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DISCUSSION AT OAK RIDGE ON UO₃ ANALYSIS

The writer visited Oak Ridge on March 10 and 11, and had opportunity to discuss with K-25 personnel various problems relating to the analysis of UO₃ produced at Hanford.

Several lots of Hanford-produced UO₃ have been processed at K-25 in the fluorinating train. Details of the observation are described in a separate report from F. W. Hurd, which the writer transmitted to you. The particular difficulties were observed in processing this material. In the first place, a low conversion to UF₆ was obtained -- on the order of about 70%. As a consequence, an excessive amount of free fluorine is required to complete the transition to UF₆. Since the facilities at Oak Ridge for preparing free fluorine are limited, the use of additional fluorine for processing Hanford material would aggravate the bottleneck that already exists. The second difficulty was the formation in the fluorinating tower of a heavy deposit that almost completely throttled the flow. Portions of the Hanford material were processed in both the "A" and "B" processing lines, and this deposit was observed in both cases. The deposit consisted, in part, of a fluffy, light colored material, and in part, of a hard, glass-like substance containing alternately light and dark colored

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laminated layers. Several analyses on some portions of this material showed the sum of U + F to be 96%. Other portions of the deposit were found to be very difficult to place in solution which suggests the presence of calcined alumina. Although the fluorinating towers contain an "ash pit" for the purpose of collecting such residues, the quantities formed in these cases were much greater than previously obtained with other oxides. The formation of large quantities of the materials is of particular concern because of the presence of plutonium and beta and gamma emitting fission products. The comment was made that the deposit found after processing oxide material obtained from Oak Ridge Purex process runs contained as high as 100 ppm plutonium.

The properties of Hanford oxide that are of particular concern to K-25 personnel are the specific surface and the impurities. Hurd believes the former to be more critical and suggests that the lower surface of our material may be related to the high impurity content.

Analyses of Hanford oxide were completed at Oak Ridge during the last week in February. Since several discrepancies were observed, analytical personnel at both sites have since examined the questionable determinations in rather complete detail. Observations and modification of methods at both sites appear to have eliminated the originally observed discrepancies. On the basis of our discussions it would appear that the composition of material recently shipped from Hanford is about as follows:

UO ₃	97.5%
H ₂ O	.5%
NO ₃	.5%
U ₃ O ₈	.3 - 2%
Na	2500 ppm
P	5 - 200 ppm (?)
Fe	500 ppm
Al	2000 ppm
Bulk Density	2.0 g/cc
Surface Area	1.6± m ² /g
Pu	5 - 10 ppb
Fission Product Beta	7% (of natural U)
Fission Product Gamma	50% (of natural U)

Other impurities are found to be essentially insignificant at both sites.

UO₃

K-25 has consistently shown a 1-2% higher UO₃ content. In addition, it is observed that the summation of their analyses tends to run somewhat over 100%. In view of the unexpectedly high impurity content of the samples, however, they are inclined to agree with us that their procedure, which involves simple ignition to U₃O₈ and correction for impurities, is not accurate. As a result, they are installing their X-ray photometer to make these analyses, and the writer agreed to furnish them with our procedure and with details of the instrument modifications that we have developed. Both sites expect that agreement will be obtained after installation of the new method. Since my return, we have discovered that Hanford results have tended to be slightly low as a result of an error in a standard solution; the error is on the order of 0.4%

H₂O

The specification limit for water in Hanford oxide was set with the intent of keeping the content sufficiently low so that saking of the material did not occur. Since the samples have shown considerably more than the 0.1% tentative specification, and since the powder has been observed to flow freely in all cases, Oak Ridge personnel believe that the limit is too strict.

