INL/CON-05-00687
PREPRINT

Fission Product Removal From Spent Oxide Fuel By Head-End Processing

GLOBAL 2005

B. R. Westphal
K. J. Bateman
R. P. Lind
K. L. Howden
G. D. Del Cul

October 2005

The INL is a
U.S. Department of Energy
National Laboratory
operated by
Battelle Energy Alliance

Proceedings of GLOBAL 2005
Tsukuba, Japan, Oct 9-13, 2005
Paper No. 345

Fission Product Removal from Spent Oxide Fuel by Head-End Processing

B.R. WESTPHAL[1] , K.J. BATEMAN[1], R.P. LIND[1], K.L. HOWDEN[1], and G.D. DEL CUL[2]

[1]*Idaho National Laboratory, Idaho Falls, ID 83403*

Tel. (208) 533-7398, Fax. (208) 533-7471, E-mail:brian.westphal@inl.gov

[2]*Oak Ridge National Laboratory, Oak Ridge, TN 37831*

ABSTRACT: The development of a head-end processing step for spent oxide fuel that applies to both aqueous and pyrometallurgical technologies is being performed by the Idaho National Laboratory, the Oak Ridge National Laboratory, and the Korean Atomic Energy Research Institute through a joint International Nuclear Energy Research Initiative. The processing step employs high temperatures and oxidative gases to promote the oxidation of UO_2 to U_3O_8. Potential benefits of the head-end step include the removal or reduction of fission products as well as separation of the fuel from cladding. Experiments have been performed with irradiated oxide fuel to evaluate the removal of fission products. During these experiments, operating parameters such as temperature and pressure have been varied to discern their effects on the behavior of specific fission products. In general, the extent of removal increases with increasing operating temperature and decreasing pressure. Removal efficiencies as high as 98% have been achieved during testing. Given the results of testing, an explanation of the likely fission product species being removed during the test program is also provided. In addition, experiments have been performed with other oxidative gases (steam and ozone) on surrogates to determine their potential benefit for removal of fission products.

KEYWORDS: *Irradiated Oxide Fuel, Pyrometallurgical Processing, Fission Product Volatility, Decladding*

I. INTRODUCTION

A head-end processing step is being developed for the treatment of spent oxide fuel by either aqueous or pyrometallurgical technologies [1-2]. The head-end step is based on previous investigations [3-4] and employs high temperatures to promote the oxidation of UO_2 to U_3O_8 via an oxygen carrier gas. Potential benefits of the technology include the removal of volatile fission products and the separation of fuel from cladding to assist downstream processes.

During oxidation, the spent fuel experiences a 30% increase in lattice structure volume resulting in an expansion internally that stresses the cladding allowing fission products and fuel to be separated from the cladding. The release of fission products occurs either directly from the broken fuel structure or following oxidation as volatile species. The head-end removal or reduction of fission products would simplify the overall flowsheets for both aqueous and pyrometallurgical processes. In addition, separating or decladding the fuel could simplify downstream processing steps while improving the dissolution kinetics of the fuel.

Although several fission products are released by the oxidation of spent oxide fuel, three specific fission products have been targeted for removal based on their deleterious effects on downstream processes. The three targeted fission products are technetium, molybdenum, and cesium due to either the formation of insoluble fines causing process interference or heat-loading issues. A test program was initiated, both on surrogate and irradiated materials, to reduce the targeted fission products by varying the operating parameters of the oxidation cycle. Test variables included temperature, pressure, and oxidative gases. A discussion of the targeted as well as the other fission products removed by oxidation will be presented. Following is a brief description of the equipment, facility, spent fuel, and test procedures for the irradiated test program.

II. EXPERIMENTAL

The equipment utilized for testing consists of a fuel containment vessel, a cylindrical furnace capable of operation to 1050°C, and a gas delivery/collection system, see Fig 1. The containment vessel has been specifically adapted for this program so that both a vacuum can be applied and oxidative gas can be regulated during a run. A more detailed description of this equipment can be found elsewhere [5].

