THERMAL TREATMENT OF HTGR FUEL*

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Introduction

The reference fuel kernel in high-temperature gas-cooled reactors (HTGRs) is UO_2 and UC_2 finely dispersed in microspheres of porous carbon derived from weak-acid ion-exchange resins (WAR).[1,2] These resins are available commercially as sized and shaped microspheres derived from acrylic acid-divinylbenzene. Amberlite IRC-72 (manufactured by Rohm & Haas) and Duolite C-464 (manufactured by Diamond Shamrock) were used in this study.

After drying, carbonization to 900°C completes the H_2O evolution and thermally decomposes the resin, producing finely dispersed UO_2 in a porous carbon matrix. Typical properties are carbon-to-uranium ratios of from 4 to 6 with a density of 2.4 to 3.7 Mg/m^3 and 67 to 75 wt % U.

Carbothermic reduction of the UO_2 (conversion) produces UC_2 and $UC_{1-x}O_x$ with the evolution of CO. The percent oxygen removed is defined as the percent conversion (UO_2 = 0%, UC_2 = 100%). Final weight percent uranium ranges from 72 to 86% with corresponding densities from 2.4 to 6 Mg/m^3.

This work determined the effect of heating rate during carbonization on the bulk physical and chemical properties, the variation during processing of significant material properties, and the effect of conversion conditions on the thermodynamic predictions.

Experimental Procedure

Processing occurs in vertical graphite resistance furnaces containing cylindrical graphite fluidization tubes having conical bottoms. Chamber diameters are nominally 2.54 to 6.35 cm (1.00 to 2.5 in.). Temperature measurement is accomplished with sheathed Chromel-P–Alumel bed thermocouples to 700°C and optical pyrometry for higher temperatures. Fluidizing (argon) gases are supplied through calibrated flowmeters.

Thermogravimetric (TGA) and differential thermal analysis (DTA) were conducted with a Mettler recording vacuum thermoanalyzer 300. To establish the effect of heating rate during carbonization on bulk properties, Amberlite IRC-72 and Duolite C-464 were heated at controlled rates to 500°C followed by rapid heating to 1200°C.

Property variation during processing was investigated by heating both resins at 2°C/min to 500°C and then at 20°C/min to a selected temperature. Mercury density and porosimetry, BET surface area, carbon-to-uranium ratio, particle size, and bulk physical properties were determined.

Comparisons of observed and predicted conversion levels for different gas flows, resin types, temperatures and batch sizes were made in 35 experiments with gas flows from 0.295 to 7.37 ℓ of argon per gram of uranium from 1500 to 1690°C at conversion levels from 15 to 93%. Batch sizes varied from 28 to 486 g in furnace tubes from 35 to 108 mm in diameter.

Results

The Amberlite IRC-72 TGA analysis showed a gradual weight loss to 270°C for 2°C/min, a large weight loss from 360 to 440°C, and little subsequent weight loss to 1000°C. Faster heating rates increased the weight loss.

The Duolite material shows little weight loss until 210°C where a gradual loss occurred. Faster weight losses occur with lower heating rates to approximately 315°C, above which the weight loss accelerates. Above 480°C, little weight loss occurs to 1000°C. The Duolite resin requires higher temperatures for equivalent decomposition than does the Amberlite material, which is attributed to the higher degree of polymer cross-linking resulting from the higher uranium concentration. The predominance of the reaction rate in the 350 to 460°C region is apparent throughout.

The DTA results show three broad endotherms for both resins. Comparison with the TGA results indicates that the peaks correspond to the weight losses. The relative peak sizes correspond to the relative weight losses. The similar thermal behavior indicates that similar processes may be occurring in both resins above 270°C.

The effect of heating rate on Amberlite IRC-72 from 200 to 500°C, the predominant TGA region, on the weight loss, volume loss, and carbon-to-uranium ratio shows a strong linear dependence on the log of the heating rate. As carbothermic reduction to UC_2 requires a carbon-to-uranium ratio of 4, any technically feasible heating rate will be satisfactory. Duolite C-464 shows a stronger correlation with higher carbon-to-uranium ratios.

Comparisons of the carbon-to-uranium ratio are significant as a higher ratio reduces the agglomeration tendency during conversion. Both resins show reduced agglomeration tendencies with slower heating rate through the critical range. Conversion runs under comparative conditions indicate Duolite resin to be superior in resisting agglomeration.

The changes in weight loss, volume loss, and tap density are shown for Amberlite in Fig. 1. Tap density is obtained from the bulk volume occupied by the particles. The weight loss curve follows the TGA behavior. The behavior of Duolite C-464 is similar. Particle size, carbon-to-uranium ratio, and mercury density closely replicate the TGA and shrinkage curves. Mercury porosimetry shows that carbonized Duolite C-464 has 0.05-μm pores, significantly

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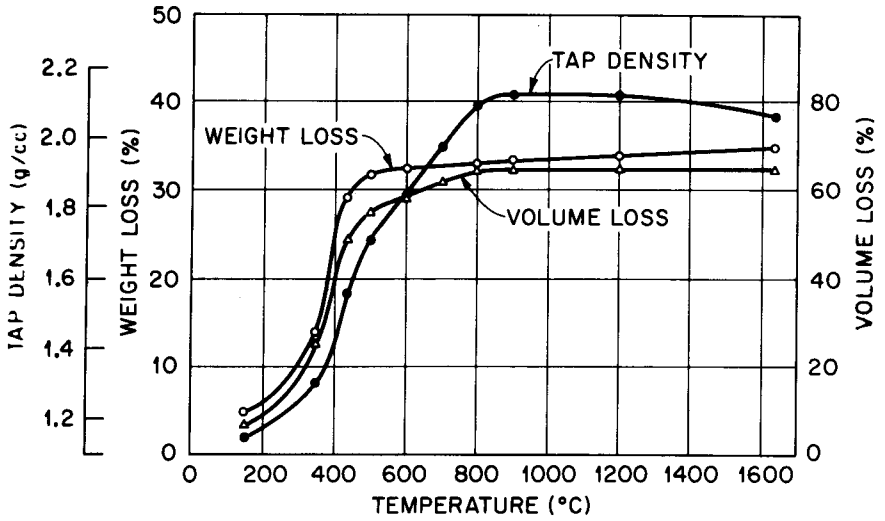