In a comparison of analytical results it is apparent that Oak Ridge results nearly double those obtained at Hanford. The Hanford analytical procedure involves a titration of the solid sample according to the Karl Fischer technique. The Oak Ridge procedure involves ignition of the sample, collection in a drying tube of the water released, and weighing. Analyses at Hanford according to the Oak Ridge procedure yielded results in exact agreement with the Oak Ridge values, which tends to confirm the thought that the Karl Fischer reagent does not leach water completely from the oxides. There still remains some question as to whether oxides of nitrogen may be picked up in the water trap and weighed and reported as water. We intend to check this point, although experiments at Oak Ridge indicate that there is no error from this source.

According to the Oak Ridge procedure, one gram of sample is placed in a combustion tube and heated for 30 minutes at 500-600°C. A stream of oxygen is passed successively through a H₂SO₄ tower and a Deydrite tower, and thence over the sample. The gas stream is then passed through a tared Anhydrome tower, which is followed by several protective drying traps.

HNO₃

The nitrate content of Hanford oxide does not appear, per se, to be of any concern process-wise, because it is expected that it is destroyed in the first process tray during hydrogen reduction. The presence of nitrate, however, is of concern in that it is an indication of metallic impurities. Oak Ridge employs a distillation, followed by colorimetric nitrate evacuation. Hanford employs a vacuum distillation, followed by acid titration. Excellent agreement has been obtained.

U₃O₈

Although U₃O₈ is readily reduced and fluorinated in the Oak Ridge process, Hurd expressed concern over the quantity of this oxide present in our material. Although he has no data to support the point, he is concerned lest overburning of oxide, as indicated by the presence of appreciable U₃O₈, has a deleterious effect on surface area. The results of analyses at both sites have shown good agreement, although there are big differences in the contents of different lots. Oak Ridge has reported analyses of the samples sent from Hanford and of drum samples obtained at Oak Ridge. In general, they show good agreement, although it is strikingly evident that their analyses on the two samples from any given lots show very wide differences in U₃O₈ content.

Oak Ridge employs a procedure involving dissolution of sample in phosphoric acid in the presence of formic acid to destroy nitrate and subsequent photometric measurement of U(IV) content. They have recently confirmed our observation that formic acid causes some reduction of U(VI) to U(IV) and have consequently reduced the quantity of formic acid

employed, thereby attaining somewhat lower results. They also report that hexavalent uranium appears to be slowly reduced photochemically, as indicated by increased photometric readings with time. Hanford has employed a procedure consisting of dissolution of the sample in HCl and determination of uranium in the insoluble U_3O_8 residue. Good analytical agreement between sites has been obtained, although we are investigating a modification of the Oak Ridge method employing hydroxylamine as a substitute for formic acid.

Spectrochemical Impurity Determinations

High impurity contents are of concern because of the caking observed in the fluorination tower, as previously described.

The procedure at Oak Ridge is the carrier distillation method using 100 mg. sample with 2% added gallium oxide. The sample is placed in a crater in a graphite electrode, pre-burned for 5 seconds and then exposed for 40 seconds. It was agreed that the limited burning period may be the source of some inaccuracy, especially in the presence of large quantities of impurities which may have a pronounced effect on burning characteristics of the sample in the arc. In many cases Oak Ridge has made analyses both direct and by 10:1 dilution of the sample with pure UO_3 ; they report acceptable agreement. The practice at Oak Ridge, as at Hanford, is to compare the spectrographic lines visually, and it is expected that results are accurate within a factor of two. Both sites report results on the sample weight basis.

Sodium

A considerable disagreement between results from the two sites was apparent on the first several analyses. After re-examination of their procedure, Oak Ridge was convinced that their original results were low. As a result, they have modified their procedure and are recording results substantially in agreement with ours. Several analyses at Hanford were made by the more tedious but more exact flame photometer technique; the results obtained were in exceptionally close agreement with the spectrographic results.

Phosphorus

The existence of high phosphorus contents is of some concern process-wise because it is expected that phosphorus will be fluorinated to form a volatile compound which will build up in the recycle HF stream.

