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TOPICAL REPORT

THE REFLECTIVITY OF ORANGE OXIDES

by

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THE REFLECTIVITY OF ORANGE OXIDES

I. Introduction

One of the basic problems associated with the production of uranium tetrafluoride is the varying reactivity of uranium trioxide (orange oxide). Separate batches of material produced by the same method may be so dissimilar that they require different sets of reaction conditions for satisfactory processing.

The term "orange oxide" is used throughout this report to describe plant-produced UO_3 . This material is almost invariably a mixture of several different types (as determined by X-ray measurements) of UO_3 which are identified when possible.

Briefly, "reactivity" is the term applied to the behavior of a given orange oxide with respect to its reduction to UO_2 and subsequent hydrofluorination to UF_4 . After reaction, the percent AOI (ammonium oxalate insoluble) fraction of the UF_4 is determined. This is a measure of the unconverted UO_2 and U_3O_8 . An orange oxide resulting in a low percent AOI UF_4 is said to be more reactive than one which results in a high percent AOI UF_4 . A more complete description of the methods, apparatus, and interpretation of reactivity measurements may be found elsewhere.^{1,2,3}

Assuming constant reaction conditions (e.g., temperature, time, and gas flow-rates) it is thought that the reactivity of an orange oxide depends, to varying degrees, on the following:

- 1) the chemical composition - different types of UO_3 , hydrates, and trace impurities which exhibit catalytic properties.
- 2) the physical makeup of the oxide - particle size, crystallite size, surface area, and porosity.

Since the evaluation of these variables by conventional reactivity tests involves a rather lengthy procedure, it is difficult to apply the reactivity test to plant denitration, reduction, and hydrofluorination problems. Consequently, a simple and rapid test is needed for reactivity, ideally one which can be applied directly to the orange oxide.

The visual examination of numerous samples of UO_3 suggested that the color of the oxide could be directly related to some of the previously noted chemical and physical properties. From this, it was deduced that color ought to be related to the reactivity of the oxide;

¹ Swinehart, B. A., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1397 (October 1, 1956) p 97-114

² Swinehart, B. A., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1385 (April 1, 1956) p 38-45

³ Swinehart, B. A., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1392 (July 1, 1956) p 24-33

and if so, its measurement would permit the desired, rapid prediction of reactivity.

Quantitative measurements of color were made in the visible region of the spectrum with a Beckman Model DU spectrophotometer adapted to reflectivity determinations. These measurements were then compared to experimentally determined reactivities.

II. Summary

Reflectivity measurements have been used to qualitatively identify type III UO_3 ,⁴ type II UO_3 , $\text{UO}_3 \cdot \text{H}_2\text{O}$, and amorphous UO_3 . In addition, a method was devised for the quantitative estimation of amorphous UO_3 in an orange oxide. Ultimately, a simple and rapid test was devised for predicting the relative reactivity of any given UO_3 toward reduction and subsequent hydrofluorination. The method requires only two to four measurements of reflectivity and can be completed in 15 minutes.

The simplicity of the test suggests several possible plant applications. For example, it could be used to help control denitration conditions to yield a standardized orange oxide. This, in turn, would make it possible to adopt the most satisfactory reduction and hydrofluorination conditions. Moreover, in the case of non-standard orange oxides it should be possible to predict the reactivity and indicate when changes in plant reaction conditions are needed to minimize thermal damage⁵ and sintering.

It should be pointed out that some of the relationships presented are empirical, particularly those between reflectivity and reactivity; however, the promise of direct plant application requires that they be included in this report.

III. Experimental and Discussion

A. Apparatus

All reflection measurements were made using a Beckman Model DU spectrophotometer equipped with a reflectance attachment. A magnesium carbonate block was used as the reflection standard. A description of the instrument and its optical system is included in Section A of the appendix.

B. Sample Preparation and Measurement

The orange oxide to be tested is sampled and a small quantity of the powder placed in

⁴ Katz, J. J. and Rabinowitch, E., *The Chemistry of Uranium*, McGraw-Hill Book Co., New York (1951) p 275-277.

⁵ Swinehart, B. A., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1399 (January 1, 1957) p 31.

a pill-box top. The surface is smoothed by exerting fingertip pressure on a metal cover plate. The cover is removed, the sample placed in the spectrophotometer, and the percent reflectivity measured at the selected wavelengths. A definition of reflectivity appears in Section B of the appendix. In general, measurements were made over the range 350-950 $m\mu$ at 10 $m\mu$ intervals; however, the percent reflectivity (r) shows very little change above 660 $m\mu$ and, consequently, the r vs. λ (wave length) curves are reproduced only up to about 700 $m\mu$.

