DP-1201

AEC RESEARCH AND DEVELOPMENT REPORT

A MASS SPECTROMETRIC - THERMOGRAVIMETRIC TECHNIQUE FOR EVALUATING THE GAS RELEASE POTENTIAL OF SINTERED THORIA

P. CHASTAGNER

Savannah River Laboratory
Aiken, South Carolina

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Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy $3.00; Microfiche $0.65

DP-1201

Chemistry
(TID-4500,UC-4)

A MASS SPECTROMETRIC - THERMOGRAVIMETRIC TECHNIQUE FOR EVALUATING THE GAS RELEASE POTENTIAL OF SINTERED THORIA

by

Philippe Chastagner

Approved by

R. L. Folger, Research Manager
Analytical Chemistry Division

September 1969

E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, S. C. 29801

CONTRACT AT(07-2)-1 WITH THE
UNITED STATES ATOMIC ENERGY COMMISSION

ABSTRACT

A mass spectrometric - thermogravimetric technique coupled with electrochemical moisture determinations is described for the characterization of sintered thoria. The data obtained can be used to evaluate the gas release potential of thoria during reactor irradiation to produce ^{233}U.

INTRODUCTION

Thoria is irradiated in nuclear reactors to produce ^{233}U. At the Savannah River Plant, the thoria target elements are fabricated by filling specially designed aluminum containers with sintered thoria. These elements are irradiated in the reactor in contact with the heavy water which serves both as neutron moderator and coolant. During irradiation, the thoria in the center of the target element may reach temperatures hundreds of degrees higher than that of the moderator which is below its boiling point at atmospheric pressure. Under these conditions, gases that are sorbed or combined with the thoria may be released with resulting pressurization and failure of the element. Therefore, the gas release characteristics of each lot of thoria must be evaluated to determine its suitability for irradiation and to provide data for the design of satisfactory target elements. Such evaluation is readily accomplished by the combination of mass spectrometric - thermogravimetric analyses and electrochemical moisture determinations described and illustrated in this report.

EXPERIMENTAL

Equipment

A Bell and Howell CEC Model 26-321A Solids Moisture Analyzer was modified by replacing the furnace with a quartz tube furnace that could be operated at temperatures up to 1000°C. The furnace was mounted outside the analyzer and was connected to it with Teflon® tubing.

The mass spectrometric - thermogravimetric analyzer consisted of a Cahn Model RH Electrobalance® in a glass vessel with an Associated Electrical Industries Model MS10 mass spectrometer attached to the pumping line. The hangdown tube was 57 mm in diameter, and both it and the sample crucible were quartz. The hangdown wire and crucible support were Nichrome®. The hangdown tube was heated with a high temperature furnace with an upper

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Electrobalance - Cahn Division, Ventron Instruments Corp.
Nichrome - Driver-Harris Co.

temperature limit of 1200°C. The furnace temperature was controlled with a power proportioning programmer. The system was evacuated through a 5-cm-diameter stainless steel line by a diffusion pump equipped with a liquid nitrogen cooled baffle and backed by a mechanical pump. Provisions were made for collecting samples of effluent gases and for operation with controlled atmospheres. Viton® gasketed joints and valves were used throughout the high vacuum system. Thermocouple and cold cathode ionization gages were used to monitor pressures. The effective pumping speed at the sample was about 15 liters per second; pressures of 1×10^{-7} torr were obtained readily in the absence of an outgassing sample. The temperature, sample weight, and mass spectrometric data were continuously recorded.

Procedure

One-gram samples of thoria were heated from 300 to 1000°C in the electrochemical moisture analyzer to determine water content. The weight of water lost in the various temperature intervals was subsequently subtracted from the thermogravimetric values to determine the weight loss due to volatile species other than water.

Ten-gram samples of thoria were analyzed by the mass spectrometric - thermogravimetric system to determine weight loss characteristics between 25 and 1000°C and to determine the composition of the effluent gases. The detection limit for weight changes was about 0.4 ppm. In an analysis, a sample was first outgassed overnight at pressures of about 1×10^{-7} torr. The sample was then heated from 25 to 1000°C at a programmed rate of 5°C per minute. Mass spectrometric scans were made over the mass range 2-45 at frequent intervals.

RESULTS AND DISCUSSION

Experimental Observations

Data from mass spectrometric - thermogravimetric analyses and moisture analyses of two batches of sintered thoria are shown in Figures 1 and 2. These two batches had been similarly processed, but "A" was sintered in steel while "B" was sintered in graphite crucibles and therefore contained traces of carbon. As shown in Table I, thoria "B" also contained more alkali and alkaline earth impurities than "A".

TABLE I

Alkali and Alkaline Earth Impurities in Thoria

	Concentration, ppm				
	Ca	Na	Mg	Ba	K
Sample "A"	60	140	130	9	1
Sample "B"	370	400	100	15	2

The moisture analyses showed that the evolution of water from the thoria was essentially complete at about 500°C, as expected. The thoria-water system has been studied extensively by Fuller, Holmes, and Secoy,(1) and is not discussed here.

