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by

Donald E. Vance
Maynard E. Smith
Glenn R. Waterbury

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DETERMINATION OF TOTAL AMOUNT OF VOLATILES IN MIXED - OXIDE REACTOR FUEL PELLETS

by

Donald E. Vance, Maynard E. Smith, and Glenn R. Waterbury

ABSTRACT

Mixed-oxide reactor fuel pellets are heated inductively to 1600°C in a vacuum extraction apparatus to evolve the adsorbed volatiles which are measured volumetrically. Water vapor in the volatiles is removed by $\text{Mg}(\text{ClO}_4)_2$ dessicant, and the remaining gases are collected using a Toeppler pump. The pressure, volume, and temperature of the collected gases are measured, and the volume at standard conditions is calculated. The total amounts of volatiles measured other than water ranged between 0.020 and 0.059 cm^3/g for one lot of samples. A mass spectrometric study of the volatiles evolved from 200 to 1800°C identified H_2 , He, CO, CO_2 , N_2 , NO, O_2 , and Ar.

I. INTRODUCTION

A property of sintered mixed oxides important to their use as reactor fuels is the quantity of gas, including water vapor, evolved at reactor operating temperatures. Because of the small quantities of volatiles generally found in sintered fuel pellets, a sensitive method was required. A vacuum extraction system having a small calibrated volume for measuring the evolved gases without excessive dilution or contamination was designed and tested. The design requirements of the vacuum extraction system precluded the simultaneous determination of water with the other volatiles because the large-diameter tubing and valves, water-cooled pumps, and large-volume glassware presented considerable opportunity for adsorption of water vapor before it could be measured. Consequently, the water was determined separately.¹

II. APPARATUS AND REAGENTS

A. Apparatus

Bucket, made from 4-mil tungsten foil, 1 in. high, 3/8-in. o.d. (Fig. 1).

Calibrated sample tube, made of graduated glass

tubing, approximately 1.25-ml total volume (Fig. 2). Calibrate by weighing the amounts of mercury required to fill to each graduation mark and calculating the respective volumes.

Chain, gold, with welded links approximately 1 mm long.

Chain, platinum, 2-in.-long welded links made from 0.010-in. platinum wire.

Desiccant tube, borosilicate glass, filled with anhydrous magnesium perchlorate (6 to 8 mesh) and plugged with glass wool in each end to contain the reagent dust.

Diffusion pumps, glass, two required, Consolidated Vacuum Corporation (CVC), type GHG-15, or equivalent pump which will continue to pump with relatively high forepressures. Water-cooled, rather than nitrogen-cooled, condensers were used on these pumps to avoid condensation of volatiles from the pellets, and gold foil was placed in the entrance arm of the condenser nearest the induction furnace as a barrier to back-diffusion of mercury vapor into the furnace.

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Fig. 1. Sample manipulator.

Diffusion pump, metal, CVC type MHG-180, or equivalent.

Electric timers, 30-sec. two required, Industrial Timer Corporation, or equivalent. Wired so that one timer controls the vacuum half of the Toepler pump cycle and the other alternately controls the pressure half of the cycle.

Furnace adapter, borosilicate glass (Fig. 3).

Furnace tube, fused-silica (Fig. 4). The furnace tube is surrounded by a water jacket in which the wire induction coil is inserted. The outer tube is sealed to the induction coil terminal blocks with epoxy cement to make a water-tight seal and the inner tube (furnace tube) is sealed with Viton O-rings as shown. This furnace design yielded the lowest apparatus background of several designs tested.

Gloved enclosure, suitable for handling plutonium oxide. The enclosure contains only the induction furnace tube and furnace fittings.

Induction generator, 25 kW, LASL drawing No. 26Y-76681, or equivalent.

Mass spectrometer, Consolidated Electrodynamics Corporation, Model 21-620, or equivalent.

McLeod gauge, constructed of borosilicate glass tubing of the same diameter used in the sample tube (Fig. 2).

Pressure controls, Mercoid Corporation, or equivalent, three required to turn off diffusion pump heaters in case of cooling-water failure.

Regulator, high pressure, Victor Equipment Company, or equivalent.

Regulator, low pressure, 0 to 50 in. of water range, Moore Products Company, Model 40-2, or equivalent regulating device.

Regulator, low pressure, Matheson Company, Model 2403-M2, or equivalent.

Sample loader, borosilicate glass (Fig. 3).

Sample manipulator, borosilicate glass (Fig. 1).

Sight glass, borosilicate glass (Fig. 3).

Solenoid valves, Skinner Electric Valve Division, one No. V5D3870 or equivalent and one V5D1680CR or equivalent required; Automatic Switch Company, one No. 827616R or equivalent required.

