dip sampling of the molten alloys will permit accounting of the weight of U^{235} in subsequently manufactured fuel elements to within 0.8% of the absolute uranium content. Accounting for U^{235} in alloys containing about 7 wt % U may deviate by 2% from the absolute uranium content.

Increasing uranium gradients occur as the composition of the alloy deviates from the eutectic composition of 13 wt % U. Cropping of alloys in the composition range 40 to 50 wt % U is recommended to improve homogeneity in resultant fuel cores.

Due to the magnitude of segregation in alloys containing 40 to 50 wt % U, dip sampling is not considered to be a representative sampling technique. To adequately predict the U^{235} content of fuel cores from these alloys, it is necessary to sample at intervals along the rolled alloy casting.

Bottom-poured and lip-poured castings of a nominal 48 wt % U-Al alloy have comparable segregation patterns, indicating that gravity segregation mechanisms are not important in alloys produced by standard techniques.

Pouring temperatures in the limited range investigated have little effect on segregation in 45 wt % U-Al alloys.

Higher mold temperatures are more conducive to the production of homogeneous castings containing 45 wt % U. However, the temperatures required are sufficiently high to be undesirable in terms of other production considerations.

ACCURACY OF URANIUM ANALYSES

Standard analytical procedures¹ for predicting the uranium content of a fuel assembly by assay of the uranium-aluminum fuel alloy also serve as the foundation for segregation studies. Therefore the first requirement of the investigation was to establish the limits of accuracy for uranium assay over a wide range of compositions in order to differentiate between real uranium gradients and spurious results stemming from the inherent inaccuracies in the analytical method. Further, this information serves to establish minimum limits for uranium variation in a fuel element based on a completely homogeneous alloy.

The standard method at ORNL for determining the uranium content of uranium-aluminum alloys involves potentiometric titration, with a ferric sulfate solution,² of the tetravalent uranium ion. In order to quantitatively evaluate this method, 13 buttons, each weighing about 10 g, were prepared by arc-melting, with the use of a tungsten-tipped electrode, the appropriate charges on a water-cooled copper hearth. The furnace atmosphere was purified argon maintained at a positive pressure of 5 to 7 psi.

¹J. E. Cunningham and E. J. Boyle, *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955* 9, 203 (1956).

²Method 121922, "Uranium, Potentiometric Ferric Sulfate Method," *ORNL Master Analytical Manual*.

The charge for each melt was weighed to ± 0.2 mg on a standard analytical balance, and the as-cast buttons were weighed after melting to evaluate any weight changes that might have occurred during processing. The maximum weight change noted in any one button was only 2.9 mg. On the basis of these observed weight losses, the maximum possible variation in uranium content for each button was calculated, assuming that all the losses were either aluminum or uranium. The expected compositional limits were thus established and eventually compared with the analytical results. The maximum possible deviation from the true uranium content resulting from weight losses was calculated to be 0.02 wt %.

In addition, the density of each button was determined prior to chemical analysis. The buttons were then entirely dissolved in an H_2SO_4 -HCl solution to eliminate sampling errors.

Results of the analytical studies are summarized in Table 1. From the data presented, it can be seen that the analytical method is equally accurate over the entire range of compositions investigated and that the magnitude of the inherent inaccuracies is small. The extreme value (button No. 6) was 0.80% from the true uranium content and the mean-absolute deviation (i.e., the deviation without regard to sign) was 0.4%. Uranium standards, run twice daily by the Special Analyses Laboratory of the Chemistry Division, indicate an accuracy on the standards of $\pm 0.2\%$. It would therefore be expected that the 0.4% value represents the total cumulative error for individual samples.

However, it should be noted that the method is not biased in either direction but rather yields results above and below the true value with about equal frequency. Thus, in terms of production accountability over a reasonable period of time, deviations should average out. The average deviation (i.e., the deviation when considering the sign of the variation) of all 13 buttons analyzed in the present work was only -0.09% from the true uranium content.

Good correlation was obtained between actual production accountability and the projected average deviation with time of -0.09% predicted from the limited number of control samples in the present work. Analysis of production records for the Process Metallurgy Section for the 12-month period ending December 1957 indicated that 58,897 g of uranium in the form of uranium-aluminum alloys had been shipped. During this time a net loss

Table 1. Accuracy of Uranium Analysis in Uranium-Aluminum Alloys

Button No.	Intended Uranium Content (wt %)	Weight Loss During Melting (g)	Uranium Content			
			Calculated - Losses Assumed To Be Uranium (wt %)	Calculated - Losses Assumed To Be Aluminum (wt %)	Analyzed (wt %)	Deviation (%)
14	12.90	0.0000	12.90	12.90	12.86	-0.31
2	13.00	0.0001	13.00	13.00	13.09	+0.69
3	18.00	0.0007	17.99	18.00	17.93	-0.39
4	18.00	0.0005	18.00	18.00	18.04	+0.22
5	25.00	0.0013	24.99	25.00	24.82	-0.72
6	25.00	0.0000	25.00	25.00	24.80	-0.80
7	35.00	0.0009	34.99	35.00	34.86	-0.40
8	35.01	0.0017	35.00	35.02	34.96	-0.11
9	45.00	0.0019	44.99	45.01	45.01	+0.02
10	45.00	0.0013	44.99	45.01	44.88	-0.27
12	52.39	0.0002	52.39	52.39	52.70	+0.59
13	52.39	0.0029	52.38	52.40	52.23	-0.30
11	55.00	0.0013	54.99	55.01	55.03	+0.05

of 25.2 g or -0.04% was realized - a value well within the predicted limit.

The theoretical density of each button was calculated with equations derived by Aronin and Klein, based on equilibrium compositions,³ and was compared with the measured density. From these data, tabulated in Table 2, it can be observed that excellent agreement was obtained between theoretical and measured densities for as-cast alloys containing 35 wt % U or less. Some divergence of theoretical from measured density occurred in alloys containing 45 to 55 wt % U as a result of the marked porosity of alloys in this compositional range.

On the basis of the foregoing analysis of analytical inaccuracies, it appears that the standard method of potentiometric titration for uranium assay introduces insignificant errors in accountability of U²³⁵ in uranium-aluminum alloys containing up to 55 wt % U.

³L. R. Aronin and J. L. Klein, *Use of a Density (Specific Volume) Method as a Sensitive Absolute Measure of Alloy Composition, and Its Application to the Aluminum-Uranium System*, NMI-1118 (Oct. 29, 1954).

THEORY OF SEGREGATION

Macroscopic or gross segregation in multicomponent alloys can be classified as one of three primary types:

Gravity. - This type of segregation occurs when one solid phase is considerably denser than the liquid from which it nucleates and tends to settle during solidification.

Normal. - This type of segregation occurs when the solute is concentrated in the last-to-freeze regions of the casting and is the type that would be predicted solely from equilibrium diagram considerations and complete solute diffusion in the melt.

Inverse. - This type of segregation occurs when the solute-rich liquid feeds through the inter-crystalline passages to the regions where final solidification and consequent contraction are taking place. This feeding of the solute-rich phase through interdendritic channels of the pasty zone, bounded by the solidus and liquidus isotherms, results in depletion of the solute phase in the last regions of the casting to solidify. Since segregation resulting from this type of feeding is the opposite of that predicted from

Table 2. Comparison of Measured and Theoretical Densities for Uranium-Aluminum Alloys

Button No.	Intended Uranium Content (wt %)	Density		
		Theoretical* (g/cc)	Measured (g/cc)	Deviation** (%)
14	12.90	3.013	3.013	0
2	13.00	3.016	3.014	-0.07
3	18.00	3.158	3.159	+0.03
4	18.00	3.158	3.159	+0.03
5	25.00	3.381	3.382	+0.03
6	25.00	3.381	3.383	+0.06
7	35.00	3.761	3.754	-0.19
8	35.01	3.761	3.753	-0.21
9	45.00	4.236	4.194	-0.99
10	45.00	4.236	4.189	-1.11
12	52.39	4.673	4.540	-1.39
13	52.39	4.673	4.608	-2.85
11	55.00	4.850	4.798	-1.07

3.3502

* $\frac{3.3502}{(1.2408 - \text{weight fraction of U})}$

Measured density - theoretical density

** $\frac{\text{Measured density} - \text{theoretical density}}{\text{Theoretical density}} \times 100\%$

equilibrium diagram considerations, it is termed "inverse."

Although it has been shown⁴ that gravity segregation can occur in uranium-aluminum alloys solidified under very special conditions, the cooling rates achieved in conventional practice are of such magnitude that this type of segregation would not be anticipated. It has also been shown that, in general, large or slowly cooled masses of metal are prone to normal segregation but that small and rather rapidly cooled masses of metal tend to exhibit inverse segregation.⁵ It has been further demonstrated that a wide freezing range is conducive to inverse segregation, although this phenomenon is not solely limited to such systems.⁶

⁴B. C. Allen and S. Isserow, *Acta Met.* 5, 465 (1957).

⁵H. C. H. Carpenter and J. M. Robertson, *Metals*, vol. 1, p 661-676, Oxford University Press, London, 1937.

⁶A. Phillips and R. M. Brick, *Metals Technol.* 4(2), 1-17 (Paper No. 785) (1937).