A statistical study of the reproducibility of the reflectivity measurements at various wavelengths appears in Section C of the appendix.

C. Qualitative Identification of Oxides

The preparation of samples for both qualitative identification and quantitative estimation of various types of UO_3 is complicated by difficulty in obtaining materials of known composition. Two tests were used as criteria for purity: (1) the X-ray pattern and (2) the reflectivity itself. For example, if X-ray evidence indicated that two different samples of $UO_3 \cdot H_2O$ were of the same purity, the one with the highest percent r at 380 $m\mu$ was assumed to be the best sample.

Using this procedure it was possible to obtain reflectivity curves for type II, type III (the main product from MCW denitration pots), the monohydrate, and amorphous UO_3 . These curves are reproduced in Figure 1. In addition a curve for an unidentified hydrate, prepared by the hot slurry hydration of type III UO_3 , has been determined. The curve shape is quite similar to that of $UO_3 \cdot H_2O$, but the reflection peak occurs at 405 $m\mu$ rather than 380 $m\mu$. Other compounds, such as type Y,⁶ which possess characteristic X-ray patterns, have not been obtained in a form pure enough to permit assigning them specific reflectivity curves.

The distinctive curve shapes permit an identification of the major constituents in pot-produced orange oxide. The variation in reflection in the 380-400 $m\mu$ region indicates changes in the amount of hydrate. Variations in the vicinity of 660 $m\mu$ indicate amorphous UO_3 . Type II cannot be distinguished from amorphous, but the former compound is a laboratory oddity and has not been found in production-type orange oxide.

The nature of the reflection pattern in the 440-580 $m\mu$ range is complex and cannot be conveniently explained in terms of the presence of a particular compound. The possible

⁶ Paine, R. M. and Boersig, T. C., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1373 (April 1, 1955) p 57-76.

FIGURE 1
REFLECTIVITY CURVES FOR VARIOUS UO_2 SAMPLES

contributing factors are discussed elsewhere in this report.

D. Quantitative Estimation of Amorphous UO_3

Inasmuch as amorphous UO_3 is known to possess an unusually high reactivity, a method for its quantitative estimation has long been desirable. There is a good possibility that lot-to-lot variations in the reaction properties of orange oxide may be related, in part, to amorphous content. This contention is supported by the fact that several batches of UO_3 which were unusually reactive had reflectivity curves indicating the presence of a greater than normal quantity of amorphous oxide.

As indicated in Section C, the portion of the reflection spectrum, of an orange oxide, above $600\text{ m}\mu$ is sensitive to the amount of amorphous UO_3 in the preparation. As shown in Figure 1, the plot of percent r against wavelength exhibits a plateau in the vicinity of $660\text{ m}\mu$. Measurements at this wavelength were selected for the determination of the fraction of amorphous UO_3 present in an arbitrary mixture.

Since orange oxide preparations made by thermal decomposition of uranyl nitrate frequently consist of complex mixtures of compounds, it is necessary to determine any interfering substances. Up to 1.5 percent U_3O_8 and 3 percent nitrate did not correlate with the reflectivity at $660\text{ m}\mu$. Similarly, it was shown that for a constant percent amorphous UO_3 , varying amounts of type III UO_3 and $\text{UO}_3 \cdot \text{H}_2\text{O}$ had very little effect on percent r at this wavelength.

Having illustrated that U_3O_8 , undecomposed nitrate, and mixtures of type III UO_3 and $\text{UO}_3 \cdot \text{H}_2\text{O}$ do not seriously affect reflectivity measurements pertaining to amorphous oxide, a calibration curve for the quantitative estimation of amorphous UO_3 was prepared.

The calibration curve was based on two samples of orange oxide. A sample of amorphous UO_3 was obtained from Battelle Memorial Institute. There was no X-ray evidence for the presence of any other type of UO_3 . In addition, it showed the lowest percent r at $660\text{ m}\mu$ of all available oxides and was arbitrarily assumed to be 100% amorphous. Numerous samples of plant orange oxide were examined and the one reflecting the greatest amount of light at $660\text{ m}\mu$ was assumed to contain the least amount of amorphous and was arbitrarily assigned the value of 0%. Known weights of each sample were mixed and thoroughly

blended to give a series of oxides with varying weight percent amorphous UO_3 . The percent amorphous is plotted against $\log \frac{1}{r}$, where r is the reflectivity at $660 \text{ m}\mu$, in Figure 2. This plot can be used to advantage, inasmuch as there is no other convenient method for analyzing an orange oxide for its amorphous content.