This determination is the only one in which the discrepancy between sites has not been explained. Initially, we reported a number of results on the order of 1000 ppm but have since obtained evidence that the true result is more probably on the order of 200 ppm. On the other hand, Oak Ridge finds no phosphorus spectrographically and only several ppm by a photometric analysis. The latter consists of extraction of phosphomolybdate into butyl alcohol from a sulfuric acid medium and subsequent colorimetric measurement. It is our opinion that the photometric procedure should be reliable. Further attention will be given to this analysis. It is to be noted that K-25 reports ppm PO₄ whereas Hanford reports ppm P.

Aluminum

Spectrographic aluminum determinations at Oak Ridge have consistently shown about 200 ppm, whereas the Hanford results have been 5000 ppm. Re-examination of our technique during the past week gave indication that our results may actually be on the order of 2000 ppm, whereas the Oak Ridge spectrographers found no indication of error on their part. In view of the discrepancy, samples of each lot were analyzed photometrically at Oak Ridge. Tentative results reported during my visit were about 1300 ppm. Thus, as a result of the observations at the two sites, the initial wide discrepancy appears to have vanished.

Bulk Density

Both sites are using the identical procedure which involves the weight of sample required to fill a standard cup by free flow. Close agreements are obtained. During discussion of the determination it was noted, however, that Oak Ridge determines bulk density of Mallinckrodt oxide by a tap procedure. The sample is allowed to flow freely into a 100 cc graduate which has been cut off at the 25 cc mark; it is then tapped repeatedly on a solid surface until a constant volume is obtained, and the bulk density is calculated from the volume and weight of the sample. According to the free flow technique, Hanford oxide shows a density of about 2.0 and, according to the tap procedure, a density of 3.5. During my visit several samples of oxide were determined according to both procedures with the following results:

	<u>Free Flow Density</u>	<u>Tap Density</u>
Furax UMH converted at Mallinckrodt		
D-1	2.5	3.6
D-2	2.6	3.8
D-3	2.4	3.6
Normal Mallinckrodt UO ₃	2.2	3.7

In view of these data Hurd indicated his belief that the tentative specification for Hanford oxide was established on the basis of tap density and according to the free flow density method, and suggested reconsideration of the specification.

Surface Area

Identical analytical methods are used, and exceptionally close agreements have been obtained.

Plutonium

Hanford results on Lots 3, 4, and 5 have been less than 5 ppb and on Lot 6 less than 15 ppb. On all three lots Oak Ridge has shown about 10 ppb. The procedures employed at the two sites appear to be identical. Duplicate analyses at Oak Ridge have, in a number of cases, shown agreement to within 1 ppb, although it was agreed that this was abnormal in view of the relatively poor counting statistics.

Fission Product Beta

On samples through Lot 6, Hanford has reported less than 5%, whereas Oak Ridge has reported about 60%. The difference is not real, however, because our result represents only fission products, whereas the Oak Ridge result includes total beta, i.e., fission product, U-237, and uranium daughters. C. A. Kimberger, who is the radiochemist in the K-25 organization, expressed his willingness to modify the beta counting technique by employing a 25 mg/cm² gold absorber. Such an absorber would essentially eliminate beta radiation from U-237 and would result in more reproducible counting as a result of elimination of weak energy betas. Evidence at Hanford indicates that such a change would have little effect on the reported result, because uranium daughters and the fission product mixtures are attenuated to an approximately equal extent. Kimberger was in some doubt as to whether U-237 betas were to be considered a part of the specification and did not consider himself qualified to pass on the point. Since all correspondence has referred to fission product, there is apparently no argument.

Fission Product Gamma

The reported gamma results from the two sites have been on the same basis as those for beta, so that the numerical values are different. Kimberger prefers to employ the Shonka chamber for these measurements, because there is an established and familiar procedure in their laboratory, whereas they have had little experience with the gamma scintillation counter. He did agree to explore the possibility of using the latter instrument. In the meantime it appears that Hanford must employ the scintillation counter because of the difficulties resulting from the presence of undecayed U-237.

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