From the uranium-aluminum constitution diagram shown in Fig. 1, it can be seen that a rapid divergence of solidus and liquidus curves occurs on either side of the eutectic point (13 wt % U). In light of this marked divergence of solidus and liquidus curves coupled with the fact that conventionally produced uranium-aluminum alloy castings are generally small in mass and cool relatively rapidly, such alloys prepared by established techniques would be expected to manifest inverse segregation. Thus, in hypereutectic alloys (greater than 13 wt % U), a uranium-rich region should be found at the thermal center of the casting, resulting from the feeding of the aluminum-rich eutectic through interdendritic networks toward the solidifying portions which leaves behind a region of primary uranium-rich crystals. In hypoeutectic alloys the opposite effect should result, with an aluminum-rich region being located in the last-to-freeze portion of the casting.

When a very rapid cooling rate is employed, solidification throughout the casting may occur

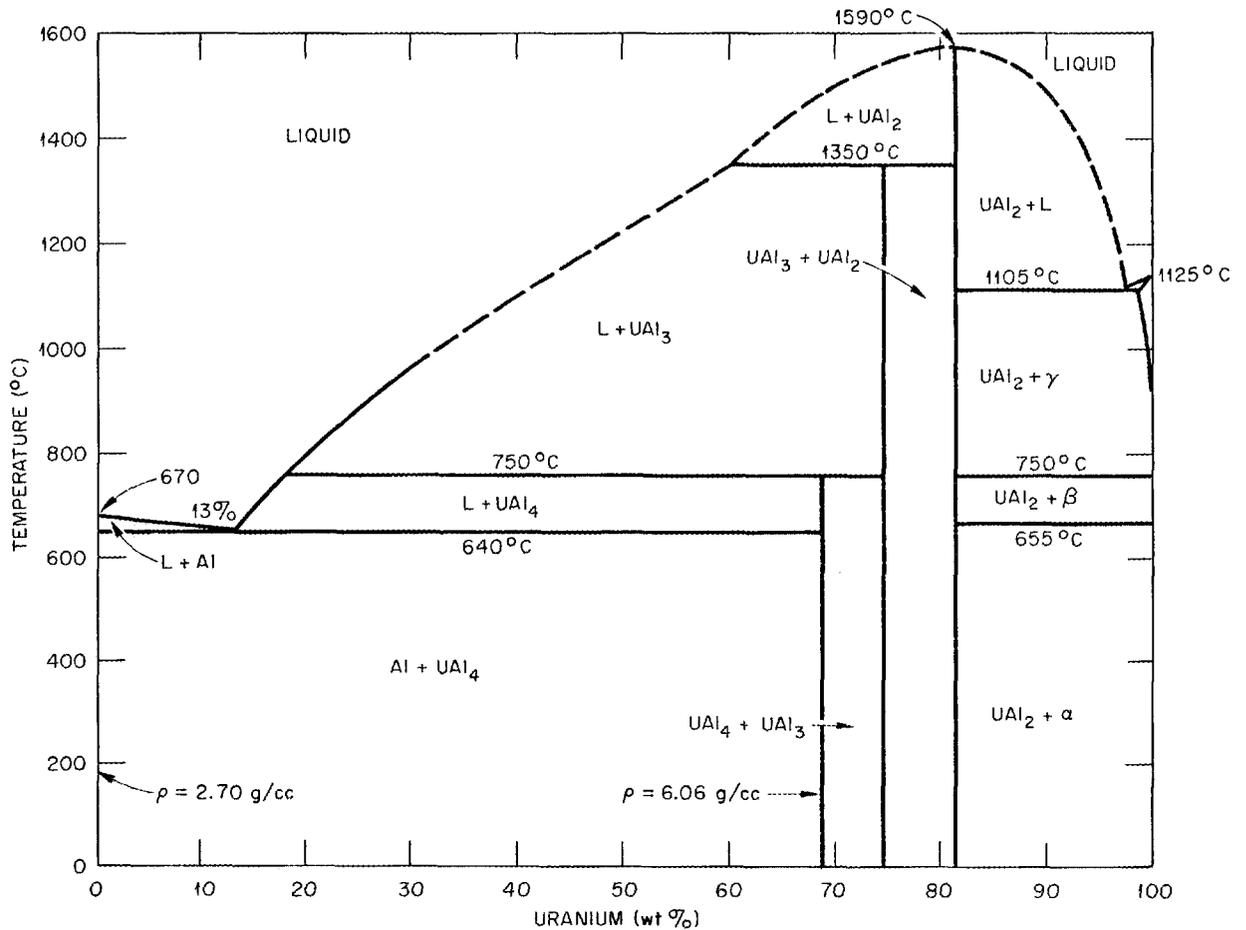


Fig. 1. Aluminum-Uranium Phase Diagram.

so quickly that feeding of the solute-rich liquid toward the solidus is greatly minimized. In such a case the casting would tend to be more homogeneous. At the other extreme, that is, with extremely slow cooling, diffusion of the solute through the liquid would be maximized and production of either a normally segregated or homogeneous casting may be possible.

The findings discussed in subsequent sections of this report substantiate the hypothesis that uranium-aluminum alloys prepared according to existing practices do, in fact, exhibit inverse segregation; also discussed are the effects of this mode of segregation on the accountability of the U^{235} isotope in fuel elements.

SEGREGATION IN ALLOYS CONTAINING LESS THAN 19 wt % URANIUM

To determine the extent of uranium segregation in uranium-aluminum alloys containing from 7 to 19 wt % U, four production heats were selected for extensive investigation. Cores obtained from these heats were ultimately used in fabricating fuel elements for initial operations in the Oak Ridge Research Reactor. The heats selected had the nominal uranium compositions of 7.30, 13.70, 16.10, and 18.65 wt %. The first composition is hypoeutectic, the second is very near the eutectic, and the last two compositions are hypereutectic.

Each heat was prepared by the appropriate charge (5000-7000 g) being melted in a graphite crucible by open-air induction and then being

poured into graphite molds at room temperature. The pouring temperature for each composition was as follows:

7.30% U	735°C
13.70% U	745°C
16.10% U	760°C
18.65% U	795°C

the mold cavity was 1.25 in. wide \times 4.75 in. long \times 10 in. deep, and the mold walls were 1 in. thick. Two castings of this size were poured from each heat.

Immediately prior to pouring the heat, the dross was skimmed from the surface of the melt and three dip-samples were taken. As established by standard procedures,⁷ two dip-samples were assayed for uranium and averaged, while the third sample was held in reserve.

Each casting was preheated to 600°C and rolled from the initial thickness of 1.25 in. to a final thickness of 0.255 in. on a 20 \times 30 in. two-high mill, 10% reductions being used per pass. Thirty-eight fuel cores 2.3 in. wide \times 2.0 in. long were punched from each hot-rolled casting, giving a total yield of 76 cores per heat. Five additional samples for uranium assay were then removed from each remaining skeleton as illustrated in Fig. 2. This skeleton sampling is not performed as standard practice for alloys in this compositional range but was employed only for the present studies. Adjacent analyses bracketed either 8 or 10 fuel cores. These samples were analyzed by the same technique (potentiometric titration) as that used for the dip-samples.

Figures 3, 4, 5, and 6 illustrate the uranium distribution in each of the eight slabs selected for study. In graphically presenting these data, it was presumed that the uranium gradient between successive analyses was linear. Also shown in each figure is the intended uranium content; the uranium content of the heat as determined by the average of two dip-samples; and the uranium content as determined by direct averaging of the 10 samples taken from the punched skeletons which was designated as the "heat average." From these figures, it will be noted that in every

case a uranium gradient occurs in those regions which were originally the top of the casting. In the hypoeutectic alloy (Fig. 3), the gradient is negative, that is, the uranium content in this region is below that of adjacent areas, while in the hypereutectic alloys the uranium gradient is positive. The sharpness of the gradient can be seen to increase as the composition deviates progressively from the eutectic; in the nominal 13.70 wt % U-Al alloy, only a very slight gradient is observed, while in the 18.65 wt % U-Al alloy a marked gradient is observed, with the composition rising in the top of one billet to 19.79 wt % U. The magnitude of these gradients correlates closely with divergence of the solidus and liquidus curves shown in Fig. 1.

The observed mode of uranium segregation is consistent with the theory outlined in "Theory of Segregation." In hypereutectic alloys the aluminum-rich eutectic feeds away from the top and center of the casting, leaving behind a uranium-rich region, while in hypoeutectic alloys, eutectic feeding creates a uranium-poor region at the top and center of the casting.

Based on the data presented in Figs. 3 to 6, the U^{235} content of a hypothetical 16-plate aluminum fuel element was predicted by several different methods and compared with the U^{235} content as determined by dip sampling. Dip sampling was selected as a base, since it is the presently accepted criterion in accounting for the U^{235} content of fuel elements. For the purposes of calculation, a constant core volume was assumed and the density equivalent to a given weight percentage of uranium was computed by calculations of the type described in "Accuracy of Uranium Analyses." On this basis, the U^{235} content was calculated by using

1. the average of two dip-sample analyses as representative of all 16 cores in the fuel element,
2. the intended analysis as representative of all 16 cores in the fuel element,
3. the "heat average" (average of all 10 skeleton samples) as representative of all 16 cores in the fuel element,
4. the average of each pair of skeleton samples as representative of the 8 or 10 cores which it bracketed and then selecting the cores by (a) random selection of two cores bracketed by each pair of samples, (b) specially selecting

⁷J. E. Cunningham and E. J. Boyle, *Proc. Intern. Conf. Peaceful Uses Atomic Energy, Geneva, 1955* 9, 205 (1956).

