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Analyze D_2O Losses from the D_2O loaded AgZ provided in FY15 By ORNL

Fuel Cycle Research & Development

Milestone M3FT-16SN030107041

DOE/Ne-Fuel Cycle R&D
Materials Recovery and Waste Form Development

Prepared for
US Department of Energy
Office of Nuclear Energy –
Materials Recovery and Waste Form Development
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Sandia National Laboratories
April 20, 2016
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Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

Develop Plan for Analysis of the Effluent from GCM Production

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Plan:
This milestone is focused on utilizing NMR and various gas chromatograph set ups (thermal conductivity and/ionizing detection) at SNL, to analyze the relative ratio of water and deuterated water in Ag-MOR samples of natural zeolite sent to SNL in FY15 by ORNL.

Samples Studied:
ORNL D_2O AgI-MOR sample(s) were I_2 and D_2O loaded, then additional treatments of:
Ag°Z-I-D_2O SHB #1: 24 hr dry air purge
Ag°Z-I-D_2O SHB #2: 4 hr dry air purge, moist air stream loading, 24 hr dry air purge

Analysis Methods:
1) The solid state MAS NMR Bruker Avance – III 600 NMR instrument using a 2.5 mm rotor spinning at 30 kHz for proton, and a 4 mm rotor spinning at 12 kHz for deuterium characterization. The ^1H NMR chemical shifts were referenced to the secondary external standard adamantane δ = 1.63 ppm with respect to TMS = 0.0 ppm. Deconvolutions were obtained using the DMFIT software.

2) Isotope measurements via Mass Spec (Finnegan MAT 271 magnetic sector mass spec). Instrument has a limitation of inherent surface composition of –OH's; even at ~100 milliTorr, the -OH levels were swamping the very low level of D_2O (if any) in the sample.

3) Isotope measurements via pulsed discharge ionization detector (PDID; Valco Instruments Co., VICI AG International), to separate D_2O and H_2O by Gas Chromatography.

Results:
NMR: In the two materials, the ^1H (proton) NMR signal is dominated by the broad water resonance near ~4.5 ppm. This resonance reflects waters that are not strongly hydrogen bonded to the surface or other functional groups, but are surface adsorbed resulting in short T2 values (see below) and broader lines. It is actually heterogeneous in nature and can be considered the overlap of several different water environments and slightly different bonding environments within the pores(See integrations in Figures 5 – 9). These results also show that the SNL D2O-X samples have the lowest concentration of water and other proton species in comparison to the other samples. The ORNL AGI-MOR sample has a the sharp resonance at ~ 9 ppm, which reflects a proton (OH of H_2O) in a relatively strong hydrogen bonding environment.

For the deuterium analysis (^2H) of the two ORNL samples: The chemical shift is consistent with water in these materials. The presence of multiple sidebands demonstrates that the water is rigid and not isotopically moving. The goal we were tasked with was to determine the relative concentration of ^2H remaining in these materials. The presence of deuterium is small in either of these samples, only a ratio between them is measurable. Since the ***total integration is related to the concentration, the ratio of the D_2O-2/D_2O-1 in these samples was found to be 13% or about a 7.7 fold reduction in the ^2H concentration following the additional air flow treatment***.

Isotope Measurement and PDID: Neither of these analyses were able to produce results to determine concentrations of D_2O in the samples. In fact, the only conclusive result here is that the quantity of deuterium was too small to detect.

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