Fig. 1. Experimental Equipment for Irradiated Testing

Irradiated testing is performed in the Hot Fuel Examination Facility (HFEF) located at the Idaho National Laboratory. The HFEF is an inert shielded hot cell requiring remote-handled operations. With the exception of the oxidative gas cylinder, all the components of the equipment are located in the HFEF argon cell.

The spent oxide fuel used for testing originated from the Belgium Reactor-3 (BR-3), a pressurized water reactor located in Mol, Belgium. The BR-3 fuel tested has a typical burnup of ~37 GWd/t with a 25 year decay time and zircaloy-4 type cladding.

Segments of approximately 2.5 cm in length are sectioned from a BR-3 spent oxide fuel rod and loaded into a stand that keeps the segments vertical while processing. The stand is then placed into an alumina crucible and loaded into the fuel containment vessel and furnace. The nominal batch size is 100 g of fuel and cladding. Heating of the fuel commences under an oxidative cover gas, either oxygen or air, until oxidation to U_3O_8 is complete, typically between 500-700°C after 1-2 hours. If a higher temperature or lower pressure test is being performed, those conditions are applied following the sequence given. Following the test, fuel removed from the cladding is sampled and analyzed for the extent of fission product removal.

III. RESULTS AND DISCUSSION

A series of experiments have been performed with the BR-3 oxide fuel to discern the degree of fission product removal following the head-end oxidation process. Chemical analyses of fuel samples taken before and after the oxidation cycle are used to calculate fission product removal.

Sixteen fission products, as well as three transuranic elements, were analyzed during the test program to assess their removal efficiencies. Of these nineteen elements, only six, all fission products, were removed to any extent during the oxidations. Removal data for the six fission products (rhodium, ruthenium, technetium, molybdenum, tellurium, and cesium) are presented and likely species are discussed.

The amount of rhodium, ruthenium, and technetium removed during the oxidation of spent fuel is shown in Fig. 2 for a wide range of temperatures. Following the oxidation cycle, heating continues to the maximum temperatures as previously described. The general trend for removal efficiencies is increasing with temperature. It should be noted that analytically Tc-99 was detected and is being reported as elemental technetium. To date, molybdenum has only been removed during one test; a low pressure test to 880°C. The removal of molybdenum was 32% for this test.

In order to understand the potential species of rhodium, ruthenium, technetium, and molybdenum being removed, a background on their chemical state following the irradiation of oxide fuel is necessary. For all four fission products, metallic precipitates or white inclusions crystallize as the spent fuel cools from reactor conditions [6-7]. Internally, the

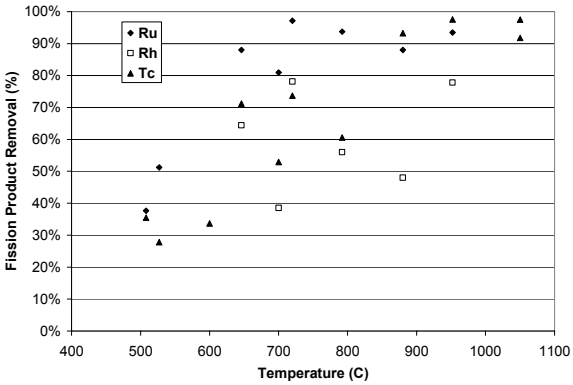

Fig. 2. Removal of Rh, Ru, and Tc versus Temperature

oxygen potential is not sufficient to promote their oxidation during irradiation [8]. The possible exception to this is molybdenum which may form small amounts of Cs_2MoO_4 [8]. Thus, the metallic inclusions of these noble metals are primarily oxidized during the head-end processing and not during irradiation.