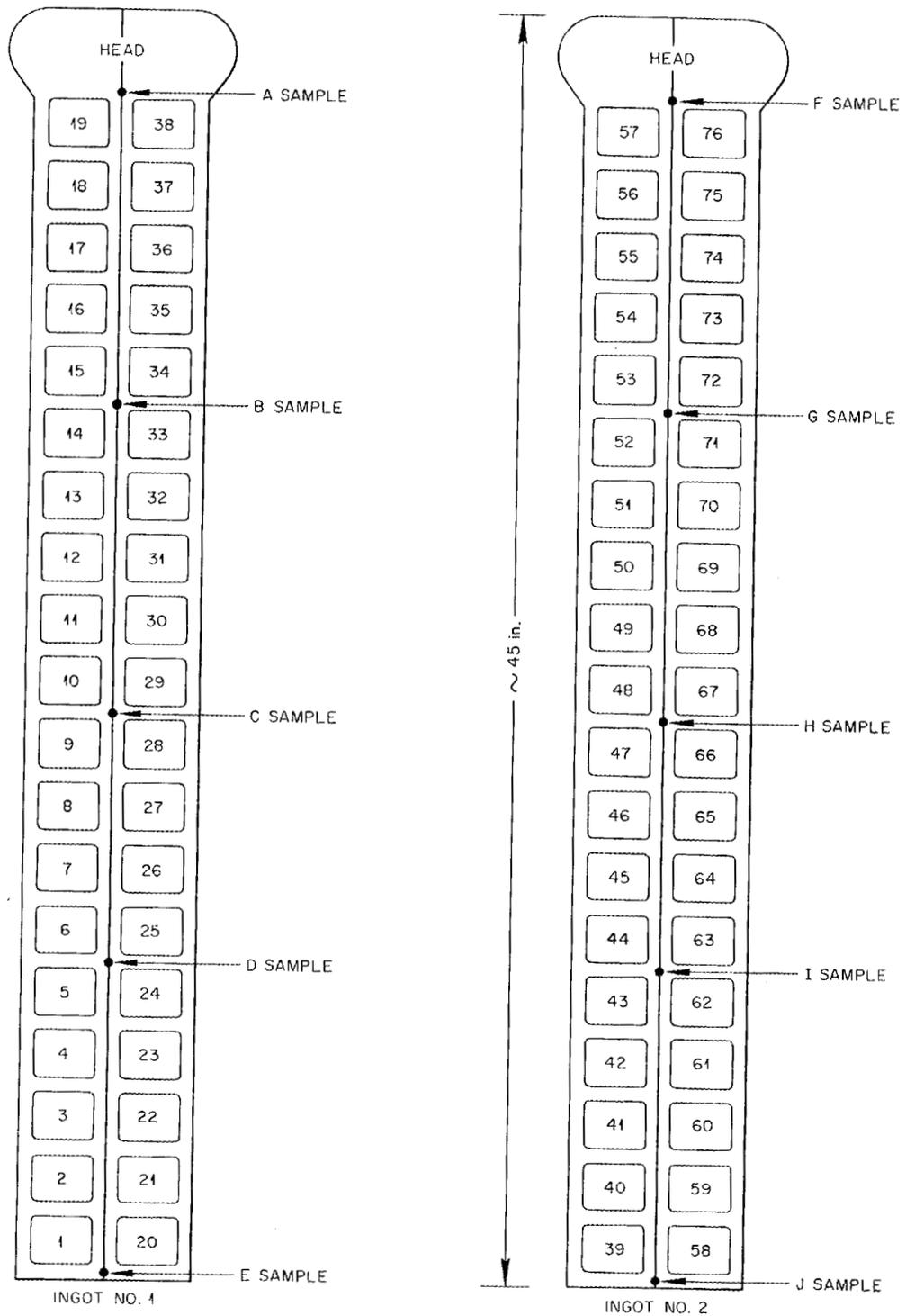


Fig. 2. Skeleton Sampling Diagram for Alloys Containing Less Than 20 wt % U.

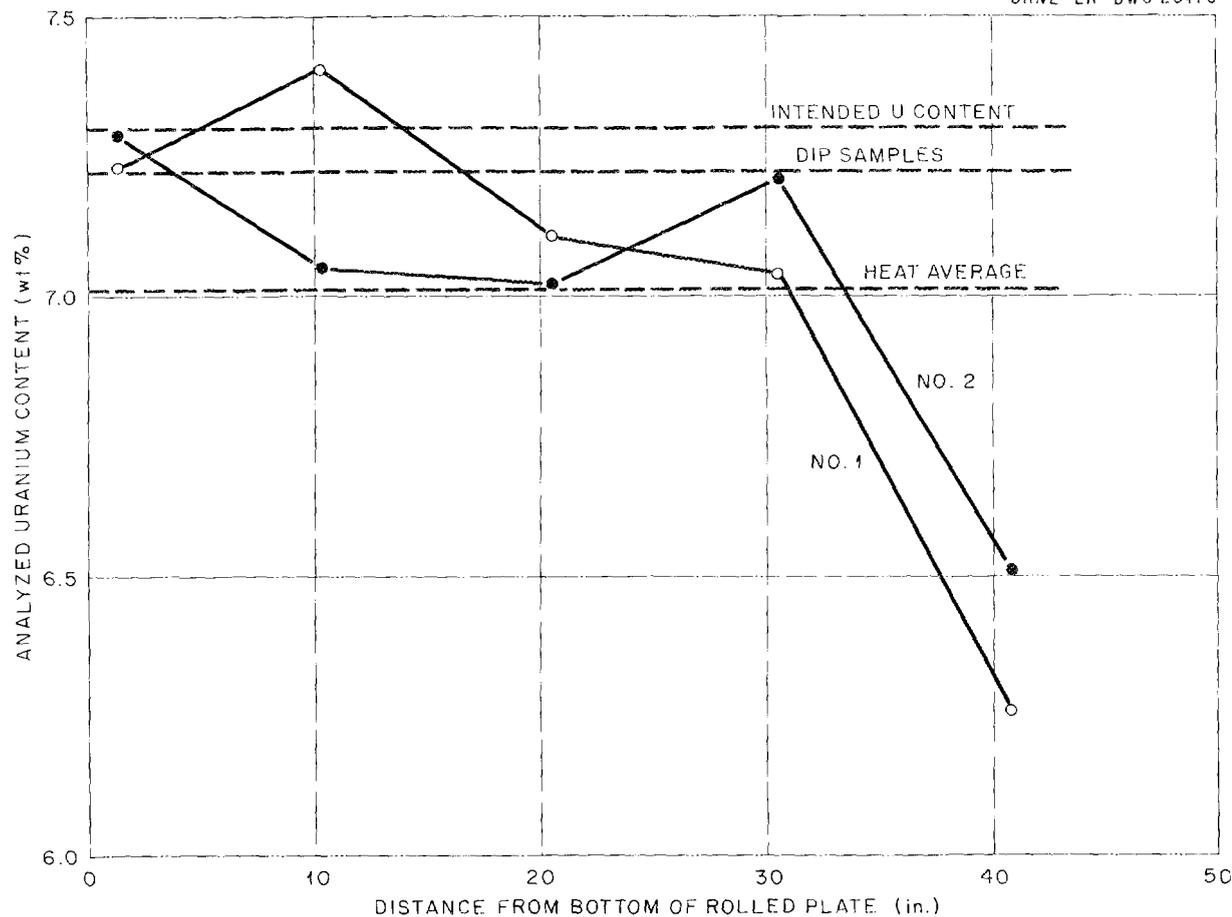


Fig. 3. Uranium Distribution in Rolled Castings of Nominal 7.30 wt % U-Al Alloy (Heat D-633R).

the 16 cores containing the greatest amount of uranium, or (c) specially selecting the 16 cores containing the least amount of uranium.

It is felt that the weighted average of method 4(a) is the most accurate method for the selection of 16 cores. Sample calculations for one heat (D665) are given in the Appendix. Similar calculations for all four heats are summarized in Table 3. Table 4 gives the differences in uranium content between the value predicted by dip sampling and the values predicted by each of the other described techniques.

Selecting the data in Tables 3 and 4 for the nominal 18.65 % U alloy for purposes of discussion, it can be seen that the difference between the uranium content determined by dip sampling and the uranium content determined by

the most accurate method (weighted average of two cores per pair of analyses, Table 3) is 1.33 g of U^{235} . This is equivalent to a measurement error of 0.8% in the U^{235} content. Further, it should be noted that in the worst conceivable case (weighted average of 16 cores of highest U content, Table 3), with all cores for a given 16-plate fuel element being selected from the top of the two billets, the difference between the uranium content as measured by dip sampling and the uranium content as determined by the weighted average and special selection is 5.59 g of U^{235} or 3.4%.

