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LOW TEMPERATURE GLASS COMPOSITE MATERIAL (GCM) WASTE FORM FOR RADIOLOGICAL IODINE CAPTURED BY Ag-ZEOLITES: OPTIMIZATION AND DURABILITY

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Abstract – *We have developed a waste form for the storage of ^{129}I which utilizes a low temperature sintering oxide glass to encapsulate AgI-mordenite (AgI-MOR) particles to form a dense and durable composite. The bismuth silica zinc (Bi-Si-Zn) oxide based glass is sintered to full density at 550°C and has excellent chemical durability. Herein, we report on the effects of a number of synthesis variables on the durability of the Sandia GCM waste form. Those variables included: AgI-MOR weight percent level, AgI-MOR particle size, organic iodine source and silver addition. We use the Single Pass Flow Through (SPFT) test to determine variables that might affect the rate at which iodine and silver are released from the waste form, and therefore its durability. The resultant GCM is an effective waste form for ^{129}I because the glass is chemically durable, I release from AgI-Mordenite is relatively slow, and Bi in the weathered glass may sorb iodide. Moreover, low temperature (< 600°C) Bi-Si-Zn glass sintering minimizes iodide release from the AgI-Mordenite during processing.*

I. INTRODUCTION

The chemical and physical controls over iodine release from candidate ^{129}I waste forms must be quantified to predict long-term waste form effectiveness. Ag-Mordenite will likely be an important waste form component because of its ability to remove ^{129}I from waste streams and convert it to AgI and/or sorb it.[1] Silver iodide is relatively insoluble in water, $K_{sp} = 10^{-16.1}$ at 20°C, so Ag-Mordenite should retain ^{129}I for long periods of time. Encapsulating ^{129}I-Ag–Mordenite (AgI–MOR) into a durable solid waste form should limit potential releases of ^{129}I further. Low temperature sintering Glass Composite Materials (GCMs) are candidates for encapsulating AgI-MOR. GCMs contain both crystalline and glass phases, and are easier to synthesize, less expensive, and can achieve higher waste loadings than traditional ceramic waste forms.[2] Herein we present the results of GCM durability studies with respect to changes in process variables such as particle size, additive concentrations, and iodine loading.

II. SYNTHESIS AND CHARACTERIZATION

II.A. Synthesis: AgI-MOR and GCM Preparation[2]

The low-sintering temperature glass used in this work was a Bi–Si-oxide glass that is available commercially (3 μm average particle size, a density of 5.8 g/ cm^3, coefficient of thermal expansion of 7.8 x 10^{-6} / °C, from Ferro Corp., Cleveland, OH). The glass has a composition of: 7.8 wt% ZnO, 63.4 wt% Bi_2O_3, 5.4 wt% Al_2O_3, 23.4 wt% SiO_2.

The ground AgI–MOR was mixed, typically at 20 wt%, with the glass powder and with an additional 5 wt% of silver flake (d <10 μm, Sigma Aldrich). The silver flake was added to assure complete capture of any adsorbed iodine released during thermal processing, and the particle size of the AgI-MOR used was typically ~150 μm. . The mixtures were uniaxially dry pressed at 70 MPa in a steel die. Samples were heated at 5°C/min in air to 550°C for 1 h to sinter the glass to form a dense GCM. Powder XRD verified that the glass phase remained amorphous after the heat treatment for all compositions. Higher sintering temperatures or longer times resulted in crystallization of the eulytite phase in the glass.

Variables in GCM synthesis studied included: weight percent loading of AgI-MOR, particle size, and weight percent Ag flake addition.

II.B. Materials Characterization

The materials were examined using powder X-ray diffraction (XRD, Siemens Kristalloflex D 500 diffractometer, Bruker-AXS Inc., Madison, WI), before and after heating in the TGA/DSC. Samples of the AgI-

MOR GCMs with varying particle sizes of AgI-MOR were examined using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM, FEI NovaNano SEM 230 and EDS, EDAX Genesis Apex 2 with an Apollo SDD detector). Optical microscopy was performed on an AM4013TL Dino-Lite Premier digital microscope.

II.C. Durability Testing

MCC-1 (ASTM C-1220)[3] and PCT-B (ASTM C1285)[4], are static aqueous dissolution tests that measure the concentration of elements that leach into solution at 90°C for 1 week. The Single-Pass Flow-Through Test (MCC-4 or ASTM C-1662) is a durability test that is frequently used to measure degradation rates of minerals and nuclear waste glasses.[5] In the SPFT test a solution at a constant temperature makes a single pass at a known flow rate through a reaction cell containing the ground up solid sample. The test roughly mimics the slow movement of groundwater through a waste form.

III. RESULTS AND DISCUSSION

Our studies show that independent of compositional variables, the Bi-Si-Zn oxide glass matrix dissolves at a relatively low rate.[6] Flow-through testing data indicates low GCM dissolution rates ($<10^{-3}$ g/m^2•d) across wide variable ranges including: pH, AgI-MOR loading, I loading, and AgI-MOR particle size. The Bi-Si-Zn oxide glass matrix limits the release of iodine from the otherwise relatively fast degrading AgI-MOR getter material. The formation of an amorphous AgI phase results in the limitation of iodine release during waste form degradation.

SPFT tests show pH-dependent glass degradation at rates similar to high level waste glasses, reaching a minima near neutral pH at 25°C, increasing at higher and lower pHs. Steady-state Si levels were less than 1 ppm and well below saturation with solid silica phases. Measured non-stoichiometric release rates point to formation of a Bi leach layer at the glass surface. The Ag and I release from AgI-MOR under oxidizing conditions are not affected by pH.

IV. CONCLUSIONS

The capture and safe storage of radiological iodine (^{129}I) from nuclear fuel reprocessing is of concern due to its long half-life and potential mobility in the environment. The development of durable waste forms in which to store captured iodine requires materials that are both compatible with the iodine capture phases and durable to repository environments. To that end, a low temperature sintering Bi-Si-Zn oxide glass composite waste form has been developed and herein is studied for its durability. Traditional iodine capture material Ag-Zeolite (Mordenite, MOR) is studied in this waste form. Single Pass Flow Through (SPFT) tests, Product consistency test (PCT-B) and chemical durability (MCC-1) tests were performed on both the individual components of the GCM and the complete GCM though fabricated with variable procedures. Results indicate that multiple features of the AgI-MOR/Glass/Ag flake GCM make it an effective waste form for ^{129}I.

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