

TEST PLAN FOR MEASURING THE THERMAL CONDUCTIVITY OF CRYSTALLINE SILICOTITANATE

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1. BACKGROUND

Crystalline silicotitanate (CST) is being investigated as an inorganic ion-exchange media to remove cesium from the supernatant stored in the high-level radioactive waste tanks at the Savannah River Plant (SRP). The supernatant is primarily a mixture of aqueous sodium nitrate and sodium hydroxide with smaller concentrations of other species. The total sodium concentration is around 5.6 *M*. Although the cesium concentration is low, $<1.4 \times 10^{-4}$ *M*, the ^{137}Cs accounts for much of the radioactivity of the supernatant. Sorption of the cesium from the supernatant results in concentrating the ^{137}Cs into the much smaller volume of the CST bed. In concentrated form, the ^{137}Cs becomes a compact source of significant thermal energy. Engineering designs of the CST sorption column must handle this thermal load; otherwise hot spots could develop within the column and degrade the performance of the ion-exchange process. Development of adequate mathematical models to aid the design of the CST ion-exchange column requires information on the thermal properties of the CST. The heat capacity has been measured (Bostick and Steele, 1999), but data on thermal conductivity is lacking.

The commercial source of the granular form of CST is UOP Molecular Sieves, LLC, Mt. Laurel, New Jersey. It is sold under the trade name IONSIV[®] IE-911[™]. The objective is to measure the effective thermal conductivity of IE-911[™].

2. RATIONALE FOR SELECTING MEASUREMENT CONDITIONS

In one of several viable alternatives, the equipment implemented to remove ^{137}Cs from tank waste supernatant is a simple vertical tube filled with granular CST – that is, an ion-exchange column. During normal operation of the column, liquid supernatant flows downward through the porous bed of CST granules. In this mode of operation, heat generated by radioactive decay of sorbed ^{137}Cs is transferred from the solid particles to the liquid phase. The particle size of the CST is very small (average particle diameter ~400 μm). Should the thermal conductivity of the individual solid particle be poor, a large temperature difference between the surface and center of the particle is unlikely to arise because of the small distance involved. It may be surmised that convective heat transfer dominates the temperature variations within the column under normal circumstances.

Radiolysis of water in the column will produce free hydrogen and oxygen gas. Production of bubbles within the bed displaces the liquid, leaving a zone of wetted particles with

most of the interstitial voids filled with hydrogen and oxygen gas. Prior tests (Welch et al., 1999) have shown that small bubbles move through the column. Because these bubble are rapidly replaced with liquid, they probably have little effect on the temperature gradients. The column does retain a steady-state void fraction of ~7% and some larger bubbles were observed to adhere to the wall of the column. Retained and immobile bubbles represent locations in the column where cooling by the flowing supernatant is interrupted. Heat transfer in these zones is limited by thermal conductivity.

If the liquid flow is halted, then the mode of heat transfer changes character. The bed of granulated material tends to stabilize the liquid with respect to natural convection, so the liquid remains quiescent. The contents of the column must be cooled from the outer surfaces or with heat exchange tubes imbedded in the bed of particles. Heat transfer is limited by the thermal conductivity of the heterogeneous solid-liquid media (solid particles with the interstitial voids filled with liquid). If a localized hot spot develops so that the temperature approaches the boiling point of the liquid (probable range of 100°C to ~120°), then the expanding water vapor can displace the fluid leaving a wetted zone of particles (solid particles wetted with the liquid but with most of the interstitial voids filled with water vapor). This is similar to voids caused by non-condensable radiolysis products. Prolonged heating will cause the water to fully evaporate from the particles leaving precipitated salts on the particles with the interstitial voids filled with water vapor.

There appear to be three general physical conditions where thermal conductivity controls the removal of heat from the ion-exchange column. Within these general conditions, subsets of specific chemical make-up can be identified.

2.1 Dry Solid Particles

A dry solids bed may result when the water in a wetted bed completely evaporates (not counting waters of hydration). A drained bed of solids retains only a fraction of the liquid associated with an immersed bed. When the water is removed, the crystallized salts remaining are a small fraction of the mass of the CST granules. The crystallized solids coat the granule with little effect, but solids that crystallize within the pores of individual CST grains might cause more substantial effects on the thermal conductivity of an individual grain.

2.2 Immersed Solid Particles

In this condition the solids bed is submerged in the liquid. For practical purposes, all the fluid within the interstitial bed of solid particles may be considered to be the liquid phase. The thermal conductivity of the supernatant simulant has been measured in previous studies (Bostick and Steele, 1999). Data are not available on the thermal conductivity of the solid particles.

2.3 Wetted Solid Particles

A wetted solids bed is formed when the liquid is displaced by a gas. The liquid may be displaced by radiolytically produced non-condensable gas or by thermally produced water vapor

(steam). Most of the interstitial void space of the solids bed is filled with the gas and the particles themselves are coated with a thin film of liquid. This condition may be simulated by draining the liquid from an immersed solids bed; for example, by gravity filtration of the solids on a frit. Two subsets of this condition are evident; one in which the gas is a mixture of hydrogen and oxygen, and another in which the gas is water vapor. The thermal conductivity of these gases is available from the literature.