On the basis of the preceding analysis, it appears that the uranium content of a given fuel assembly determined by dip sampling will deviate from the best estimate by about 2% for alloys

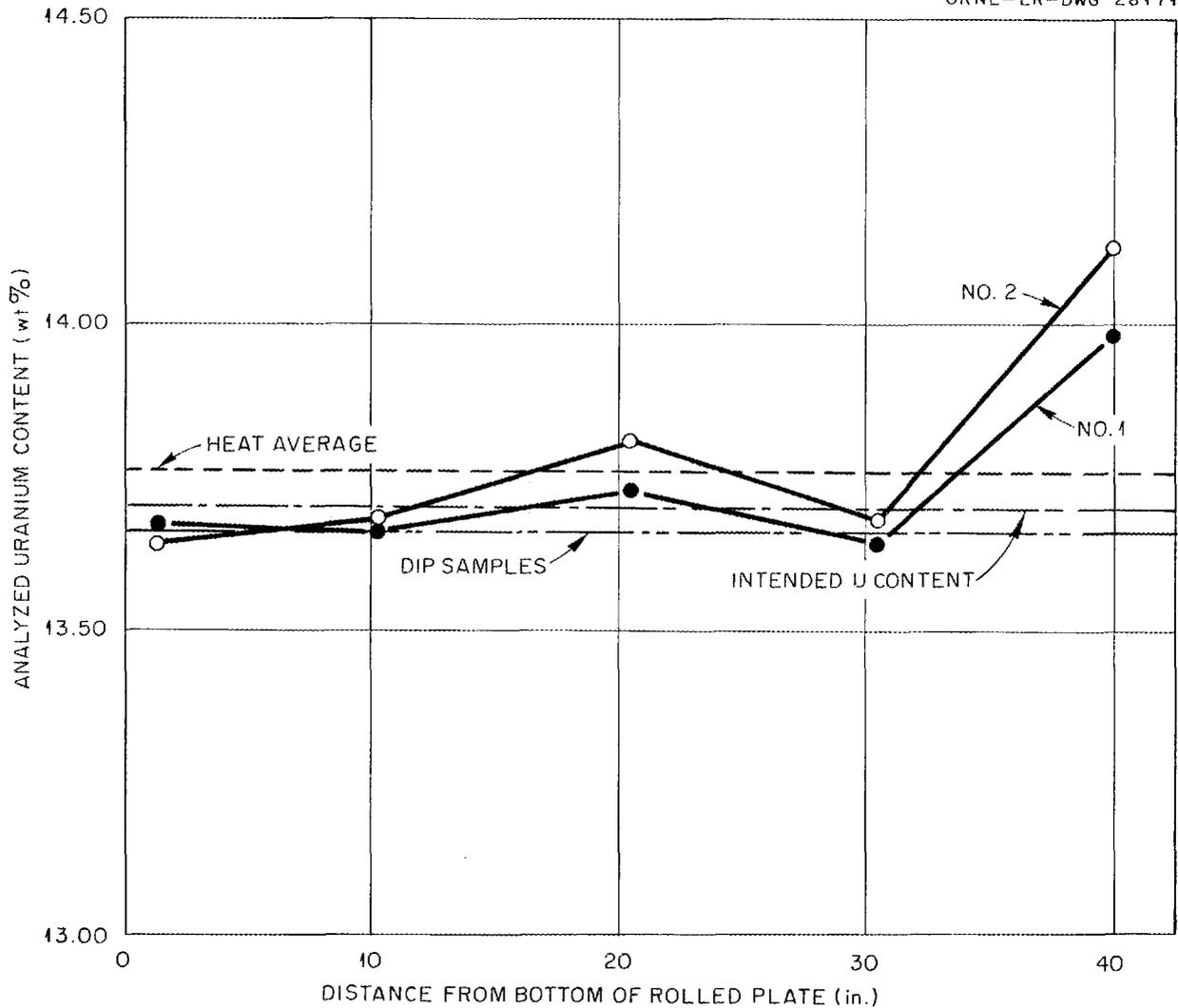


Fig. 4. Uranium Distribution In Rolled Castings of Nominal 13.70 wt % U-Al Alloy (Heat D-640).

Table 3. Fuel Content of 16-Plate Fuel Element as Predicted by Several Sampling Techniques*

Heat**	Intended Uranium Content (wt %)	U ²³⁵ Content (g)					
		Based on Dip Samples	Based on Intended Analysis	Based on "Heat Average"	Based on Weighted Average of 2 Cores per Pair of Analyses	Based on Weighted Average of 16 Cores of Highest U Content	Based on Weighted Average of 16 Cores of Lowest U Content
D-633R	7.30	57.39	58.06	55.63	56.07	58.05	53.27
D-640	13.70	114.91	115.28	115.86	115.63	116.87	114.88
D-651	16.10	139.16	138.47	140.07	139.54	142.73	137.23
D-665	18.65	163.33	164.29	165.41	164.66	168.92	162.90

*For alloys containing uranium enriched 93.5% in U²³⁵ isotope.
**Two castings per heat.

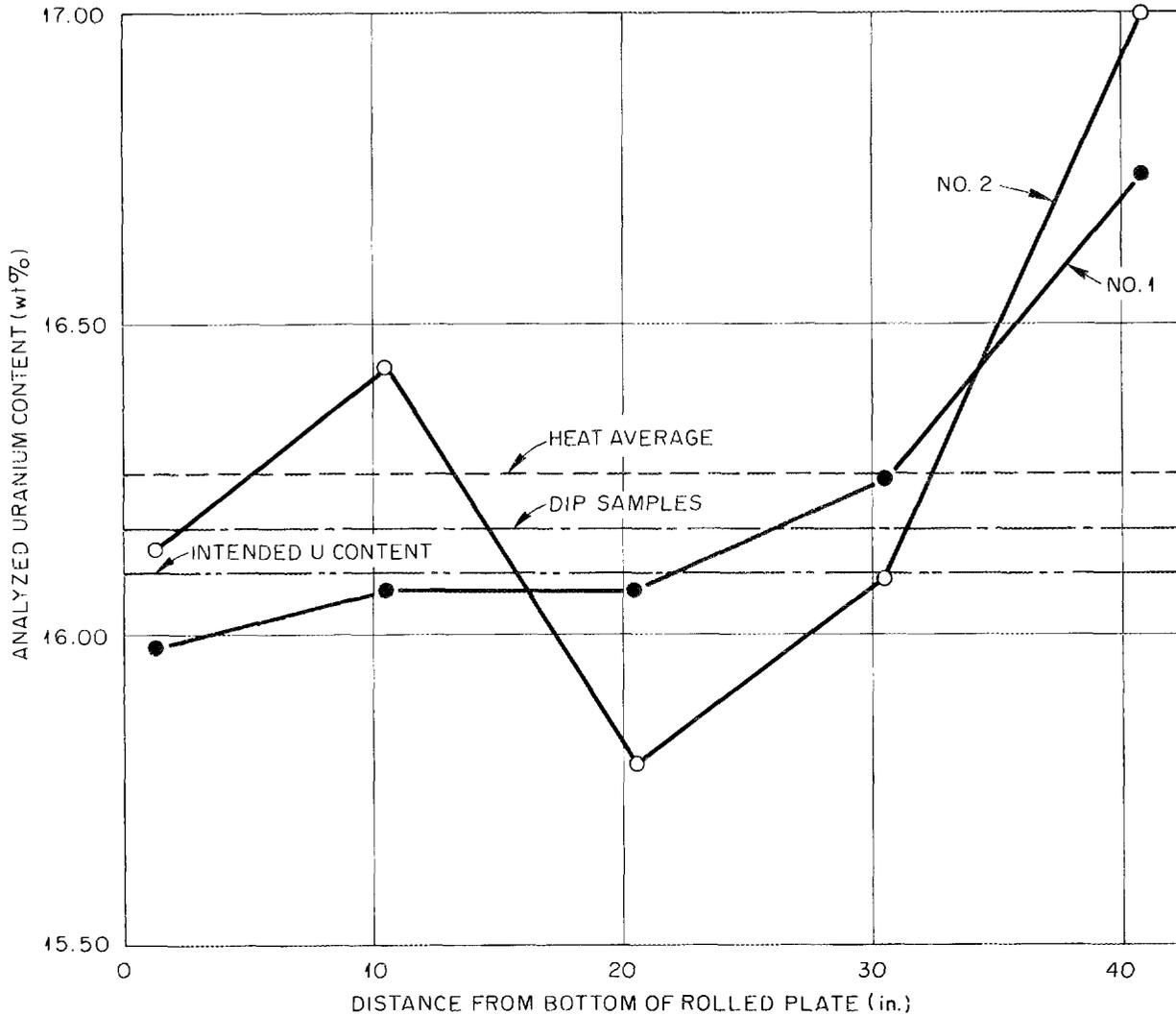


Fig. 5. Uranium Distribution in Nominal 16.10 wt % U-Al Alloy (Heat D-651).

