

2
Conf-900466--105

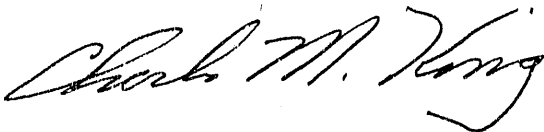
WSRC-RP-89-1098

Spectroscopic Probes of the Structure of Hydrrous Uranium Oxide Precursors to UO₂ Ceramic Fuel

by

WSRC-RP--89-1098

Major C. Thompson
Charles M. King



4 DE92 009838

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina

and

R. Bruce King

Department of Chemistry
University of Georgia
Athens, GA

An abstract proposed for presentation and publication
Materials Research Society: Better Ceramics Through Chemistry
San Francisco, CA
April 16-21, 1990

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

*This paper was prepared in connection with work done under Contract No. DE-ACO9-76SR00001 (now Contract No. DE-ACO9-88SR18035) with the U.S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

MASTER

M9004017

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

SPECTROSCOPIC PROBES OF THE STRUCTURE OF HYDROUS URANIUM OXIDE PRECURSORS TO UO₂ CERAMIC FUEL

MAJOR C. THOMPSON*, CHARLES M. KING* AND R. BRUCE KING**

*Westinghouse Savannah River Company, Savannah River Site, Aiken, SC 29802

**Department of Chemistry, University of Georgia, Athens GA 30602

ABSTRACT

Fourier Transform infrared spectroscopy, x-ray powder diffraction and thermal analysis show that one example of "ammonium diuranate" observed as an intermediate in the U(VI) sol-gel process is a layered hydrous uranium oxide with a proposed structural formula of $(\text{NH}_4)_2[(\text{UO}_2)_8\text{O}_4(\text{OH})_{10}] \cdot 8\text{H}_2\text{O}$, an ammonium ion intercalate. Examples of polyamine intercalation compounds of hydrous uranium oxide are also given.

INTRODUCTION

Beginning in the late 1950s, sol-gel processes were developed for the preparation of nuclear reactor fuels of U, Th, and Pu in the form of microspheres. The Oak Ridge National Laboratory (ORNL) has developed a process using U(VI) based on "internal" gelation of colloidal sols by methods previously studied in the Netherlands [1,2]. In the ORNL sol-gel process, a solution of uranyl nitrate with urea is mixed at 0°C with a solution of hexamethylene tetramine (HMTA) resulting in hydrolysis of the uranyl cation to a hydrous uranium oxide. HMTA functions as a weak base for hydrolysis and is assumed to decompose when heated in the next process step releasing ammonia (which causes gelation) and formaldehyde. The gelled uranium, which has been implied to be "ammonium diuranate", is washed with aqueous ammonia solution to remove ammonium nitrate and formaldehyde. This report describes our efforts to identify the intermediates in the sol-gel process in order to better understand the chemical mechanisms involved in the process.

EXPERIMENTAL

Fourier Transform infrared spectra (FTIR) were recorded with a Nicolet 20-DX Fourier Transform interferometer after preparation of dried gels and solids in a potassium bromide matrix compressed to 10,000 psig. X-Ray powder diffraction (XRPD) patterns were recorded on a Siemens Diffrac-500 x-ray diffractometer using CuK α radiation and a scintillation detector. Uranium samples were handled in a completely contained Siemens apparatus. X-Ray diffraction patterns of experimental samples were compared to reference patterns using the International Centre for Diffraction Data Joint Committee on Powder Diffraction Standards (JCPDS) files for graphic pattern evaluation including phase identification and "d" spacing. Thermal analyses were performed with a Du Pont Thermal Analyzer programmed to record weight loss and calculate differential weight loss.

Gel samples were prepared by the Oak Ridge method with HMTA solution being mixed with a solution of urea and uranyl nitrate. Uranium compounds were precipitated from uranyl nitrate or chloride solutions by addition of solutions of ammonia, HMTA, diazabicyclooctane (DABCO), or aliphatic polyamines.

RESULTS

FTIR spectra of pure HMTA, HMTAH⁺, and NH₄⁺ compounds and synthetic uranates show that these cations are resolvable based on absorptions in the region from 1000 to 1300 cm⁻¹. Figure 1 shows the absorptions in the area of interest for several of the compounds. HMTA is a symmetric compound which gives single absorptions at 1250 and 1030cm⁻¹ due to the symmetric C-N stretch [3]. Addition of H⁺ to one of the nitrogens causes lengthening of two of the C-N bonds resulting in a splitting of each of the C-N bands in HMTA into two peaks [3]. NH₄⁺ has no absorptions in this region of the spectrum. The FTIR spectra illustrate that the protonated forms of the polyamine (HMTAH⁺) structures are stable in the uranate composition and are believed to be interstitial or "intercalation" cations.

Several synthetic uranyl compounds of ammonia, HMTA, and DABCO were analyzed by thermogravimetry. In addition to relative weight loss depending on the cation, the differential weight loss curves are also characteristic of the cation. Figure 2 shows some examples of the different compounds. Figure 2 also shows a DABCO uranate before and after treatment with ammonia. Clearly, most of the DABCO has been replaced by ammonia illustrating the ion exchange properties of these uranates. The scale for the DABCO uranate differential weight loss is 5 times greater than the ammonia uranates shown in Figure 2, illustrating the higher molecular weight of the "intercalation" cation.