Thermometer, mercury, two required, one having a range of -10 to +510°C, and one suitable for measuring ambient temperature.

Toepler pump, 250 ml, Eck and Krebs Scientific Laboratory Glass Apparatus, Incorporated, or equivalent.

Tongs, stainless steel, 12 in. long, modified so that the tips spread outward when the handle is compressed, to remove and replace the crucible in the induction furnace.

Tubing, 304 stainless steel, 0.75-in. o.d., for construction of vacuum manifold.

Vacuum gauges, two required, NRC Equipment Corporation, Type 701, or equivalent.

Fig 2. Vacuum extraction system. A, induction furnace assembly; B, monel bellows; C, wall of gloved enclosure; D, low pressure regulator, 0 to 50 in. of water; E, vacuum gauge thermocouple; F, water-cooled condensers; G, glass diffusion pumps; H, 28/12 semi-ball joints; I, $\text{Mg}(\text{ClO}_4)_2$ trap; J, calibrated sample tube; K, Toepler pump; L, McLeod gauge; M, mercury reservoir; N, metal diffusion pump; O, water-cooled baffle; P, vacuum gauge thermocouple; Q, mechanical forepump; R, low pressure regulator; S, needle valve; T, solenoid valves; U, solenoid valves; V, cycle counter; W, Toepler pump timers; X, mechanical vacuum pump; V1 and V14, Hoke valves No. 4551Q4M; V2 through V13, V15 and V16, stainless steel bellows valves.

Vacuum manifold, stainless steel tubing, valves, bellows, and fittings; welded joints throughout (Fig. 2). Tees were drawn in the tubing, using the method described by Ruess,² to permit 100% penetration in the welded joints and to provide optimum gas flow characteristics.

Vacuum pumps, mechanical, W. M. Welch Manufacturing Company, Model 1405H, and Cenco Hyvac, Catalog No. 91105.

Valve, bellows, stainless steel, Heraeus Englehard Vacuum, Incorporated, or equivalent, 14 required.

Valve, Hoke No. 4551Q-4M or equivalent, two required.

Variable transformers, 10-A, two required for operation of the glass diffusion-pump heaters.

B. Reagents

Argon, tank.

Grease, silicone, Dow-Corning high-vacuum.

Magnesium perchlorate, anhydrous, reagent grade.

Mercury, triple-distilled

Wax, Apiezon W.

III. SAMPLE PREPARATION

Inspect the sample for obvious impurities such as lint, and remove any foreign material. Because pellet storage conditions are not yet rigidly specified, analyze sample pellets as received without further preparation. It has become obvious, however, from this and other work,¹ that storage under dry conditions would alleviate problems in the use of the pellets as reactor fuel, and also simplify the analytical methods for measuring volatiles and water.

IV. RECOMMENDED PROCEDURE

CAUTION: Health and safety rules for handling of radioactive materials must be rigidly followed, and adequate protection for the operator must be ensured by the use of suitable gloved enclosures and protective clothing.

Fig. 3. Induction furnace adapter, sample loader, and sight glass.

1. Keep the apparatus under forepump vacuum at all times when not in use. Turn on the diffusion pumps about 12 h before samples are to be analyzed.

2. Isolate the furnace tube by closing valves V2 and V3 (Fig. 2), and disconnect the sample loader while flushing the furnace with argon through valve V1.

3. Fill the loading arm with the fuel pellets to be analyzed and reconnect the sample loader to the furnace, sealing the joint with silicone grease.

4. Evacuate the furnace by closing valves V1, V4, V5, V7, V8, V10, V12, and V16, opening valves V15, V13, V11, V9, and V6, and slowly opening valve V3 so as not to cause violent agitation of the mercury in the Toepler pump. When the thermocouple gauge, P, indicates a pressure of 100 microns or less, close valves V3, V6, V9, V13, and V15, and open valves V16, V12, V10, V8, V7, V5, V4, and V2.

5. Heat the empty crucible slowly to increase its temperature to 1600°C during 4 to 6 h.

Fig. 4. Induction furnace and fused-silica furnace tube.

6. Slowly open the three-way stopcock to allow air to enter the mercury reservoir, M, until mercury rises about halfway up the side-arm leading to the Toepler pump.

7. Close valve V11 and start the Toepler pump timers, W.

8. After about 35 min (70 cycles of the Toepler pump), close the stopcock above the reservoir bulb of the Toepler pump with the mercury at the top of its cycle, and turn off the timers.

9. Allow more air to enter the reservoir, M, until the mercury reaches a suitable graduation on the sample tube, J.

10. Record the temperature, volume, and difference in millimeters pressure between this level of mercury and the level of mercury in the McLeod gauge.