Table 4. Difference in U²³⁵ Content Predicted by Dip-Sampling Technique* and That Predicted by Other Methods

Heat No.	Intended Uranium Content (wt %)	U ²³⁵ Content									
		Based on Intended Analysis		Based on "Heat Average"		Based on Weighted Average of 2 Cores per Pair of Analyses		Based on Weighted Average of 16 Cores of Highest U Content		Based on Weighted Average of 16 Cores of Lowest U Content	
		Grams	Per Cent	Grams	Per Cent	Grams	Per Cent	Grams	Per Cent	Grams	Per Cent
D-633R	7.30	-0.67	-1.2	1.76	3.1	1.32	2.3	-0.66	-1.2	4.12	7.3
D-640	13.70	-0.27	-0.2	-0.95	-0.8	-0.74	-0.6	-1.96	-1.7	0.03	0
D-651	16.10	0.69	0.5	-0.91	-0.7	-0.38	-0.3	-3.57	-2.6	1.93	1.4
D-665	18.65	-0.96	0.6	-2.08	-1.3	-1.33	-0.8	-5.59	-3.4	0.43	0.2

*For alloys containing uranium enriched 93.5% in U²³⁵ isotope.

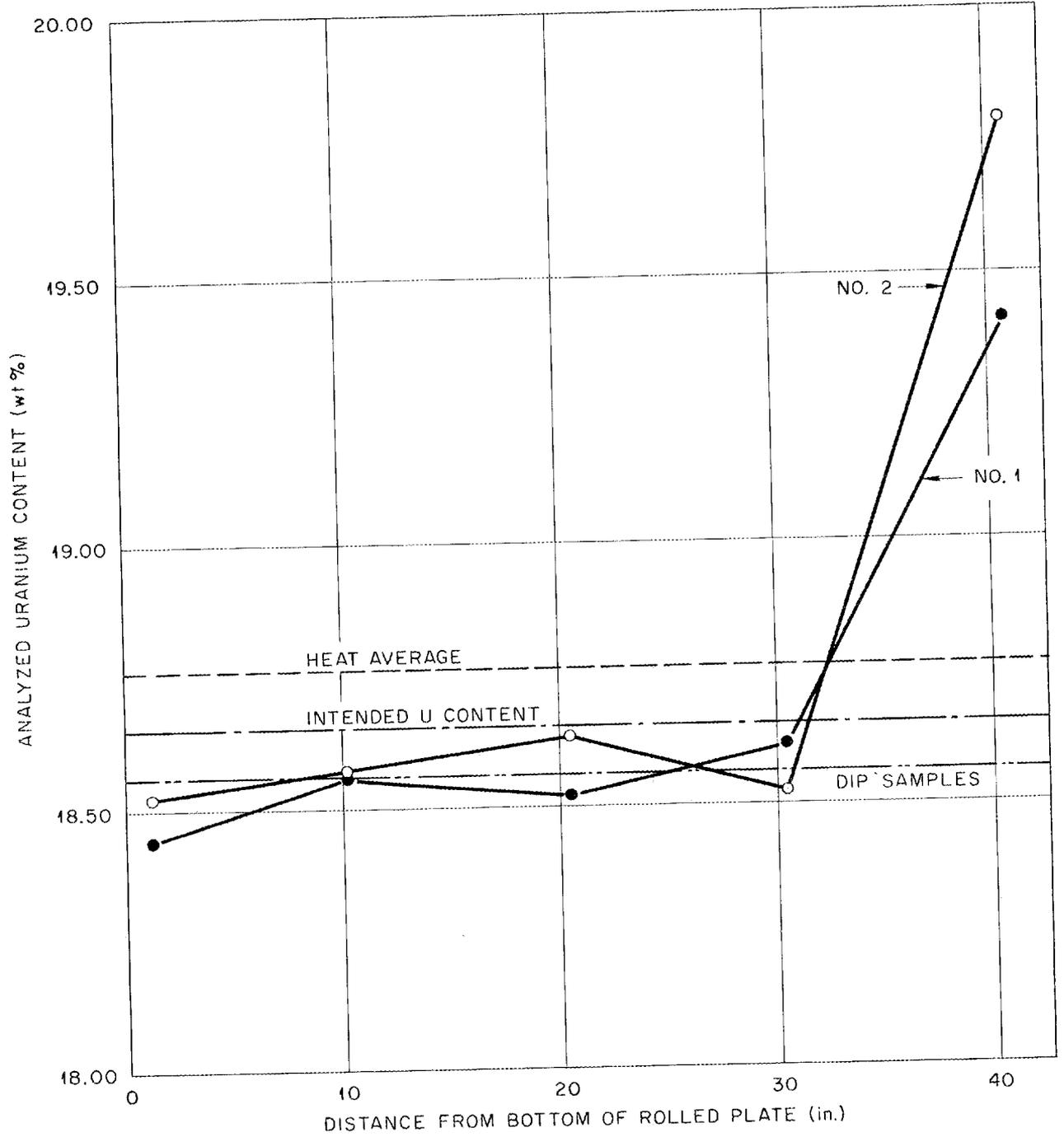


Fig. 6. Uranium Distribution in Rolled Castings of Nominal 18.65 wt % U-Al Alloy (Heat D-665).

containing 7.30 wt % U and by less than 0.8% for alloys containing 13 to 19 wt % U. Reactivity measurements of MTR fuel elements verify this conclusion, and portions of such data have been reported previously.⁸ However, it is conceivable that larger variations are possible, if a fortuitous selection of cores is made.

SEGREGATION IN ALLOYS CONTAINING 40-50 wt % URANIUM

Alloys in the composition range 40 to 50 wt % U are treated separately in this report, not because of any anticipated differences in mode of segregation but rather because these alloys are of specific interest for Foreign Reactor Program fuel elements where enrichment in the U²³⁵ isotope is limited to 20%. Although no differences in the mode of segregation would be predicted on the basis of the previously described solidification mechanism, differences in magnitude would certainly be expected by virtue of the wide temperature gradient between solidus and liquidus and the wide compositional gradient between the first freezing solid (UAl₃) and the last freezing solid (eutectic mixture). For example, considering a 45 wt % U-Al alloy, the temperature gradient existing between the initiation and completion of crystallization is about 510 Centigrade degrees and the compositional gradient of the uranium for the same alloy is 61 wt %.

In view of the expected magnitude of segregation, attention was directed toward determining the effect of two basic casting variables on the homogeneity of these alloys: mold temperature and pouring temperature.

Although the liquidus temperature for alloys of less than 25% U has been determined,⁹ the liquidus curve can only be estimated for alloys richer in uranium. The inferred liquidus temperature for a 45 wt % U-Al alloy, shown in Fig. 1, is 1150°C. Consequently a standard pouring temperature of 1175°C was adopted for this particular composition. To compare the segregation in castings poured at 50°C above, as well as below, the selected 1175°C pouring temperature, a series of three cylindrical billets was prepared. In each case the molten uranium-

aluminum alloy at the desired temperature was poured into a graphite mold 1 $\frac{3}{4}$ in. in diameter \times 8 in. in depth, whose wall temperature was 50°C. The cylindrical castings were sectioned along a vertical center line, and drillings were taken at 1-in. intervals from bottom to top for chemical analyses. Results of this study, which are presented in Fig. 7, indicate that in the range of temperatures considered, pouring temperature has virtually no effect on the mode or magnitude of uranium segregation. Further, the observed segregation pattern is a striking illustration of the inverse segregation occurring in these alloys under the described conditions.

Investigation of the effects of mold temperature on segregation was accomplished with a similar series of castings. In this case the pouring temperature was maintained at 1175°C, and the mold temperature varied from subzero to furnace-cooling of the melt. On the basis of the inverse segregation theory, where feeding of eutectic liquid is the controlling factor, it was envisioned that the very rapid cooling rates would minimize flow of the eutectic liquid through the interstices. In such a situation, a relatively homogeneous billet would be anticipated. It was also felt that with very slow cooling rates (furnace cooling) the diffusion processes would predominate and a homogeneous product might again be produced. To test these hypotheses, one casting was poured into a mold chilled with liquid nitrogen to about -185°C, and another casting was melted, heated to 1175°C, and allowed to furnace-cool in the crucible. In addition, intermediate mold temperatures of 25, 160, and 500°C, where appreciable inverse segregation was anticipated, were investigated. These results are summarized in Fig. 8. From the data presented it can be observed that castings of the described shape poured into molds at 500°C or furnace-cooled exhibited only random segregation; this observation substantiates the conjecture that, when a melt freezes under either of these conditions, diffusion supplants feeding as the mode-controlling process, creating randomly or normally segregated billets. As was predicted, billets poured into molds at 160 and 25°C exhibited pronounced inverse segregation. The casting poured into the mold, chilled with liquid nitrogen to -185°C, also exhibited a marked degree of inverse segregation, suggesting that the cooling rate obtained was

⁸W. C. Francis, *Examination of Boron Content in ETR 1-4 Fuel Element by Means of Fuel Scan and Transmission Measurements*, IDO-16354 (May 25, 1956).

⁹H. A. Saller et al., *A Study of Aluminum-Uranium Alloys*, BMI-1066 (Jan. 19, 1956).