3. OBJECTIVES

No data are available on the thermal conductivity of IE-911™ from UOP Molecular Sieves. The thermal conductivity of the supernatant simulant has been measured and reported (Bostick and Steele, 1999). It is anticipated that the effective thermal conductivity of the granular CST will be strongly dependent on the properties of the fluid that fills the interstitial voids.

The objectives are to measure the effective thermal conductivity in up to three conditions; (1) granular CST that has been treated for use in the ion-exchange column and then dried, (2) the same material as item 1 but immersed in supernatant simulant, and (3) the same material as item 2 with the liquid supernatant gravity filtered from the solid.

In the first test the interstitial voids of the dry granular CST will be filled with air. The thermal properties of air are known, so it is possible that simple models may be developed to separate the thermal conductivity of the solid from the measurement of the mixture. In operating columns, gases likely to fill the interstitial voids of dry CST are water vapor, hydrogen, oxygen, and mixtures of these three gases. The properties of these gases are also known, and the thermal conductivity varies within a small range. Based on measurements made in air, computation of the effective thermal conductivity for systems with different interstitial gases should yield acceptable results.

In the second test, the effective thermal conductivity of IE-911™ immersed in simulant will be measured experimentally. The value will be estimated theoretically from the measurements made in the first test and the previously reported thermal conductivity of supernatant simulant. The experimental and calculated values will be compared.

The third test is optional and the decision to proceed with it will depend on the outcome of the first two tests. In that test, a similar measurement of the effective thermal conductivity of IE-911™, wetted with simulant and gravity drained of bulk liquid will be performed. The interstitial gas will be air. Thermal conductivities of drained solids with interstitial gases other than air may be computed from the properties of those other gases.

4. EXPERIMENTAL APPARATUS AND REAGENTS

4.1 Equipment

Thermal conductivity of air dried CST and a mixture of CST with supernatant waste simulant will be measured using a transient plane source method. The equipment that will be used is a Hot Disk Thermal Constants analyzer, the same equipment that was previously used to measure the thermal conductivity of waste simulant (Bostick and Steele, 1999).

4.2 Materials

4.2.1 Supernatant Simulant

Supernatant simulant will be prepared using a recipe supplied by SRS personnel and used in previous tests at ORNL (see Table 1). Deionized water will be used to prepare the solution. Chemicals used in the preparation of the supernatant will be of reagent grade, purchased from commercial sources.

Table 1. SRS average supernatant waste composition. ^a

Component	Average Concn. (<i>M</i>)
Na ⁺	5.6
Cs ⁺	0.00014
K ⁺	0.015
OH ⁻	1.91
NO ₃ ⁻	2.14
NO ₂ ⁻	0.52
AlO ₂ ⁻	0.31
CO ₃ ²⁻	0.16
SO ₄ ²⁻	0.15
Cl ⁻	0.025
F ⁻	0.032
PO ₄ ³⁻	0.010
C ₂ O ₄ ²⁻	0.008
SiO ₃ ²⁻	0.004
MoO ₄ ²⁻	0.0002

^a Source: Welch et al., 2000.

4.2.2 Granulated CST

CST used for these tests will be the commercial, granular form of the sorbent, IONSIV[®] IE-911[™] (UOP Molecular Sieves, Mt. Laurel, NJ). The as-received CST will be pre-treated using the steps recommended by the manufacturer and agreed upon by ORNL and SRS. This includes backwashing to remove fines and treatment with dilute sodium hydroxide to adjust the pH at ~13 prior to use. The material will then be drained and air-dried. The bulk density and particle size distribution of the dried material will be measured.

5. EXPERIMENTAL CONDITIONS

The thermal conductivity of the test specimens will be measured at various temperatures, which represent a physically plausible range. Redundant measurements will be made as required to obtain for statistical estimation of the relative error in the results. The tests will be performed at the prevailing atmospheric pressure. Barometric pressure will be recorded. Refer to Sect. 2 for a description of the solids-liquid mixture.

5.1 Dry CST Solid Particles

The thermal conductivity will be measured at the following temperatures: 25°C, 50°C, 100°C, 150°C, and 200°C.

5.2 Immersed CSR Solid Particles

The thermal conductivity will be measured at the following temperatures: 25°C, 50°C, and 100°C.

5.3 Wetted CST Solid Particles (optional, dependent on results from 5.1 and 5.2)

The thermal conductivity will be measured at the following temperatures: 25°C, 50°C, and 100°C.

6. REFERENCES

D. T. Bostick and W. V. Steele, "Thermal and Physical Property Determinations for Ionsiv[®] IE-911 Crystalline Silicotitanate and Savannah River Site Waste Simulant Solutions, ORNL/TM-1999/133, Lockheed Martin Energy Research, Oak Ridge National Laboratory, August 1999.

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7. APPROVALS

B. B. Spencer, Task Leader Date

T. D. Welch, Reviewer Date

R. T. Jubin, CERS Section Head Date