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EXTRACTION OF HYDROGENOUS MATERIAL FROM CEMENTED WASTEFORMS BY SUPERCRITICAL FLUID CARBONATION

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INTRODUCTION

We are conducting experiments on an innovative transformation concept, using a traditional immobilization technique, that may significantly reduce the volume of hazardous and/or radioactive waste requiring transport and long-term storage. The standard practice at LANL for the stabilization of radioactive salts and residues is to mix them with portland cement, which may include additives to enhance immobilization. Many of these wasteforms do not qualify for transportation or underground disposition, however, because they do not meet Department of Energy regulations for free liquids, decay heat, and/or head-space gases.[1,2,3,4] The present treatment method alters the bulk properties of a cemented wasteform by greatly accelerating the natural cement-aging reactions, producing a chemically stable form having reduced levels of free liquids and organic compounds, as well as reduced porosity, permeability and pH. These structural and chemical changes should allow for greater actinide loading, as well as reduced mobility of the anions, cations, and radionuclides in aboveground and underground repositories.

DESCRIPTION OF WORK

The attractiveness of supercritical fluids as solvents stems from their unique combination of liquid-like and gas-like properties. The table below gives an order of magnitude comparison of viscosity, density and (solute) diffusion coefficient of a typical liquid, gas and supercritical fluid. The high, liquid-like

	Viscosity $\left(N \cdot s/m^2\right)$	**Density** $\left(kg/m^3\right)$	**Diffusion coefficient** $\left(cm^2/s\right)$
liquid	10^{-3}	1000	10^{-5}
supercritical fluid	10^{-4}	700	10^{-4}
gas	10^{-5}	1	10^{-1}

densities of supercritical fluids allows for substantial solubilities, while the gas-like transport properties permit extractions to be performed on dense, microporous matrices.

The natural curing reactions which occur in a standard portland cement involve the formation of calcium hydroxide (portlandite), $Ca(OH)_2$, as well as calcium silicate hydrates (CSH). Over time, the cement abstracts CO_2 from the air, converting the calcium hydroxide and CSH to calcium carbonate. It turns out, however, that this secondary conversion results in the closure and/or blockage of pores, impeding the ingress of the reactant (CO_2) and the egress of reaction product (H_2O), drastically slowing the reaction rate with time. These long reaction times make it difficult to predict the long-term behavior of cemented wasteforms. By exposing a portland cement to $SCCO_2$, it is found that the carbonation reaction can be greatly accelerated. This acceleration is due to the ease of penetration of the supercritical fluid into the micro-pores of the cement, providing continuous availability of fresh, hyper-stoichiometric reactant, as well

DISCLAIMER

as the solubility of the reaction product in the supercritical fluid, facilitating its removal. Any organic compounds contained within the cement will be extracted along with the water.

We give in this presentation the initial results of a systematic study optimizing the processing conditions of

- (a) supercritical fluid pressure
- (b) supercritical fluid temperature
- (c) treatment time
- (d) cement chemistry (additives, cement/water ratio, etc.)

for their influence on the resulting Type I/II portland cement properties of

- (a) hydrogenous content
- (b) degree of chemical conversion
- (c) porosity
- (d) permeability
- (e) mechanical strength
- (f) leachability

RESULTS

Our results show that there is sensitive interplay between the curing time of the cement and the degree of structural/chemical conversion produced by the supercritical fluid treatment. As more time is allowed for the cement to approach a more fully-cured condition, the permeability decreases, necessitating longer treatment times to achieve the same degree of conversion. This effect is clearly shown in petrographic analysis and by compressive strength measurements, where the *relative* strength enhancement for the treated versus untreated cements is greatest for shorter curing times. This limitation can be overcome by increasing the water/cement ratio, which results in a cured cement of increased permeability. We are also examining the use of a "pulsed-pressure" treatment, where the supercritical fluid pressure is cycled. We also present the first results of porosity and permeability measurements made under saturated flow conditions,[5] as a function of the water/cement ratio and supercritical fluid treatment time.

Future studies will concentrate on additional mechanical, chemical, mass transport, and leachability measurements using both reference cements and cements loaded with surrogate and actinide salts.

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1. U.S. DOE, "TRUPAC-II User Requirements Document",. Rev. February 2, 1992.

2. U.S. DOE, "TRUPAC-II Content Codes (TRUCON)", Rev. 10, December 1996, DOE/WIPP 89-004.

3. DOE WIPP Project Office, SOP 9.4, "Waste Acceptance Criteria Certification Committee (WACCC)", December 7, 1988.

4. Jerome C. Barton, "The Los Alamos SuperScrub : Supercritical Carbon Dioxide System Utilities and Consumables Study", LA-12786 UC-321, June, 1994.

5. "Test Method for Determining Unsaturated Hydraulic Conductivity in Porous Media by Open-Flow Centrifugation", Accepted to ASTM D18.21 Subcommittee on Ground Water for general balloting

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