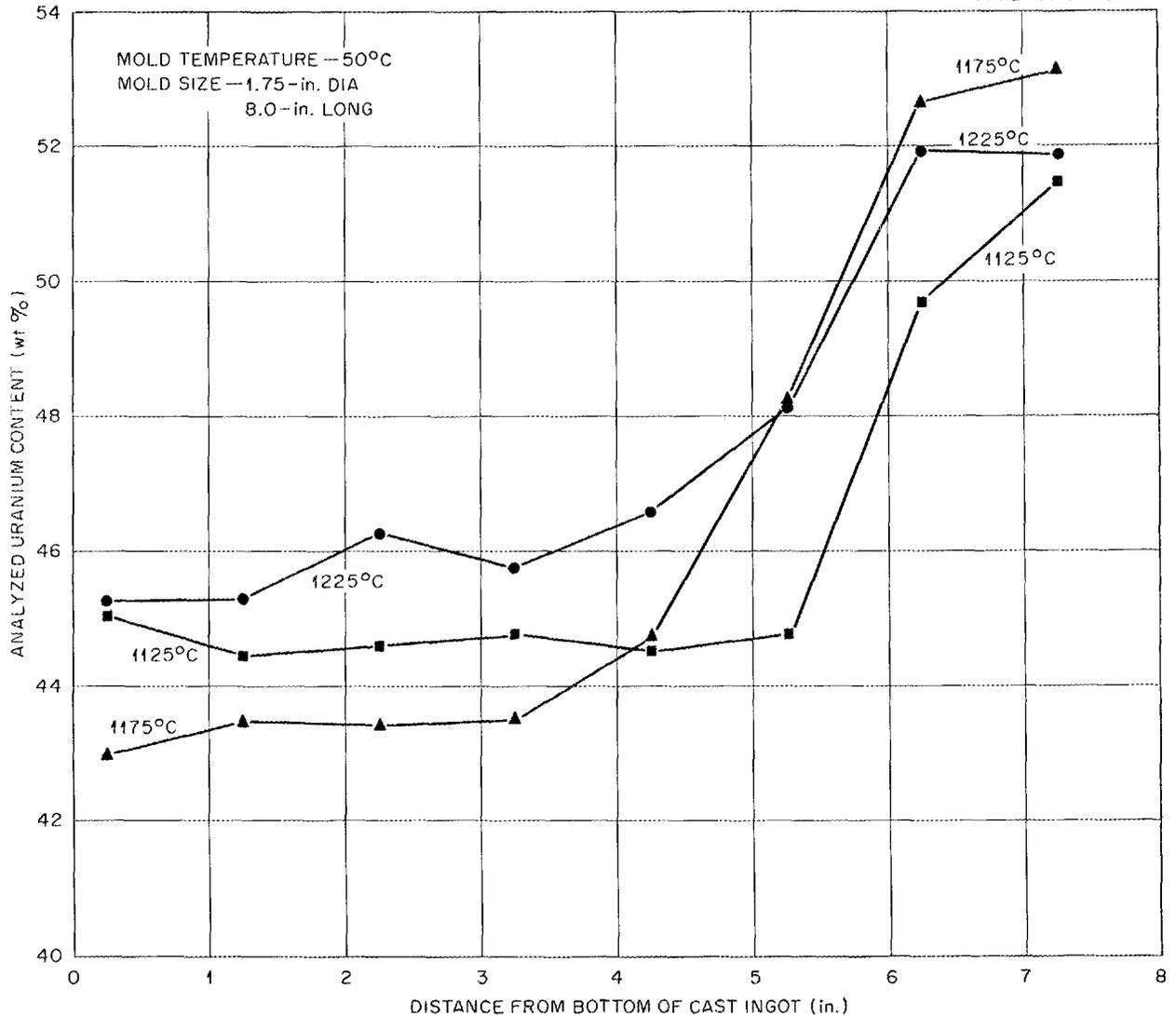


Fig. 7. Effect of Pouring Temperature on Uranium Segregation in 45 wt % U-Al Alloys.

insufficient to eliminate interdendritic feeding. It should be pointed out that although such practices are theoretically of interest, the attainment of very rapid or very slow cooling rates may not be desirable from a manufacturing point of view, and economics may dictate selection of a method which is partially or entirely conducive to inverse segregation.

A mold temperature of 300–350°C was finally adopted as a compromise condition for the production of fuel alloy slabs at ORNL, and pouring temperatures were maintained at 1175°C except for certain experimental heats.

In producing alloy slabs containing 40 to 50 wt % U for fuel element application, two different alloys were used. One was a nominal uranium-aluminum alloy and the other was a uranium-aluminum alloy containing a ternary addition of 3 wt % Si. The silicon additions were made to suppress the peritectic reaction occurring at 750°C, wherein UAl_3 transforms to UAl_4 . These modified alloys are more easily fabricated because of the reduced volume of intermetallic compound for a given weight percentage of uranium. Cooling curves made on the ternary alloy indicated that the eutectic temperature was, within the accuracy

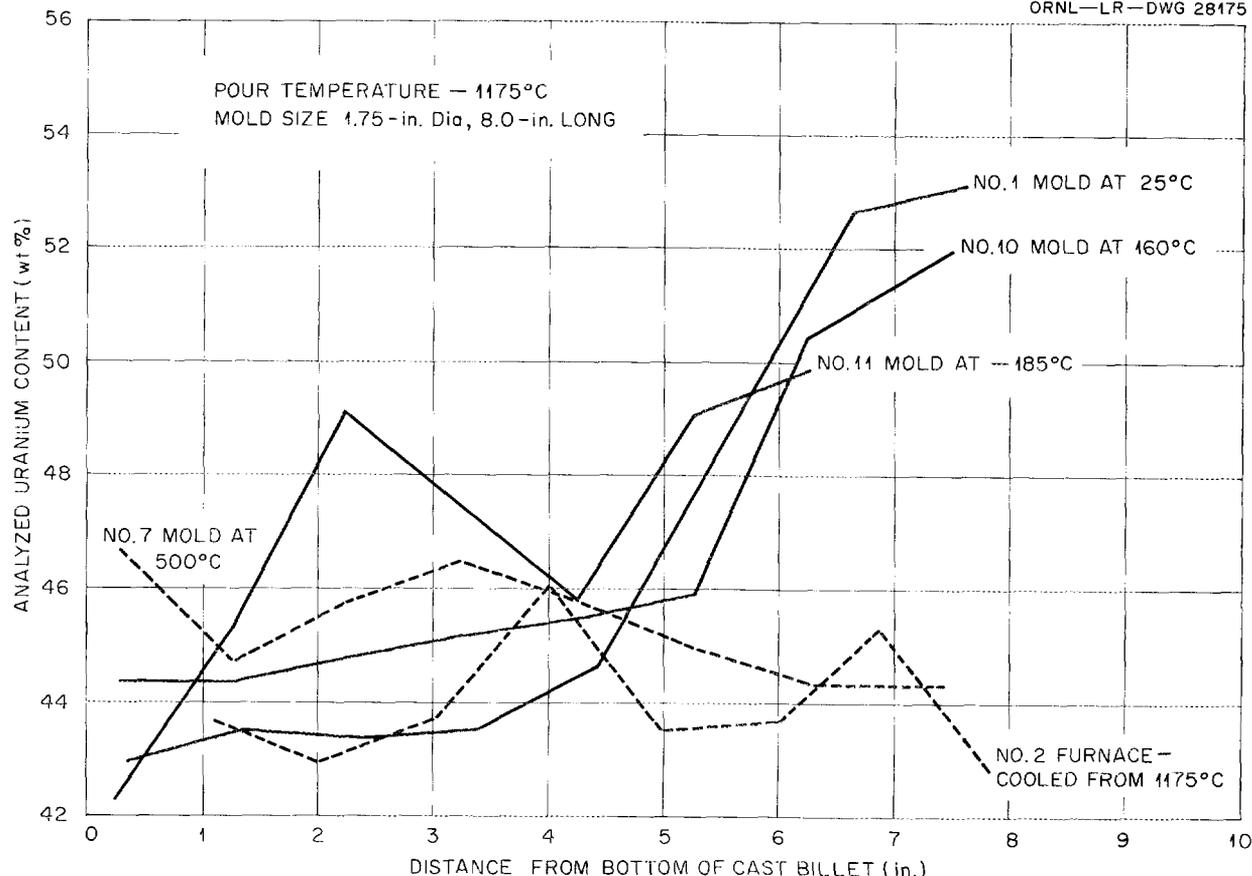


Fig. 8. Effects of Mold Temperature on Segregation in 45 wt % U-Al Alloys.

of the measurements ($\pm 5^\circ\text{C}$), unchanged from the reported value of 640°C . In view of these considerations, it was presumed that the mode of segregation in both the silicon-free and silicon-modified alloys would be identical. Data presented in Fig. 9 substantiate this supposition. Comparison of the data for billets Si-7-S, a silicon-free alloy, and Si-36-S, a silicon-modified alloy, indicates that the magnitude and pattern of segregation were about the same for each casting.

In all the experiments with high-uranium-content alloys the possibility existed that the selected pouring temperature of 1175°C was actually below the liquidus temperature and that primary UAl_3 could nucleate and then settle in the crucible under the influence of gravity prior to lip pouring. The manifestations of such segregation in the solidified casting would be identical to those which have been ascribed to feeding segregation. To prove that this was not the case, a casting identical

to Si-36-S was bottom-poured. If the segregation pattern in the bottom-poured casting was the same as that of the lip-poured casting, then, of course, the gravity segregation hypothesis could be eliminated. The uranium distribution for this bottom-poured billet (Si-35-S), which is also included in Fig. 9, indicates that the mode of segregation is indeed identical to that for the lip-poured alloys.

Since appreciable gradients are present in the upper portions of these castings, this segregated region was removed by cropping at a point $9\frac{1}{2}$ in. up from the bottom as indicated in Fig. 9, yielding reasonably homogeneous stock for subsequent fabrication.