Based on thermodynamic data [9-10], the most probable volatile species for rhodium, ruthenium, technetium, and molybdenum are RhO_2, RuO_4, Tc_2O_7, and Mo_3O_9, respectively, according to equations (1) through (4). Unlike technetium and molybdenum, rhodium and ruthenium are oxidized through intermediate states to reach their final volatile species.

$$2Rh_2O_3 + O_2(g) = 4RhO_2(g) \quad (1)$$

$$RuO_2 + O_2(g) = RuO_4(g) \quad (2)$$

$$Tc_2O_7 = Tc_2O_7(g) \quad (3)$$

$$3\ MoO_3 = Mo_3O_9(g) \quad (4)$$

Vapor pressure curves are shown in Fig. 3 for RhO_2, RuO_4, Tc_2O_7, and Mo_3O_9 [9-10]. Considering the temperature and pressure conditions during most of the oxidation tests, the removal of ruthenium and technetium is to be expected. The boiling point of $RuO_4(g)$ at standard conditions is 155°C and that of $Tc_2O_7(g)$ is 310°C. Less than 100% removal of these fission products may be due to partial vaporization, incomplete oxidation to the volatile species, or the formation of non-volatile complex oxides.

The removal of molybdenum as $Mo_3O_9(g)$ during normal testing would not be expected given typical operating pressures greater than 600 Torr. It follows then if the pressure is reduced to less than 1 Torr that the partial removal of molybdenum would be observed.

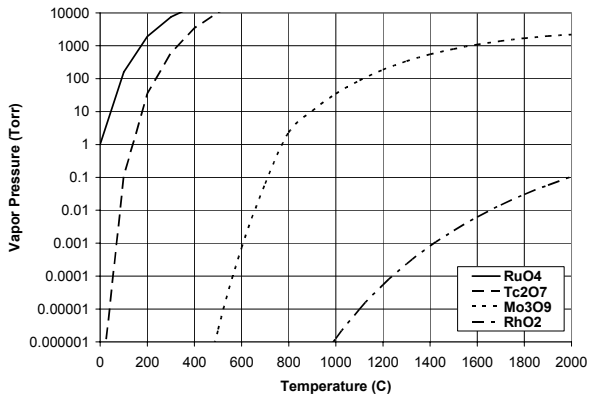

Fig. 3. Vapor Pressures of RhO_2, RuO_4, Tc_2O_7, and Mo_3O_9

In contrast to ruthenium, technetium, and molybdenum, the removal of rhodium as $RhO_2(g)$ would appear to be difficult given the vapor pressure data and operating conditions. Thus, its removal is unexpected. A few plausible explanations for this are incomplete dissolution of samples submitted for chemical analyses, unreliable vapor pressure data, misidentified vapor species, or perhaps contamination during testing. Further investigations are required to determine the species of rhodium being removed.

The final two fission products removed during oxidation testing were cesium and tellurium, Fig. 4. Again, the general trend of removal is increasing with temperature, although not to the extent of the noble fission products. In addition, the removals track each other except for the high temperature tellurium data point. Cesium removal is calculated based on Cs-137 detection.

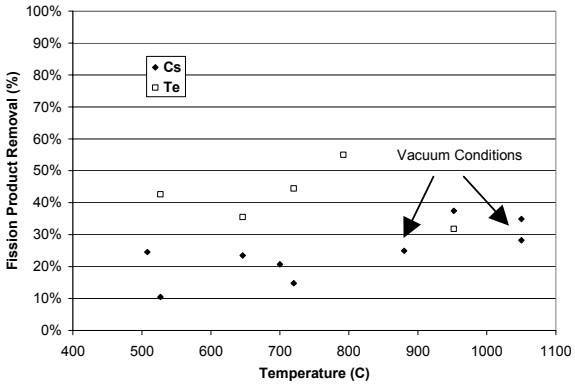

Fig. 4. Removal of Cs and Te versus Temperature

In spent oxide fuel, it is expected that cesium forms cesium iodide (CsI), cesium oxide (Cs_2O), cesium metalates ($Cs_xM_yO_z$ where M could be Zr, Mo, U, or Te), or remains in the metallic state [6-8]. Tellurium may combine with cesium to produce Cs_2Te and Cs_2TeO_3, with zirconium for Zr_3Te, or exist in elemental form [6-8]. Unlike the noble metals, the exact speciation of cesium and tellurium is complex and contradictory thus, several compounds have been suggested.