A series of synthetic uranates were analyzed by XRPD [4] and the basal spacings determined by comparison with the spacings for known structures. The synthetic uranates are isostructural by XRPD, but the basal spacing varies with the size of the cation incorporated in the "intercalation" sites. Table I shows the deduced spacings with the spacings from a recent study of some natural uranate minerals [5].

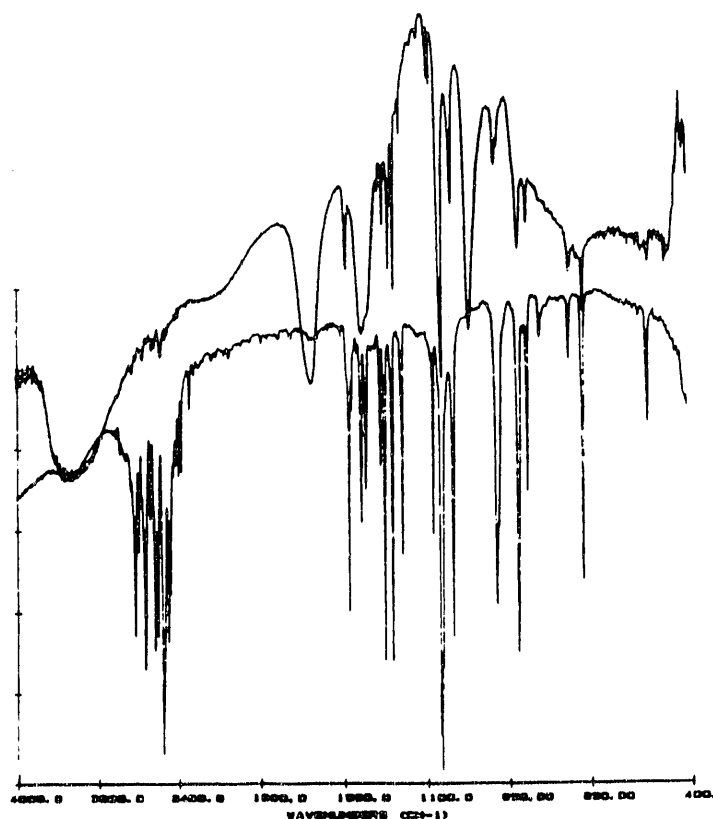


Figure 1 FTIR of Synthetic HMTAH⁺ Uranate (Upper) and HMTA·HCl (Lower)

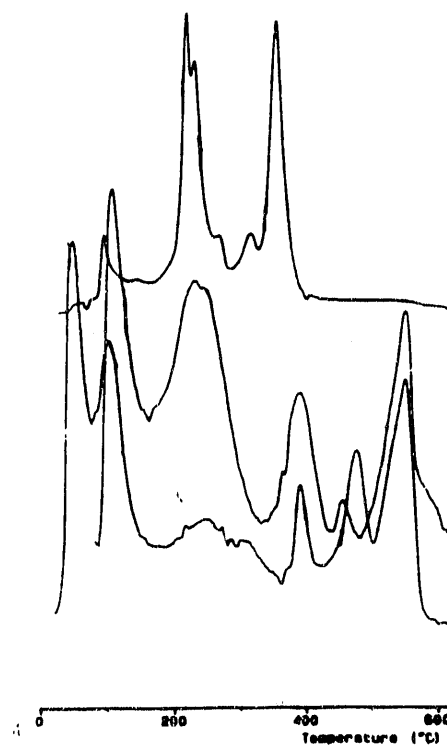


Figure 2 Differential weight loss of DABCO uranate (Upper), NH₄⁺ uranate (Lower) and NH₄⁺ exchanged DABCO uranate (Middle). Scale: DABCO = 5X, Other = 1X

DISCUSSION

The nature of the polymer in the post-washed gel formed in the ORNL process was studied by Lloyd, et. al., under various chemical conditions and was found to be consistent with a complex composition of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, $4\text{UO}_3 \cdot \text{NH}_3 \cdot 7\text{H}_2\text{O}$ and $2\text{UO}_3 \cdot \text{NH}_3 \cdot 3\text{H}_2\text{O}$ based on x-ray diffraction analysis [7]. Our results compliment the Lloyd, et. al., interpretation and provide insight on the structure of the hydrous uranium oxide polymer and the washing step.

The data from FTIR studies of uranium gels before and after washing with aqueous ammonia show that protonated HMTA is present initially and is removed by washing, being replaced by ammonium ion via an ion exchange process. At the same time, further condensation of the uranyl polymer occurs to polyanionic hydrous uranium oxide in what is believed to be a layered configuration. The HMTAH^+ and NH_4^+ ions are incorporated as "intercalation" cations to balance the negative charge of the hydrous uranium oxide layer. This was confirmed by XRPD measurements on gels and synthetic compositions [4].