For the sake of comparison with the highly enriched production heats discussed in the previous section, two production heats of a nominal 48.5 wt % U-3 wt % Si-Al, which was enriched 20% in the U^{235} isotope, were analyzed

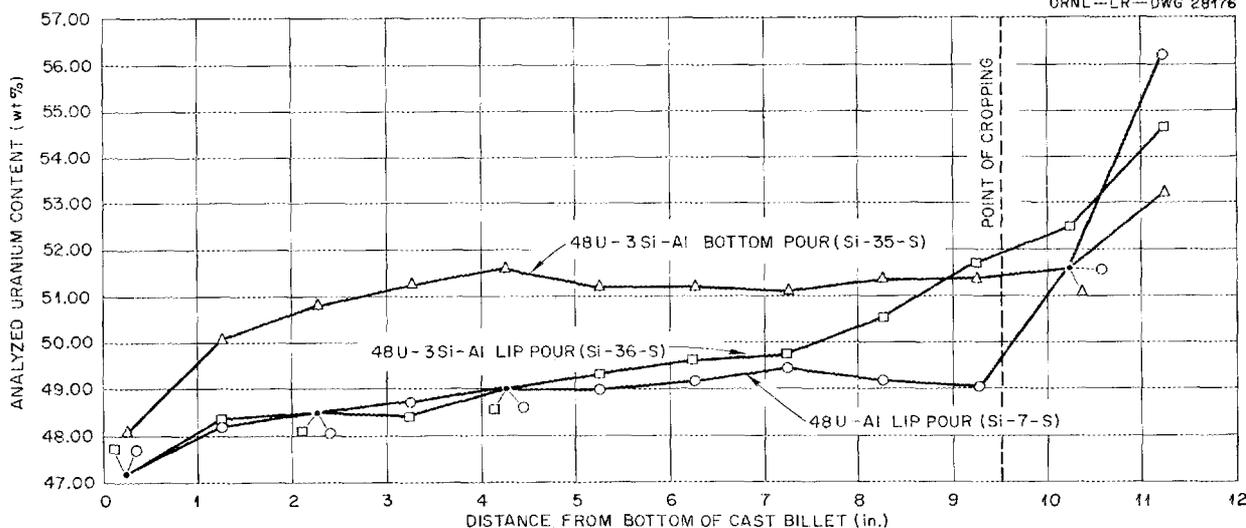


Fig. 9. Uranium Distribution in Nominal 48 wt % U-Al Alloy Castings.

in a similar fashion. (A more extensive analysis of segregations in nominal 48 wt % U-Al alloys has been described previously.¹⁰)

No dip samples were taken from either of these heats, since a heavy dross forms in these highly concentrated uranium alloys, rendering the removal of dip samples a questionable practice. Unlike the lower uranium-bearing alloys, only one slab was obtained per heat. Each slab was cropped $9\frac{1}{2}$ in. from the bottom as previously mentioned and hot-rolled at 600°C to a thickness of 0.227 in. Since alloys in this compositional range are inherently brittle and prone to edge cracking, a core yield of only 16 cores 2.3 in. wide \times 3.0 in. long was obtained from each heat. The skeleton remaining after the cores were punched was sampled in a manner somewhat similar to that shown in Fig. 3. The actual sampling plan for these two heats is shown in Fig. 10. For the purposes of subsequent analysis, the pairs of side-by-side samples (A + F, B + G, etc.) were averaged together, and the average of adjacent bottom-to-top pairs of analyses was then taken as representative of the four cores bracketed. Figure 11 plots the averaged side-by-side samples as a function of location for the two selected heats. It is obvious from the data presented that

even after cropping and hot-rolling, manifestations of inverse segregation remain, with a uranium spread from bottom-to-top in the rolled and cropped alloy of about 2 wt %. Also shown in this plot are the intended uranium level and the uranium content predicted by the previously described "heat average" method.

For each of these heats the U^{235} content of the hypothetical 16-plate fuel element was determined in four different ways by performing calculations¹¹ similar to those described in the Appendix. Since all 16 cores from each heat were required for the hypothetical fuel element, only one weighted average calculation could be made instead of the maximum, minimum, and best-estimate calculations employed with the highly enriched alloys. The dip-sample method used for alloys containing highly enriched uranium was for the sake of the present analysis, replaced by a uranium assay based on the mean of the top and bottom samples only.

Results of the above calculations are shown in Table 5. The data, based only on the usable portion of the alloy, reveal that the average uranium concentration in the alloy is 2.4% less than the intended concentration. This difference

¹⁰W. C. Thurber, J. H. Erwin, and R. J. Beaver, *The Application of a Nominal 48 wt % U-Al Alloy to Plate-Type Aluminum Research Reactor Fuel Elements*, ORNL-2351 (Feb. 25, 1958).

¹¹The core volume for alloys in the range 40 to 50 wt % U was assumed to be 25.62 cm^3 instead of 18.54 cm^3 used for alloys containing less than 20 wt % U.

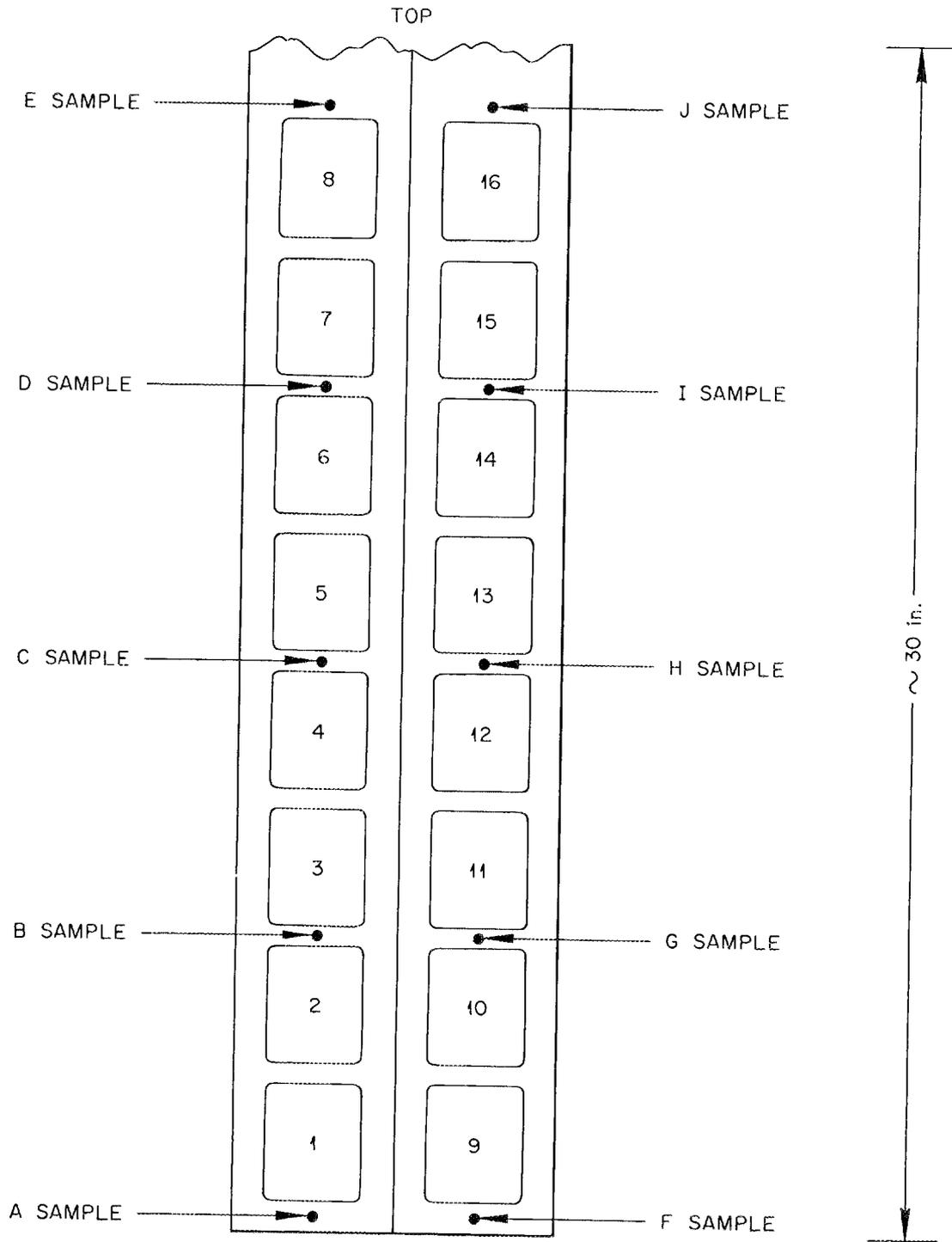


Fig. 10. Skeleton Sampling Diagram for Alloys Containing 40-50 wt % U.

