SINTERED BENTONITE CERAMICS FOR THE IMMOBILIZATION OF CESIUM- AND STRONTIUM-BEARING RADIOACTIVE WASTE

A Dissertation

by

LUIS HUMBERTO ORTEGA

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2009

Major Subject: Materials Science and Engineering

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Approved by:

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ABSTRACT

Sintered Bentonite Ceramics for the Immobilization of Cesium- and
Strontium-bearing Radioactive Waste. (December 2009)
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Chair of Advisory Committee: Dr. Sean M. McDeavitt

The Advanced Fuel Cycle Initiative (AFCI) is a Department of Energy (DOE) program, that has been investigating technologies to improve fuel cycle sustainability and proliferation resistance. One of the program's goals is to reduce the amount of radioactive waste requiring repository disposal.

Cesium and strontium are two primary heat sources during the first 300 years of spent nuclear fuel's decay, specifically isotopes Cs-137 and Sr-90. Removal of these isotopes from spent nuclear fuel will reduce the activity of the bulk spent fuel, reducing the heat given off by the waste. Once the cesium and strontium are separated from the bulk of the spent nuclear fuel, the isotopes must be immobilized.

This study is focused on a method to immobilize a cesium- and strontium-bearing radioactive liquid waste stream. While there are various schemes to remove these isotopes from spent fuel, this study has focused on a nitric acid based liquid waste. The waste liquid was mixed with the bentonite, dried then sintered. To be effective sintering temperatures from 1100 to 1200°C were required, and waste concentrations must be at least 25 wt%. The product is a leach resistant ceramic solid with the waste elements embedded within alumino-silicates and a silicon rich phase. The cesium is primarily incorporated into pollucite and the strontium into a monoclinic feldspar.

The simulated waste was prepared from nitrate salts of stable ions. These ions were limited to cesium, strontium, barium and rubidium. Barium and rubidium will be co-extracted during separation due to similar chemical properties to cesium and strontium. The waste liquid was added to the bentonite clay incrementally with drying steps between each addition. The dry powder was pressed and then sintered at various temperatures. The maximum loading tested is 32 wt. percent waste, which refers to 13.9 wt. percent cesium, 12.2 wt. percent barium, 4.1 wt. percent strontium, and 2.0 wt. percent rubidium. Lower loadings of waste were also tested. The final solid product was a hard dense ceramic with a density that varied from 2.12 g/cm^3 for a 19% waste loading with a 1200°C sintering temperature to 3.03 g/cm^3 with a 29% waste loading and sintered at 1100°C.

Differential Scanning Calorimetry and Thermal Gravimetric Analysis (DSC-TGA) of the loaded bentonite displayed mass loss steps which were consistent with water losses in pure bentonite. Water losses were complete after dehydroxylation at ~650°C. No mass losses were evident beyond the dehydroxylation. The ceramic melts at temperatures greater than 1300°C.

Light flash analysis found heat capacities of the ceramic to be comparable to those of strontium and barium feldspars as well as pollucite. Thermal conductivity improved with higher sintering temperatures, attributed to lower porosity. Porosity was minimized in 1200°C sinterings. Ceramics with waste loadings less than 25 wt% displayed slump, the lowest waste loading, 15 wt% bloated at a 1200°C sintering. Waste loading above 25 wt% produced smooth uniform ceramics when sintered >1100°C.

Sintered bentonite may provide a simple alternative to vitrification and other engineered radioactive waste-forms.

I am very fortunate to have a loving family and friends who gave their unwavering support, my sister and her husband Mary Helen and Terry Ormseth, my mother and father Maria Elena and James Resley, and my uncle Guillermo Ortega; my close friends Andy Walter, Red Knaak, Frank Williams, Matt Murawski, Flint Taylor, Michael Robbins, Mike Aussem, Sarah Harcum, Barry Goode, Matt Hartman, Rob Cruz, Edith Cassell and Karie Badgley. I would also like to thank God for everything.

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NOMENCLATURE

AFCI	Advanced Fuel Cycle Initiative
BSE	Backscattered Electron Image
CTE	Coefficient of Thermal Expansion
DOE	Department of Energy
DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive Spectroscopy
FPEX	Fission Product Extraction Process
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
LFA	Light Flash Analysis
NAA	Neutron Activation Analysis
NERI	Nuclear Energy Research Initiative
SEM	Scanning Electron Microscopy
TCLP	Toxicity Characteristic Leach Procedure
UREX	uranium extraction process
WDS	Wave Dispersive Spectroscopy
XRD	X-Ray Powder Diffraction

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