Carbon dioxide constituted the major part of gases evolved from the samples. The evolution occurred primarily between 300 and 800°C, with the maximum at about 600°C, indicating the source to be primarily from decomposition of alkali and alkaline earth carbonates. The quantities of metal impurities, if present as carbonates, were more than sufficient to account for the CO_2 evolved, which was calculated to be approximately 80 ppm for thoria "A" and 400 ppm for thoria "B".

While some CO was evolved from thoria "A", a larger amount of CO and also some H_2 was evolved from thoria "B". The water gas reaction between the carbon impurity and water vapor is probably responsible for this production of CO and H_2.

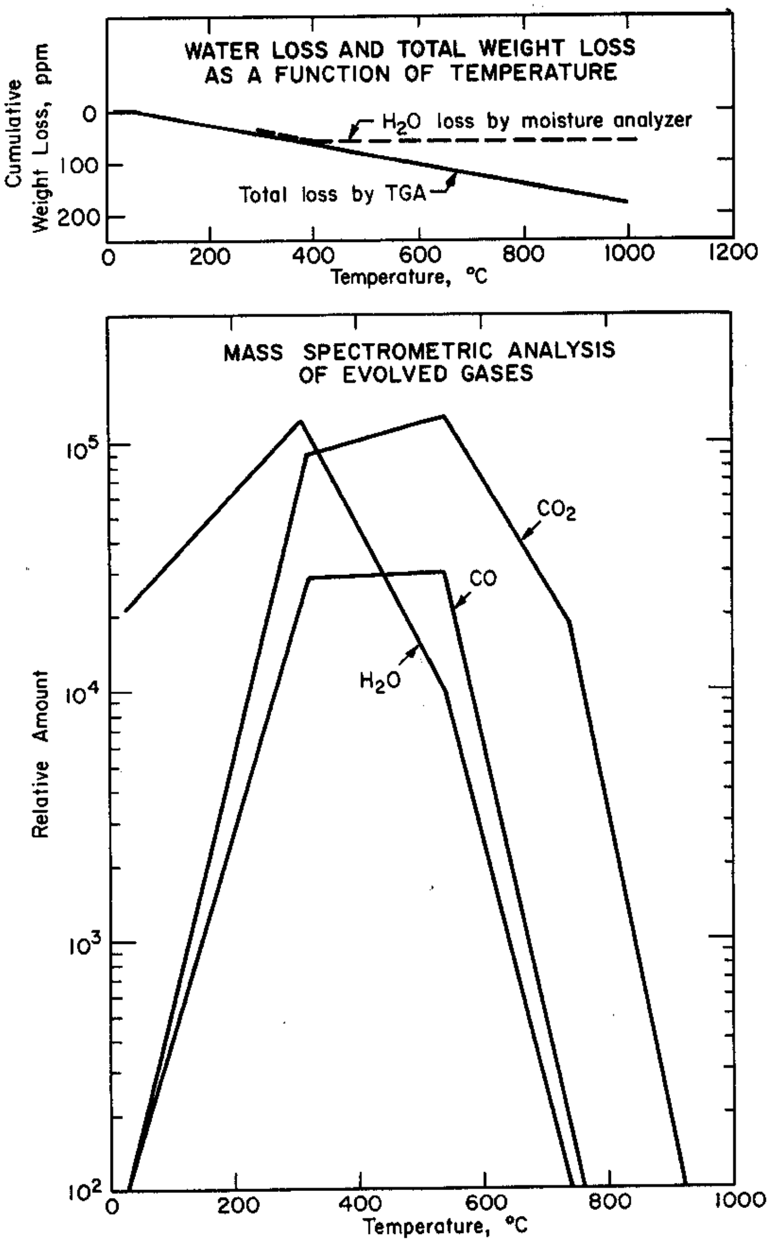

FIG. 1 THORIA SAMPLE "A"