11. Calculate the amount of gas trapped in the sample tube (apparatus background) using Eq. (1).

$$\text{Volume at standard conditions} = \frac{PV}{2.782 T} \quad (1)$$

in which:

P = difference in millimeters pressure,

V = sample volume (cm^3), and

T = temperature of sample tube ($^{\circ}\text{K}$).

12. Repeat steps 6 through 10 until the apparatus background decreases to a stable value of less than 0.010 cm^3 at standard temperature and pressure; turn off the induction generator and allow the crucible to cool to approximately room temperature.

13. Use a magnet to move the iron push-rod up the side arm of the sample loader until the first pellet drops into the crucible. Determine the gas evolved from the sample by repeating steps 6 through 11 while heating the crucible at 1600°C .

14. Subtract the amount of gas measured in Step 10 above to calculate the gas released from the pellet.

15. Alternate determinations of the apparatus background and samples.

V. EXPERIMENTAL

Reaction between the hot tungsten crucible and the water evolved from the fuel pellets was suspected of producing hydrogen which would cause an error in the results for the total volatiles. For this reason, the reaction was investigated by heating tungsten powder in a moist argon atmosphere and analyzing the argon for hydrogen contamination with a mass spectrometer. No reaction was detected after heating at 350°C for 45 min, but hydrogen was detected in the argon after heating at 400°C for 20 min and also after heating at 500°C for 10 min.

The compositions of the effluent gases from the fuel pellets at various temperatures were determined. To assure accurate temperatures, the power settings of the induction generator were calibrated by measuring the temperatures produced with either a mercury thermometer for the 200-to- 500°C range or an optical pyrometer for higher temperatures. The thermometer was inserted

through a 1-hole rubber stopper fitted into the top of the furnace tube with the thermometer bulb touching the bottom of the empty crucible in the furnace. The furnace was then evacuated and the temperature within the crucible measured as the generator power settings were changed. Power settings for each temperature of interest above 500°C were determined using a completely evacuated furnace fitted with a sight glass through which the temperatures were measured with an optical pyrometer. The empty crucible was heated slowly to prevent too rapid outgassing and subsequent deposition of tungsten oxides on the furnace walls.

The method selected as the most reliable and convenient for handling the pellets for the tests at various temperatures utilized a manipulator (Fig. 1) to remove and replace the pellet in the crucible while maintaining the vacuum in the induction furnace tube. A fuel pellet was placed in the side-arm of the manipulator, the manipulator was placed on the furnace, and the apparatus was evacuated. The empty tungsten-foil bucket was then lowered into the crucible and both bucket and crucible were outgassed at 2000°C . When repeated measurements showed the apparatus background at 2000°C to be low and reproducible, the bucket temperature was lowered to 200°C and held there until a stable apparatus background was attained at the lower temperature. The gas collected in the sample tube during the last measurement of the apparatus background was analyzed with a mass spectrometer.

The crucible was allowed to cool, and the bucket was raised to a position immediately below the sample side-arm. A magnet was used to move the iron rod that pushed the pellet out of the side-arm so it would fall into the bucket. The bucket and pellet were then lowered into the crucible and heated to 200°C . At the end of the heating period the gas collected in the sample tube was analyzed, using the mass spectrometer, for H_2 , He, CO, N_2 (and NO), O_2 , Ar, and CO_2 . The percentage composition and number of micromoles of each gas were calculated after subtracting the apparatus background. The bucket and pellet were then raised into the side-arm of the manipulator containing the winch, and the empty crucible heated to a temperature equivalent to a bucket temperature of

500°C. The apparatus background at this temperature was determined. The bucket and pellet were lowered into the crucible and heated to 500°C. This procedure was repeated at 800, 1000, 1300, 1600 and 1800°C, and the collected gas samples from the empty crucible and from the crucible-plus-pellet at each temperature were analyzed with the mass spectrometer.

The amount of gas contributed by the bucket during the heating of the pellet was considered insignificant compared to the effluent variations between the individual pellets analyzed. At temperatures up to 1300°C (Table I) the principal component of the evolved gas was H₂, and CO was the principal component at 1600 and 1800°C.