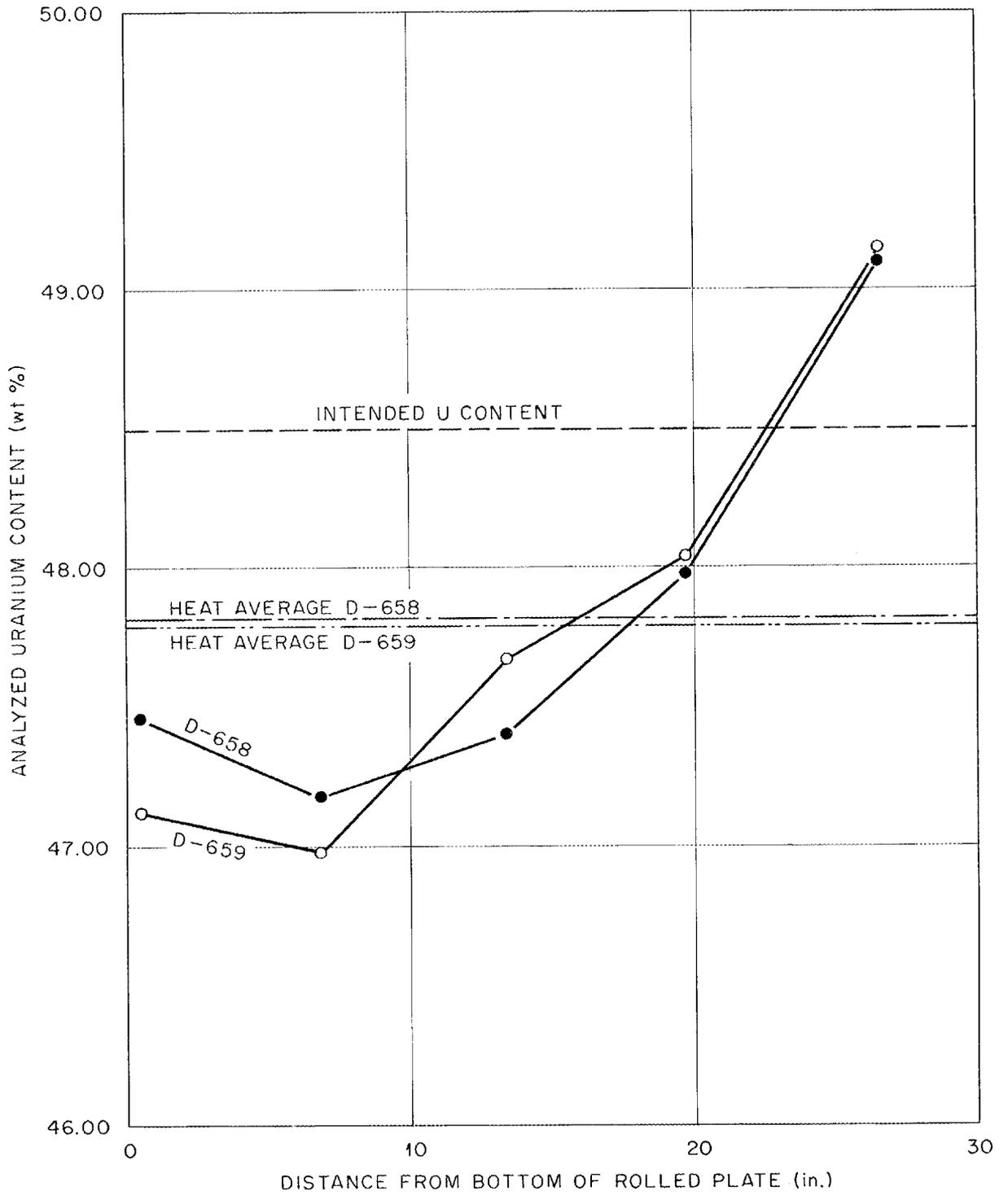


Fig. 11. Uranium Distribution in Rolled Castings of a Nominal 48.5 wt % U-3 wt % Si-Al Alloy.

Table 5. Fuel Content of 16-Plate Fuel Element as Predicted by Several Sampling Techniques*

Heat No.**	Intended Alloy Composition (wt %)	U ²³⁵ Content (g)			
		Based on Intended Analysis	Based on "Heat Average"	Based on Weighted Average of 4 Cores per Pair of Analyses	Based on Average of Top and Bottom Samples Only
D-658	48.5	176.20	172.17	171.56	174.89
D-659	48.5	176.20	172.00	171.59	173.99

*For alloys containing uranium enriched 20% in U²³⁵ isotope.

**One casting per heat.

is readily explained by the fact that the uranium segregates to the "head" of the casting, which is subsequently cropped and scrapped. It is apparent that an increase of this order of magnitude (2.4%) must be made in the uranium charged for a given heat to compensate for the loss of uranium in the usable portion of casting, due to the segregation pattern. The prediction of the U²³⁵ content based on the weighted average of four cores per pair of analyses is considered to be the most accurate figure, and it can be seen that the values based on the "heat average" agree to within 0.4% of this best estimate. However, the values based on the average of the top and bottom samples only

are nearly 2% higher. Such a limited sampling method is not considered adequate. Either the heat average or weighted average technique appears to be acceptable.

ACKNOWLEDGMENT

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Appendix

SAMPLE CALCULATION OF URANIUM CONTENT OF FUEL ELEMENT CONTAINING NOMINAL 18.65% U-AL ALLOY (HEAT D-665)

Assumptions

Core volume, 18.54 cm³

U²³⁵ enrichment, 93.5%

Number of cores per fuel element, 16

$$E = \frac{3.3597}{1.2443 - x}, \text{ where } E \text{ is density in g/cm}^3 \text{ and } x \text{ is the weight fraction of uranium}^{12}$$

Assay of samples from heat D-665

Intended analysis, 18.65 wt % U

Dip-samples analyses, 18.56 wt % U

Skeleton analyses, wt % U (see Fig. 2), where

A = 19.41	F = 19.79
B = 18.61	G = 18.52
C = 18.52	H = 18.63
D = 18.56	I = 18.57
E = 18.44	J = 18.52

U²³⁵ Content of Fuel Element Based on Intended Analysis

$$E = \frac{3.3597}{(1.24 \times 43 - 0.1865)} = 3.176 \text{ g/cm}^3$$

$$\begin{aligned} U_i &= \text{core density} \times \text{core volume} \times \text{U content of alloy} \times \text{U}^{235} \text{ enrichment} \times \text{number of} \\ &\quad \text{plates per element} \\ &= 3.176 \times 18.54 \times 0.1865 \times 0.935 \times 16 \\ &= 164.29 \text{ g of U}^{235} \end{aligned}$$

U²³⁵ Content Based on Dip-Sample Analyses

$$E = 3.173 \text{ g/cm}^3$$

$$\begin{aligned} U_i &= 3.173 \times 18.54 \times 0.1856 \times 0.935 \times 16 \\ &= 163.33 \text{ g of U}^{235} \end{aligned}$$

U²³⁵ Content Based on "Heat Average" of All 10 Skeleton Analyses

$$E = 3.179 \text{ g/cm}^3$$

$$\begin{aligned} U_i &= 3.179 \times 18.54 \times 0.1876 \times 0.935 \times 16 \\ &= 165.41 \text{ g of U}^{235} \end{aligned}$$

¹²L. R. Aronin and J. L. Klein, *Use of a Density (Specific Volume) Method as a Sensitive Absolute Measure of Alloy Composition, and Its Application to the Aluminum-Uranium System*, NMI-1118 (Oct. 29, 1954).

**U²³⁵ Content Based on Weighted Average of Adjacent Pairs of Skeleton Samples
and Selection of Two Cores from Between Each Pair of Analysis**

$$\frac{A + B}{2} = \frac{19.41 + 18.61}{2} = 19.00 \text{ wt \% U}$$

$$E_{AB} = \frac{3.597}{(1.2443 - 0.1900)} = 3.187 \text{ g/cm}^3$$

$$U_{AB} = 3.187 \times 18.54 \times 0.1900 \times 0.935 \times 2 \text{ (cores)} \\ = 20.99 \text{ g of U}^{235}$$

Calculating similarly,

$$U_{BC} = 20.42 \text{ g of U}^{235}$$

$$U_{CD} = 20.40 \text{ g of U}^{235}$$

$$U_{DE} = 20.34 \text{ g of U}^{235}$$

$$U_{FG} = 21.20 \text{ g of U}^{235}$$

$$U_{GH} = 20.44 \text{ g of U}^{235}$$

$$U_{HI} = 20.47 \text{ g of U}^{235}$$

$$U_{IJ} = 20.40 \text{ g of U}^{235}$$

$$U_i = U_{AB} + U_{BC} + U_{CD} + U_{DE} + U_{FG} + U_{GH} + U_{HI} + U_{IJ} \\ = 164.66 \text{ g of U}^{235}$$

**U²³⁵ Content Based on Weighted Average of Adjacent Pairs of Skeleton Samples
and Selection of the 16 Cores of Greatest Uranium Content**

$$U_i = \frac{U_{FG}}{2} \times 10 \frac{U_{AB}}{2} \times 6 \\ = 168.92 \text{ g of U}^{235}$$

(U_{FG} and U_{AB} must be halved because these values were calculated above, assuming that only 2 cores were taken between bracketing analyses, where, in this case, 10 and 6 cores, respectively, were selected.)

**U²³⁵ Content Based on Weighted Average of Adjacent Pairs of Skeleton Samples
and Selection of 16 Cores of Least Uranium Content**

$$U_i = \frac{U_{DE}}{2} \times 10 \frac{U_{IJ}}{2} \times 6 \\ = 162.90 \text{ g of U}^{235}$$

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