Reviewing available vapor pressure data for cesium and tellurium species [10-11], Fig. 5, the removal of cesium and tellurium as Cs(g) and $Te_2(g)$ would be expected under typical pressure conditions. Under vacuum conditions, CsI and perhaps Cs_2O would volatize increasing the amount of cesium removal. Cesium telluride would not be expected to be removed even under vacuum conditions. Only a slight increase in cesium removal was observed for lower pressure, Fig. 4, and that was probably due to temperature more than pressure. Thus, CsI, Cs_2O, and Cs_2Te do not seem likely to be the species being removed during testing. Several additional data confirm this statement. A water dissolution of the fuel after oxidation has been performed to determine the presence of Cs_2O since it is soluble in water. Since negligible cesium was detected in the water wash, it was concluded that very little Cs_2O exists in the fuel after oxidation. It is known that Cs_2Te vaporizes incongruently to Cs(g) and $Te_2(g)$ and not as $Cs_2Te(g)$ [11]. In addition, samples taken from the off-gas collection system reveal cesium and tellurium in ratios consistent with the dissociation of Cs_2Te.

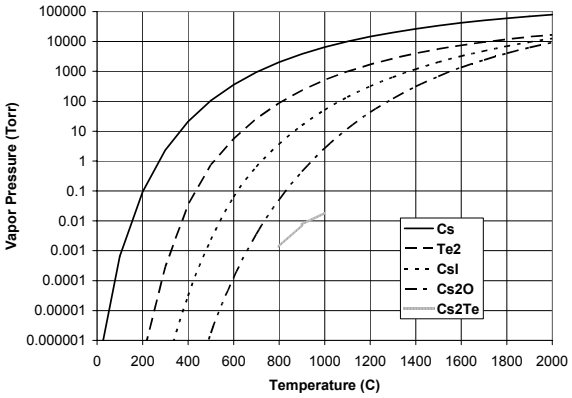

Fig. 5. Vapor Pressure of Cesium and Tellurium Species

Regardless of the cesium and telluride species present prior to oxidation testing, the most probable species being removed during oxidation are Cs(g) and $Te_2(g)$. Cesium iodide may also be removed though its existence in spent oxide fuel is not entirely conclusive [6, 8].

A couple potential areas may exist for increased cesium removal. Since a large fraction of the cesium exists as complex oxides, produced either from reactor operations or during the oxidation cycle, attention to these species seems warranted. Two complex cesium oxides, Cs_2UO_4 and Cs_2ZrO_3, are known to decompose at temperatures near 1000°C [12-13]. Thus, temperatures in excess of 1000°C may decompose these species and allow for greater cesium

removal. Another area for investigation is the removal of cesium in the presence of alternative oxidative gases. Tests, utilizing a TGA and surrogate cesium (Cs_2O), have been performed that show enhanced cesium removal using ozone and water, see Fig. 6. The onset of cesium removal is achieved at lower temperatures with minor additions of ozone and water to oxygen. Tests with irradiated fuel and other oxidative gases may yield additional removal of cesium.