A synthetic sample made by ammonia treatment of a uranyl solution at pH 4.5 had an approximate formula of $4\text{UO}_3 \cdot \text{NH}_3 \cdot 7\text{H}_2\text{O}$. The XRPD pattern of this sample is in good agreement with the literature pattern of Garner [6]. Garner classified his composition in the orthorhombic system as a layered structure with a basal reflection of 7.55 Å, but with atomic arrangements undefined. In addition, a very interesting structural analogue in the uranium mineral family [5] has been useful in the structural interpretation of the hydrous uranium oxide network. Pogoaga, et. al., published complete structures of several hydrous oxide minerals showing them to be layered structures with pentagonal coordination by oxygen around uranium and with cations occupying intercalation sites between the layers [5]. A comparison of the XRPD pattern of our synthetic ammonium, gel-like derivative with the mineral billietite shows a close match [4]. Therefore, we believe that the ammonium uranates made here and their isostructural amine analogues (Table I) are layered structures with the cations between the layers in intercalation sites. We conclude that "ammonium diuranate" observed as an intermediate in the U(VI) sol-gel process is a layered hydrous oxide with a proposed structural formula of $(\text{NH}_4)_2[(\text{UO}_2)_8\text{O}_4(\text{OH})_{10}] \cdot 8\text{H}_2\text{O}$ [4].

The following mechanism for gelation during the sol-gel process is postulated from this and other work reported at this symposium [4] and work reported by ORNL [8]. Uranyl nitrate starts to hydrolyze when the NO_3/U ratio is lowered. Urea at low temperature complexes the hydrolyzed species preventing precipitation. HMTA acts as a weak base reacting with H^+ ions in solution and causing further hydrolysis, favoring a trimeric species with pentagonal coordination around uranium [4]. Heat causes further hydrolysis and polymerization resulting in layered structures with HMTAH^+ as the cation neutralizing the negative charge in the polymeric layers. HMTA also acts as a water structuring agent through hydrogen bonding to the remaining nitrogen atoms. Washing replaces the HMTAH^+ with NH_4^+ and induces additional polymerization because the pH is much higher. Replacing the HMTAH^+ with NH_4^+ is essential because NH_4^+ is more easily removed at lower temperatures before all the water is gone and the structure is more open to gas release.

Table I: Basal Spacings of Uranates

<u>Compound or Mineral</u>	<u>Crystal Class</u>	<u>Basal Spacing</u>	<u>Reference</u>
$(\text{NH}_4)_2$ Uranate	Orthorhombic	7.5 Å	6
$(\text{HMTA})_2$ Uranate	Orthorhombic	7.8 Å	This work
Na_2 Uranate	Orthorhombic	7.9 Å	This work
DABCO Uranate	Orthorhombic	9.9 Å	This work
$(\text{TMA})_2$ Uranate*	Orthorhombic	7.2 Å	This work
TETA Uranate*	Orthorhombic	7.7 Å	This work
Becquerelite	Orthorhombic	7.50 Å	5
Billietite	Orthorhombic	7.50 Å	5

* TMA = Trimethylamine; TETA = Triethylene Tetraamine

ACKNOWLEDGMENTS

This work was conducted under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy. The authors gratefully acknowledge the assistance of Dr. Jack-Collins of ORNL on useful literature and process insight. Coworkers of the WSRC included Mrs. Nancy Gregory, Mrs. Arlene Ray and Mr. Joel Livingston (Radiochemistry), Mrs. Joyce L. Hunter (XRPD) and Mr. William Kerrigan (Thermal Analysis). Their tireless effort is gratefully acknowledged. The authors also thank Dr. M. Katherine Pagoaga of the NIST (Boulder, CO) for helpful discussions, literature and approval to use Hydrrous Uranium Oxide structural data.

REFERENCES

1. P. A. Haas, J. M. Begovich, A. D. Ryon, and J. S. Vavruska, *I&EC Prod. Res. & Dev.* **19**, 459 (1980).
2. J. B. W. Kanji, A. J. Noothout, and O. Votocek, Sol-Gel Processes for Fuel Fabrication, IAEA-161, (International Atomic Energy Agency, Vienna, 1974), p185.
3. I. S. Ahuja, R. Singh, and C. P. Rai, *Spectrochim. Acta* **35A**, 193 (1979).
4. C. M. King, R. B. King, A. R. Garber, M. C. Thompson, and B. R. Buchanan in Better Ceramics Through Chemistry IV, Edited by C. J. Brinker, D. E. Clark and D. R. Ulrich (Mater. Res. Soc. Proc., April, 1990).
5. M. K. Pagoaga, D. E. Appleman, and J. M. Stewart, *Amer. Miner.* **72**, 1230 (1987).
6. W. Garner, *J. Inorg. Nucl. Chem.* **21**, 380 (1960).
7. M. H. Lloyd, K. Bischoff, K. Peng, H. U. Nissen, and R. Wessicken, *J. Inorg. Nucl. Chem.* **38**, 1141 (1976).
8. J. L. Collins, M. H. Lloyd, and R. L. Fellows, *Radiochim. Acta* **42**, 121 (1987).

END

DATE

FILMED

4 1301 92