E. The Reflectivity of Orange Oxide and Its Relation to Reactivity

As was pointed out in the introduction, the ultimate goal of the reflectivity study was to attempt to relate the color of orange oxide to the reactivity toward reduction and subsequent hydrofluorination. The region of the spectrum found most sensitive was that of greatest slope, the $480\text{-}580 \text{ m}\mu$ range. It was shown empirically that the ratio $\frac{\text{percent } r_{540 \text{ m}\mu}}{\text{percent } r_{520 \text{ m}\mu}}$ gives the best index of reactivity. This relationship will be discussed quantitatively, but for the present, a qualitative picture of the contributing factors will be considered.

Unfortunately, the reflection in this range appears to be a function of both composition and particle size (as determined by standard screen distributions). So far, the complexity has not permitted a breakdown of the observed reflectivity. That is to say, the effect of some variables on reflectivity is not known.

The percent r curves for four different samples of orange oxide appear in Figure 3. Note that the ratio of $\frac{\text{percent } r_{540 \text{ m}\mu}}{\text{percent } r_{520 \text{ m}\mu}}$ generally decreases as the amorphous content increases:

Percent Amorphous	$\frac{\text{Percent } r_{540 \text{ m}\mu}}{\text{Percent } r_{520 \text{ m}\mu}}$
10	1.90
19	1.58
27	1.60
39	1.40

If the curves for mixtures of type III and $\text{UO}_3 \cdot \text{H}_2\text{O}$ are examined (Figures 4 and 5), it is seen that the ratio decreases as the amount of hydrate increases:

Percent Hydrate	$\frac{\text{Percent } r_{540 \text{ m}\mu}}{\text{Percent } r_{520 \text{ m}\mu}}$
20	1.87
33	1.74
47	1.61
60	1.49

FIGURE 2
CURVE FOR THE QUANTITATIVE ESTIMATION
OF AMORPHOUS UO_2 IN ORANGE OXIDE

FIGURE 3
REFLECTIVITY CURVES FOR MIXTURES OF AMORPHOUS AND TYPE III UO_2

FIGURE 4
REFLECTIVITY CURVES FOR MIXTURES OF $\text{UO}_2 \cdot \text{H}_2\text{O}$ AND TYPE III UO_2

FIGURE 5
REFLECTIVITY CURVES FOR MIXTURES OF $\text{UO}_2 \cdot \text{H}_2\text{O}$ AND TYPE III CO_2

Thus, this data illustrates that, if either amorphous or $\text{UO}_3 \cdot \text{H}_2\text{O}$ is added to type III UO_3 , the reflectivity ratio decreases, but for different reasons. See Figures 3, 4, and 5. The amorphous tends to decrease the amount of light reflected while the hydrate increases the light reflected. In addition, it is thought that the so-called type Y⁷ UO_3 contributes in this region. However, type Y has not been positively identified and, consequently, it has not been possible to associate its presence with changes in the reflectivity curve.

There are several indications that a correlation exists between particle size and reflectivity of UO_3 . This can best be illustrated by observations of percent r at 500 $m\mu$ for powders of known average particle size:

- 1) Percent r is slightly greater for fine powders than for coarse powders.
- 2) Mechanical grinding of a coarse orange oxide increases its reflectivity.
- 3) The reflectivity at 500 $m\mu$ of a series of plant-produced orange oxides was compared to the average particle diameter as determined with a Fisher Sub-sieve Analyzer.

Though not conclusive, Figure 6 certainly suggests a correlation between the two.

At the present, then, it may be said that reflectivity measurements in the vicinity of 500 $m\mu$ are a function of several variables, not all of which can be treated quantitatively. Consequently, the relationship between percent r and reactivity is empirical, and there is no way to justify the use of $\frac{\text{percent } r \text{ } 540 \text{ } m\mu}{\text{percent } r \text{ } 520 \text{ } m\mu}$ except to say that it works.

As has been previously reported,⁸ it is relatively easy to distinguish among oxides differing widely in reactivity. To illustrate this, the reflectivity ratio has been calculated for six different orange oxides and then compared to the time required for 90% complete hydrofluorination in a thermobalance. See Table I. Small reflectivity ratios indicate a high reactivity. Essentially, the same relationship is found when the conversion of UF_4 is accomplished in the reactivity chamber rather than in the thermobalance. See Table II.

⁷ Paine, R. M. and Boersig, T. C., MCW-1373, p 57-76.

⁸ Swinehart, B. A., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1401 (April 1, 1957) p 35-39.