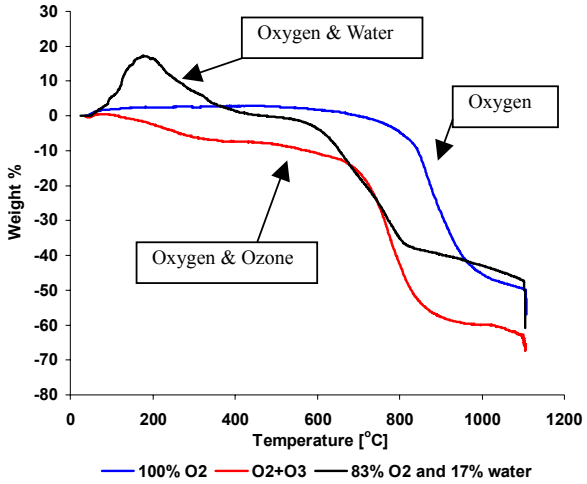

Fig. 6. TGA of Cesium Oxide with O_2, O_3, and H_2O

IV. CONCLUSIONS

- Six fission products have been partially removed during oxidation testing on spent oxide fuel.
- The removal of the noble fission products is characterized by oxidation of the metals to volatile oxides.
- Although cesium and tellurium removal is more difficult to characterize, volatile elemental species are being removed consistently.
- For the three targeted fission products, technetium removals up to 98% have been achieved while cesium and molybdenum removals as high as 30-40% have been demonstrated.
- Of the three targeted fission products, only molybdenum is affected by vacuum conditions.
- Additions of ozone and water to oxygen have shown promise for a greater removal of cesium.

ACKNOWLEDGMENTS

The authors would like to acknowledge the HFEF operations and analytical laboratory personnel for their contributions to the testing program. Work supported by the U.S. Department of Energy, Office of Nuclear Energy, Science, and Technology, under DOE-NE Idaho Operations Office Contract DE-AC07-05ID14517.

REFERENCES

1. B.R. WESTPHAL et al., "Results of Phase I Testing for the DEOX Process," *Trans. Am. Nucl. Soc.*, 91, p.519-520 (2004).
2. G.D. DEL CUL et al., "Advanced Head-End Processing of Spent Fuel: A Progress Report," *Trans. Am. Nucl. Soc.*, 91, p.507-508 (2004).
3. G.E. BRAND and E.W. MURBACH, "Pyrochemical Reprocessing of UO_2 by AIROX: Summary Report," NAA-SR-11389 (1965).
4. J.E. BODINE, I.J. GROCE, J. GUON, and L.A. HANSON, "Oxidative Decladding of Uranium Oxide Fuels," *Nucl. Sci. Eng.*, 19, p.1-7 (1964).
5. K.J. BATEMAN, B.R. WESTPHAL, and M.A. STAWICKI, "Experimental Equipment Design and Testing of the DEOX Process," *Proc. 12th Int. Conf. Nucl. Eng. (ICONE)*, Arlington, VA, April 25-29, 2004, ASME (2004).
6. H. KLEYKAMP, "The Chemical State of the Fission Products in Oxide Fuels," *J. Nucl. Mat.*, 131, p.221-246 (1985).
7. H. KLEYKAMP, "The Chemical State of the Fission Products in Oxide Fuels at Different Stages of the Nuclear Fuel Cycle," *Nucl. Tech.*, 80, p.412-422 (1988).
8. E.H.P. CORDFUNKE and R.J.M. KONINGS, "Chemical Interactions in Water-Cooled Nuclear Fuel: A Thermodynamic Approach," *J. Nucl. Mat.*, 152, p.301-309 (1988).
9. C.B. ALCOCK and G.W. HOOPER, "Thermodynamics of the Gaseous Oxides of the Platinum-Group Metals," *Proc. Roy. Soc.*, 254A, p.551-561 (1960).
10. A. ROINE, HSC Chemistry Database, 5.0 (2002).
11. J. MCFARLANE and J.C. LEBLANC, "Fission-Product Tellurium and Cesium Telluride Chemistry Revisited," AECL-11333 (1996).
12. D.K. BOSE et al., "Some Thermochemical Studies of Cesium Uranate, Molybdate, and Chromate," *J. Nucl. Mat.*, 130, p.122-125 (1984).
13. R.P.C. SCHRAM and V.M. SMIT-GROEN, "Thermodynamic Properties of Caesium Zirconate Cs_2ZrO_3," *J. Chem. Thermo.*, 31, p.43-55 (1999).