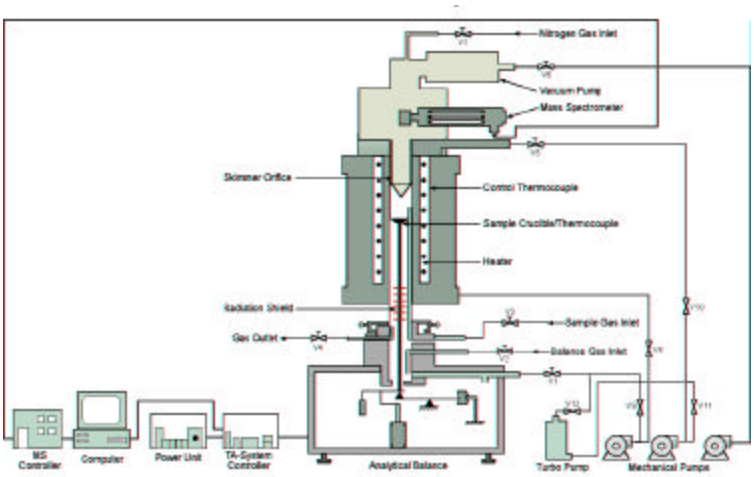
Enhanced Thermo-Gravimetric Analysis (TGA) Instrument

The Challenge

A method is needed to measure the oxidation rate and the rate of water evolution (drying) at various temperatures for samples of N Reactor fuel and associated sludge. Such an apparatus should have the ability to detect oxidation by weight gain and water evolution by weight loss. The detection of other evolved gases, such as hydrogen and fission gases, which may elucidate chemical reaction mechanisms, is also desirable.



A Schematic of the TGA/MS/DSC System

Irradiated N Reactor spent fuel has been stored in the water-filled Hanford K Basins for more than 15 years. A concerted effort is underway to move this fuel away from its current location near the Columbia River. The fuel will be placed in Multi-Canister Overpacks (MCOs) which will, in turn, be placed in interim storage at the Canister Storage Building after fuel drying is accomplished. Since much of the fuel is currently in a fractured condition and significant uranium fuel surface area is exposed to the surroundings, understanding the rate of reaction of fuel with oxygen and moisture is important for safety analysis calculations. Such oxidation reactions are a source of chemically-produced heat which must be carefully balanced against the surrounding heat removal capability during the various stages of drying and storage. Furthermore, since the drying process will take place at relatively low temperatures, it is inevitable that some amount of residual water will accompany the fuel into interim storage. This includes both water bound to the fuel itself, and water contained in sludge which may be trapped in the cracks associated with breached fuel. Quantification of the kinetics for release and decomposition of this water is important to the future pressurization of the MCOs as they sit in storage.

Current Approach

The initial attempts to quantify the oxidation behavior of N Reactor fuel were performed in a small clam-shell furnace where the depletion of oxygen in the flowing gas stream was taken as an indication of oxygen uptake by the sample. Measurement of this oxygen depletion via a gas chromatograph was not nearly as accurate as a weight measurement would be and some of the oxygen depletion could be ascribed to uptake by the furnace structure

Benefits and Features

- Continuous weight change measurement for large samples and extended operating temperature range
- Operates in vacuum, moist and dry gas environments
- Glove box installation for control of contamination
- Built-in mass spectrometer for gas composition monitoring

rather than the sample. The drying behavior of sludge was initially studied using very small samples (milligram quantities) in an inferior thermo-gravimetric analysis (TGA) instrument which had no capability to attain vacuum conditions and no capability to analyze gases driven off from the sample. This less-sophisticated instrument was installed in a fume hood which limited the ability to control contamination from large quantities of radioactive particulate and fuel.

New Technology

An enhanced TGA instrument with the capability to run gram-size samples enabled the analysis of macroscopic pieces of N Reactor fuel. This is a significant improvement since smaller microgram samples may not always contain the inhomogeneities which can initiate rapid oxidation. The temperature capability ranged from 70°C to 1000°C and vacuum operation is routine. The instrument also included a mass spectrometer capable of monitoring a wide range of atomic and molecular masses. The instrument was installed in a glove box (to control contamination spread).

The capability to introduce moist gas was attained through the addition of a bubbler and flow controller. Gas inputs were rerouted so as not to introduce moist gas (condensate) into the balance section of the instrument. A moisture monitor was added for more accurate gauging of the gas water content. An oxygen monitor was also added since oxygen additions have a known effect on the ability of water to oxidize uranium.

The instrument has been successfully used to demonstrate the degree to which irradiated N Reactor fuel (a uranium alloy) follows the correlations published in the literature for oxidation rate in dry air, moist air, and moist helium. This has led to increased confidence in the use of these correlations and the safety factors applied to these equations during design activities.

The TGA instrument has also been used to dry sludge recovered from both the bottom of K Basin fuel canisters and from the subsurface cracks in fuel elements. Here, vacuum conditions are important to exactly match the vacuum drying conditions that the fuel will see during processing. Coatings taken from the surface of fuel element cladding have also been run. The kinetics of water release from these hydrated materials, with increasing temperature, have been determined thus improving the understanding of the drying process and the knowledge related to residual moisture.

Information Contacts

John Abrefah, Pacific Northwest National Laboratory (PNNL), (509) 373-0927
B. J. Makenas, Fluor Daniel Hanford, Inc. (FDH) Spent Nuclear Fuel (509) 376-5447
G. T. Frater, FDH Technology Management (509) 372-4291
R. A. Wible, DOE-RL Science and Technology Programs, (509) 372-4776

Technology Vendor

Netzsch Instruments, Inc.
37 Industrial Boulevard, Suite D
Paoli, Pennsylvania 19301
Mr. John Kelly
(610) 722-0522

Funding for technology deployment was provided by the U.S. Department of Energy.

Fluor Daniel Hanford, Inc., Technology Management
TM-DEP-99-004