FIGURE 6
THE EFFECT OF PARTICLE SIZE ON REFLECTIVITY

Table I

Comparison of Rate Data and Reflection Properties of Various UO_3 Samples

Source of UO_3 Tested	Hydrofluorination			
	Reduction Temperature $^{\circ}\text{C}$	Temperature $^{\circ}\text{C}$	Time to 90 Percent Completion min	Reflectance Ratio Percent r 540 $m\mu$ Percent r 520 $m\mu$
MCW-Micronized ⁹	540-42	545-50	3.25	1.29
Amorphous-Battelle Memorial Institute ¹⁰	540-45	452-56	4.5	1.37
Fernald ¹⁰ Lot 3E-16-706	548-56	549-51	40.	1.46
Port Hope ¹⁰ Lot 244	548-61	510-17	60.	1.60
Fernald ¹⁰ Lot 3E-16-1027	542-50	554-56	85.	1.93
MCW-Typical Production Material ¹¹	545	545-50	>100.	2.02

⁹ Ludwig, F. J., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1399 (January 1, 1957) p 47-62.

¹⁰ Ludwig, F. J., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1397 (October 1, 1956) p 115-311.

¹¹ Ludwig, F. J., *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, MCW-1399 (January 1, 1957) p 47-62.

It has been shown that orange oxide samples of widely differing reactivities can be ranked by reference to their reflection spectra. The most important aspect of the technique, however, lies in its application to plant-produced orange oxide. The reactivity of plant material is known to vary from lot to lot, but not so strikingly as the materials whose properties are summarized in Table I and II. Even so, the use of reflectivity measurements provides a rapid and fairly dependable means of characterizing plant orange oxide. The results of typical reactivity tests are summarized in Table III and IV.

Table II

Comparison of Reactivity Data and Reflection of Orange Oxide

Source of UO ₃	Hydrofluorination for 1½ hours			
	Reduction Temperature °C	Temperature °C	Percent AOI of Product	Percent r 540 mμ Percent r 520 mμ
Vacuum Denitrated	620	457	0.31	1.42
Port Hope	620	470	0.94	1.71
MCW	625	470	5.2	2.00
Fernald	620	480	7.0	2.05

Table III

Comparison of Reactivity and Reflectivity Data
for MCW Pot Denitration Samples

UO ₃ Sample	Reduction Temperature °C	AOI after Hydrofluorination			
		Reflectivity Ratio Percent r 540 mμ Percent r 520 mμ	at 540°C %	at 580°C %	at 600°C %
A1	775	1.78	6.2	3.0	1.6
A2	775	1.91	8.8	5.3	3.0
A3	775	2.15	11.2	6.8	4.4
A4	775	2.27	9.9	6.0	3.4

Table IV

Comparison of Reactivity and Reflectivity Data
for MCW Pot Denitration Samples

UO ₃ Sample	Reduction Temperature °C	Reflectivity Ratio $\frac{\text{Percent } r \text{ 540 m}\mu}{\text{Percent } r \text{ 520 m}\mu}$	AOI after Hydrofluorination		
			at 470°C %	at 530°C %	at 590°C %
B1	610	1.84	6.9	1.6	0.2
B2	610	1.93	14.0	4.6	0.3
B3	610	1.96	17.9	7.0	0.6
B4	610	2.00	14.6	4.6	0.6
B5	610	2.02	19.6	7.8	2.1

It has been shown that reflectivity measurements permit the ranking, according to reactivity towards reduction and subsequent hydrofluorination, of uranium trioxides. Ideally, for a given set of reaction conditions, it should be possible to predict the AOI of the product. With this in mind, a series of orange oxide samples from several sources (including MCW, Fernald, and Port Hope production materials as well as numerous laboratory preparations) were reduced at about 625°C. The resulting UO₃ was hydrofluorinated and a "reactivity curve" plotted for each sample. Briefly the "reactivity curve" is a plot of percent AOI *vs* hydrofluorination temperature. The percent AOI at a selected temperature (for example 420°C) was then read from the curve and plotted as a function of the $\frac{\text{percent } r \text{ 540 m}\mu}{\text{percent } r \text{ 520 m}\mu}$ for the parent orange oxide. See Figure 7. A hydrofluorination temperature of 420°C was chosen for two reasons. First, for a 1½ hour reaction it is sufficient to yield a low percent AOI for reactive materials and still show a good spread for more typical oxides. Secondly, as the hydrofluorination reaction temperature is raised, the thermal damage becomes much more severe and the AOI results are not nearly so reproducible.

In summary, then, there is evidence that the relative reactivity, of an orange oxide, toward reduction and subsequent hydrofluorination can be predicted without recourse to time consuming reaction tests. Only five measurements are needed for the prediction: reflectivity measurements at 380, 520, 540 and 660 mμ along with a screen analysis of the powder. Actually, a complete screen analysis is not required since reactivity tests indicate that only the coarser fractions lead to severe thermal damage.