Fig. 1. Weight Loss, Volume Loss and Tap Density Variation from 150 to 1625°C for Uranium-Loaded Amberlite (IRC-72) Weak-Acid Resins.

larger than the 0.015 μm Amberlite IRC-72. Both resins showed similar variations from 150 to 1625°C. Smaller pores open from 150 to 440°C while thermal decomposition proceeds. From 500 to 1200°C, the pores coalesce and increase in size.

The changes in volume, weight, and density with conversion levels at 1625°C (after carbonization at 2°C/min) are shown in Fig. 2 for Amberlite IRC-72. Duolite C-464 had a similar behavior. Particle size and mercury density variation with conversion level correspond to the bulk property variation.

The conversion behavior of various batches at different gas flows is shown in Fig. 3. The gas flow is in liters of argon per gram of uranium per percent conversion obtained. The dashed-regression-line fit for $y = ax^b$ and the conversion reaction curve are shown. The two resins were not significantly different.

The strong dependence of conversion on gas flow agrees with the model described by Lindemer[2] and Beatty.[3] If sufficient porosity is available so that carbon monoxide removal is not diffusion-rate limited, conversion can be predicted from the equilibrium partial pressure of carbon monoxide.

Conclusions

1. Chemical and bulk physical properties closely reflect the TGA behavior and are sensitive to heating rate through a critical temperature range from about 350 to 460°C during the carbonization process. The carbonization process is near optimal at a rate of approximately 2°C/min through the critical range and the maximum practicable rate outside this range.

2. The carbothermic reduction of UO_2 can be accomplished at 1500 to 1750°C in a controlled manner by the rate of CO removal by the inert sweep gas and temperature as predicted by thermodynamic calculations.

References

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(3) T. B. Lindemer, *Nucl. Appl. Technol.* 9 (November 1970).

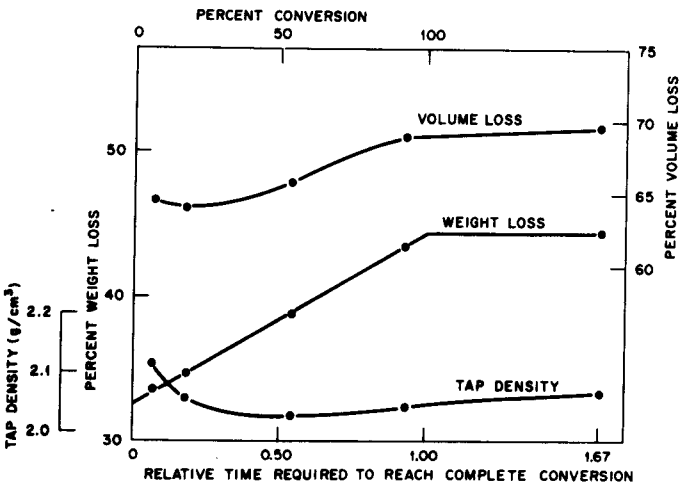

Fig. 2 (Left) Weight Loss, Volume Loss, and Tap Density Variation as a Function of Conversion Level at 1625°C for Uranium-Loaded Amberlite (IRC-72) Weak-Acid Resin.

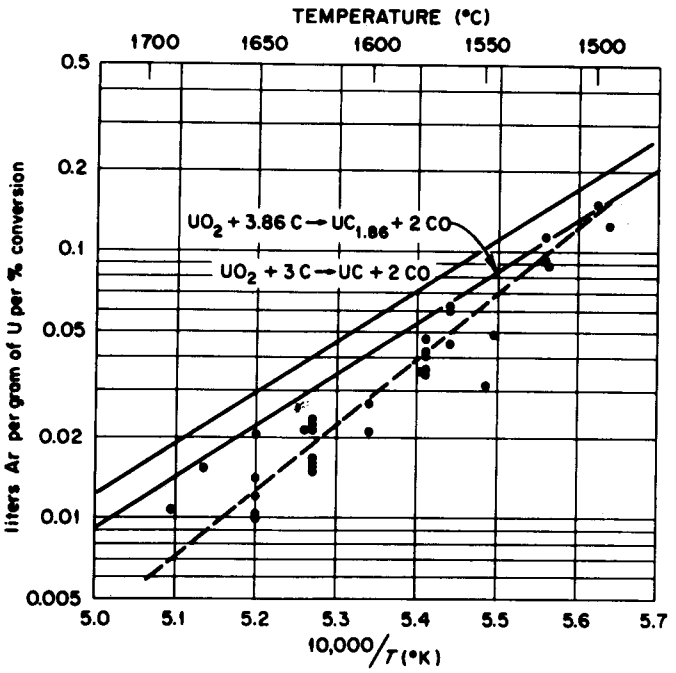

Fig. 3 (Right) Conversion Behavior of Weak-Acid Resin-Derived Fuel.