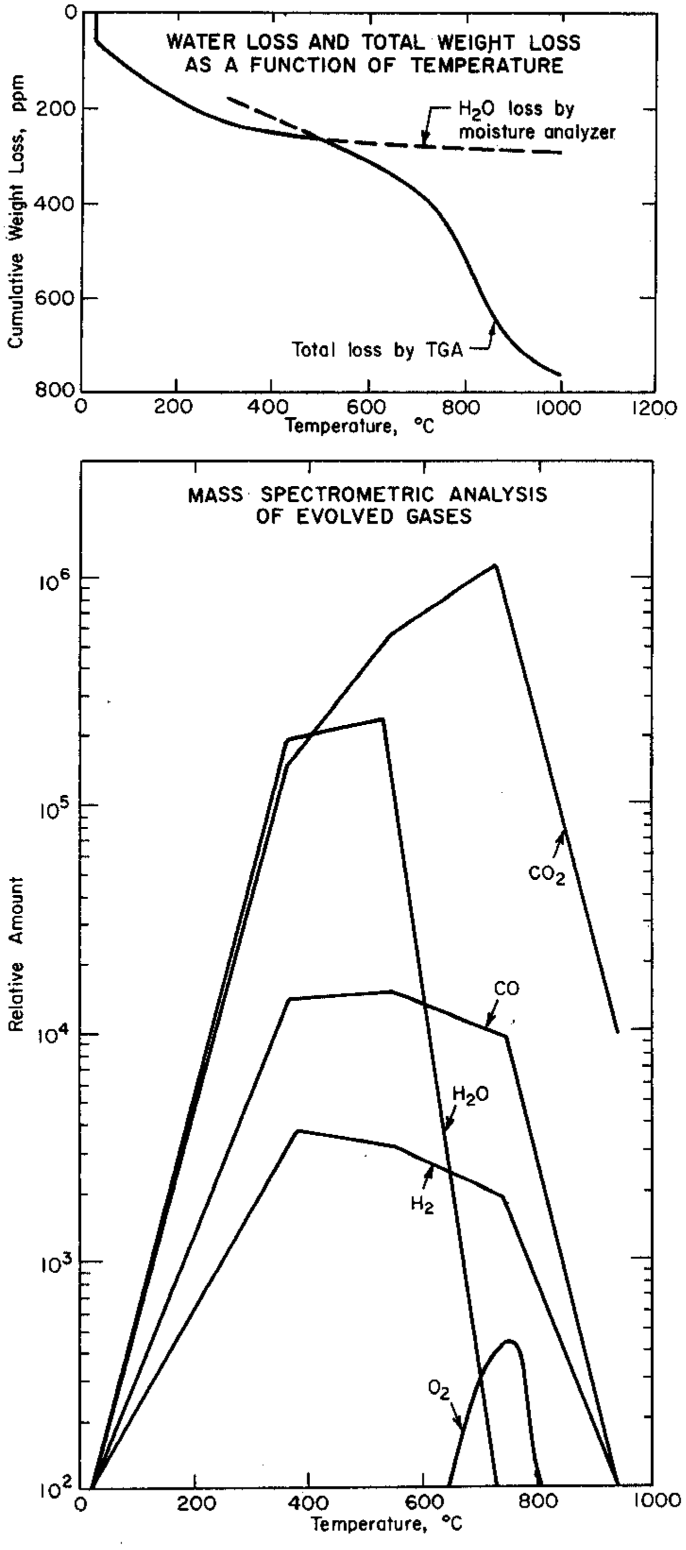

FIG. 2 THORIA SAMPLE "B"

Traces of O_2 were detected from thoria "B" at temperatures above 700°C, and the source is suggested to be from the decomposition of sodium oxide. Sodium oxide is unstable at 730°C, decomposing into sodium vapor and oxygen gas; sodium and oxygen can exist in equilibrium at 1 torr pressure at 1100°C.(2,3) Rapid attack of the quartz crucible and furnace tube during analysis of thoria "B" samples confirmed the volatilization of alkali metal.

No indication was obtained of the presence of thorium hydrides in these samples of sintered thoria. The thorium hydrides decompose predictably, Th_4H_{15} at 300 to 325°C and ThH_2 at 600°C.(4) As little as 0.0005% Th_4H_{15} would have been detected.

Prediction of Behavior During Reactor Irradiation

In a thoria target element undergoing reactor irradiation, all volatile components are confined within the aluminum container where they may interact in a variety of ways. Water would be largely desorbed at the operating temperatures, and that in excess of the quantity required to saturate the void space would condense on the cooler walls of the container. The water could react with any carbon present to produce H_2 and CO. Metal carbonates in the higher temperature zones would decompose to CO_2 and metal oxides, which could in turn decompose into the metal and O_2. The reactive metals thus formed could combine with H_2O vapor to produce metal hydroxides, which also have high vapor pressures and would tend to migrate to the container walls. There, H_2 could be produced by attack of the Al, or carbonates could be reformed by absorption of CO_2. Any oxygen liberated could react with H_2 to produce H_2O, or could attack the container to form Al_2O_3.

The total pressure generated within a thoria target element during irradiation will be the sum of the partial pressures of the fill gas (if any), H_2O vapor, H_2 generated by corrosive attack, H_2 and CO generated by a water gas reaction, desorbed CO, CO_2 produced by dissociation of metal carbonates, and O_2 produced by decomposition of metal oxides. The major contributor to the pressure will be CO_2 with the usual grades of thoria. The maximum possible CO_2 pressure can be calculated from mass spectrometric - thermogravimetric data, but the actual pressure developed is strongly dependent on the relative amounts of the various alkali metal and alkaline earth impurities. The dissociation pressures of Na_2CO_3, K_2CO_3, and $BaCO_3$ are about 0.05 atmosphere at 1200°C, while that of $CaCO_3$ is about 20 atmospheres; that of $MgCO_3$ is 470 atmospheres at 700°C.(5,6) In a hypothetical thoria element containing 500 ppm of CO_2 as $MgCO_3$ as the only impurity, the partial pressure of CO_2 would be about 10 atmospheres at an average temperature of 700°C. If the metallic impurity were Na, the pressure would be only 0.002 atmosphere. With mixed metal impurities, the CO_2 partial pressure would be a complex function of the relative amounts and decomposition pressures of the various metal carbonates and oxides present.

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