The tungsten-water reaction might produce some of the hydrogen collected at 500°C. A large fraction of the water would evolve at 200°C and not react with the crucible at this temperature. Because essentially all of the remaining water was evolved at the end of the 500°C heating period¹ (35 min at 200°C and 35 min at 500°C), it is unlikely that any hydrogen collected at higher temperatures comes from water. If all of the hydrogen measured at 500°C was from this source, which is unlikely because of the evaporation of the water and the slow rate of reaction with the tungsten, the error in the total volatiles collected would be approximately 6%. A maximum of one-fourth of the total hydrogen collected conceivably could derive from the water, but most of the evolved hydrogen probably had been adsorbed from the sintering furnace atmosphere during pellet manufacture.³

The amount of carbon monoxide increased rapidly at temperatures above 1300°C. This increase was probably caused by reduction of the uranium-plutonium dioxide by carbon impurities that reportedly average about 50 ppm⁴ in the fuel material. The amount of carbon monoxide evolved at 1800°C could cause an error in the calculated reactor conditions if these calculations were based on total volatile measurements taken at 1600°C.

Analysis for volatiles at temperatures higher than 1800°C does not appear feasible. One pellet heated to 1900°C for 35 min and then to 2100°C apparently began to volatilize at 1900°C as evidenced by a deposit formed on the walls of the induction

furnace. At 2100°C the deposition began to cause excessive heating of the furnace tube O-ring seal. When all pellet particles remaining in the furnace crucible were weighed, the loss of pellet material by vaporization was approximately 60%.

The amount of nitric oxide evolved from the pellets was not determined because a suitable standard was not available to determine the sensitivity of the mass spectrometer. If the respective sensitivities of the mass spectrometer were identical, the quantities of evolved nitric oxide and argon were about equal. These amounts would not cause significant error in the quantities of nitrogen reported.

From the results of this investigation, a temperature of 1600 to 1800°C was selected as optimum for the evolution of volatiles. If the quantities of water in these pellets increase to levels that interfere seriously in the measurement of total volatiles because of the hydrogen produced, the use of crucible materials other than tungsten will be investigated to avoid the tungsten-water reaction. A tungsten crucible and a temperature of 1600°C are used at the present time to assure uniformity in results among various laboratories.

VI. RELIABILITY

The precision and accuracy of this method could not be determined because of the lack of suitable standards and because of heterogeneity in volatiles content among individual pellets from one lot. The pooled standard deviation obtained by seven laboratories for the analysis of one lot of uranium-plutonium dioxide pellets by this and similar methods was 0.012 cm³/g at standard temperature and pressure.⁴ This precision estimate includes the between-pellet and the analytical measurement variabilities.

VII. CONCLUSIONS

A vacuum extraction method was developed for the determination of total volatiles other than water in sintered FFTF reactor fuel pellets of uranium-plutonium dioxide. A fuel pellet is heated inductively to 1600°C in a tungsten crucible for approximately 35 min. The evolved water is removed with Mg(ClO₄)₂ and the other gases are collected

TABLE I
COMPOSITION OF EFFLUENT

T (°C)	Total Micromoles	H ₂ (%)	He (%)	O ₂ (%)	Ar (%)	CO ₂ (%)	CO (%)	N ₂ & NO (%)
200	0.041	30.7	0	2.4	0.4	8.2	28.6	29.7
500	0.487	68.7	trace	1.7	0.1	4.9	10.6	14.0
800	0.625	74.9	0.3	0.3	trace	0.7	18.4	5.4
1000	0.384	67.5	0.2	0.3	trace	0.4	24.7	6.8
1300	0.457	52.9	1.1	0.4	trace	0.5	35.6	9.5
1600	1.294	1.8	0.7	0.6	0.1	0.2	95.2	1.4
1800	2.644	0	0.3	0.2	0.1	0.1	99.3	0

by a Toeppler pump and measured. The amounts of gas released by three pellets analyzed were 0.059, 0.030, and 0.022 cm³/g of pellet material. Mass spectrometric analysis of the gas collected after heating pellets to various temperatures showed the presence of H₂, He, CO, N₂, NO, O₂, Ar, and CO₂. Increasing amounts of carbon monoxide released at temperatures from 1300 to 1800°C indicate that 1800°C may be a more suitable temperature for analysis than the previously-specified 1600°C. Analysis above 1800°C does not appear feasible because of volatilization of the fuel pellets.

The accuracy of the determination of the volatiles would possibly be improved if the fuel pellets were stored in a desiccator after removal from the sintering furnace during manufacture. The pellets rapidly adsorb some moisture from the air¹ and it is later released during analysis for volatiles. The moisture may be reduced by the hot tungsten crucible to hydrogen and cause an erroneous high measurement of total volatiles evolved. The extent of this reaction during volatiles analysis is unknown but should not be appreciable with pellets containing 3 μg of water or less per gram of pellet material. During analysis, the tungsten crucible is heated to 1600°C in approximately 1 min. The rapid outgassing of water from the fuel pellet, combined with the high pumping speed of the vacuum apparatus, may cause the extent of the tungsten-water reaction to be insignificant.

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