FIGURE 7
COMPARISON OF REFLECTION AND PERCENT AOI DATA FOR UO_2
REDUCED AT 610-640°C AND HYDROFLUORINATED AT 420°C

Thus, the determination of a single sieve fraction (percent greater than 140 or 100 mesh) will usually suffice.

To compare and predict relative reactivities for two or more orange oxides, the following procedure can be used.

- 1) Compare $\frac{\text{percent } r \text{ } 540 \text{ m}\mu}{\text{percent } r \text{ } 520 \text{ m}\mu}$. The oxide having the lowest ratio can be expected to have the highest reactivity.
- 2) If the reflectivity ratios are nearly the same, refer to the percent r at 380 and 660 $m\mu$. Low reflectivity at 660 $m\mu$ and high reflectivity at 380 $m\mu$ indicate high reactivity.
- 3) Note the screen distribution of the powder; the larger the +100 mesh fraction the more likely that thermal damage (and consequently high AOI's) will occur.

IV. Appendix

A. Optics

A special attachment obtained from the manufacturer allows the Beckman Model DU Spectrophotometer to be adapted to the measurement of reflectance. Instead of passing through transmission cells, the monochromatic radiant energy is reflected by a mirror onto the sample. The radiant energy is incident approximately at 90° on the sample. The energy reflected from the sample at about 45° strikes a second mirror. This mirror, ellipsoidal in shape, reflects and focuses the energy from the sample onto a glass diffusing plate and the intensity of the diffused beam is measured with a phototube.

B. Reflectivity

Ideally, the Beckman Model DU Spectrophotometer measures directional reflectance. Directional reflectance has been defined as "the ratio of the radiance that the surface has under any specified set of irradiating and receiving conditions to the radiance that a perfectly reflecting, perfectly diffusing surface would have under the same conditions."¹² Actually, however, this ideal situation is not realized. In practice, either magnesium oxide or magnesium carbonate is used as the reflection standard. All reflection values appearing in this report are relative to the carbonate.

¹² Mellon, M. G., ed., *Analytical Absorption Spectroscopy*, John Wiley and Sons, New York, (1950) p 195.

Reflectance is the term applied to reflection measurements when the surface in question is not thick enough to completely eliminate the effect of the backing. For example, a single coat of white paint on a black surface probably would not reflect as much light as would two coats. When the backing does not affect the reflection, as was the case with the measurements of orange oxide, the term "reflectivity" denoted by the symbol r is used.

C. Statistical Study of Reproducibility of Reflectance Measurements

The reflection curve for each lot of UO_3 varies to some extent from all others. In order to distinguish between similar samples, it is necessary to have some idea as to the reproducibility of the method. Consequently, a statistical evaluation was made of the readings at several wavelengths. The general procedure was as follows: (1) A large batch of orange oxide was blended to assure homogeneity. (2) A sample was prepared. (3) Reflectance measurements were made at each of the selected wavelengths. (4) The sample container was emptied and a second portion of the large, blended batch was prepared. This procedure was repeated for each series of reflectance measurements. The wavelengths were chosen so that readings were available both for plateau and slope regions of the spectrum. The data for three different lots of orange oxide are summarized in Table A-I.

Table A-1
Reproducibility of Reflection Measurements

	Wavelength (mμ)						
Statistics	420	490	500	520	540	580	660
Sample 1							
n^a	8		8	8		8	8
$\bar{x}^b$	11.2		19.6	33.8		83.1	83.9
s_2^c	0.3186		0.4214	0.6229		0.2114	0.0340
s^d	0.56		0.65	0.79		0.46	0.18
Sample 2							
n^a	8	8			8		8
$\bar{x}^b$	15.3	25.7			66.9		91.0
s_2^c	0.146	0.3171			0.2229		0.1029
s^d	0.38	0.56			0.47		0.32
Sample 3							
n^a	8		8	8		8	8
$\bar{x}^b$	11.4		20.0	33.8		37.4	91.2
s_2^c	0.2900		1.0000	1.1400		0.1829	0.0086
s^d	0.54		1.00	1.07		0.43	0.09

^a n - The number of observations.

^b $\bar{x}$ - Mean percent reflectance of " n " samples.

^c s_2 - Variance calculated from the following equation:

$$S_2 = \frac{\sum_{i=1}^N X_i^2 - \frac{\left(\sum_{i=1}^N X_i\right)^2}{N}}{N-1}$$

Where X_i - observed percent reflectance
 N - total number of observations

^d standard deviation - $\sqrt{s^2}$