Crystalline Silicotitanate Examination Results

by

D. J. McCabe

Westinghouse Savannah River Company

Savannah River Site
Aiken, South Carolina 29808

DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.

DISCLAIMER

Westinghouse Savannah River Company
Savannah River Technology Center

To: S.D. Fink, 773-A

May 18, 1995

From: D.J. McCabe, 773-43A

Crystalline Silicotitanate Examination Results (U)

Summary

The In-Tank Precipitation (ITP) Process decontaminates radioactive waste by precipitating cesium with tetraphenylborate (TPB) and adsorbing strontium on sodium titanate (ST). An alternative method for cesium removal may offer improvements over the ITP process. One method studied is adsorption on crystalline silicotitanate (CST), a material developed by Sandia National Laboratory and Texas A&M University. Preliminary examination of the material indicates it is an effective cesium ion exchanger for Savannah River Site High Level Waste (HLW) with an overall average distribution coefficient at 25 °C of 1840 (std. dev. 106) mL/g. Unlike organic-based ion exchangers, elution is not feasible and the material would likely need to be disposed in DWPF glass.

To determine if further testing is warranted, estimates of waste processing rates and glass solubility were done. Based on calculated TiO_2 limits in glass, the cesium capacity of CST is sufficient to allow the same loading in the glass as the current

process. The radiation associated with a fully saturated CST column is extremely high and is expected to be a significant processing concern. The material would need to be in a column configuration to permit full saturation and sufficient decontamination. The crystalline silicotitanate is a fine particulate that is unsuitable for column processing, although work is underway to develop a granular supported material. Further research is needed when a granular supported material is available. Because of the inorganic nature of this material, possible advantages of CST over the organic resorcinol-formaldehyde or CS-100 resins are:

• potential for direct compatibility with glass, eliminating the need for regeneration or alternate disposal of spent resin
• probable lower radiolytic generation rates of hydrogen during processing or storage.

Introduction

The ITP Process decontaminates radioactive waste in Tank 48H by precipitating cesium with tetraphenylborate and adsorbing strontium on sodium titanate. The solids are separated from the salt solution by crossflow filters. Alternate chemicals for removal of cesium are being examined. One of these chemicals is crystalline silicotitanate, which was developed at Sandia National Laboratory and Texas A&M University.[1,2] Use of this compound would avoid generation of benzene, as occurs with TPB. Also, it is postulated that the material may be directly compatible with borosilicate glass.

Prior to proposing use of this compound as a replacement for TPB, the compatibility and effectiveness of CST must be examined. The waste solutions typically contain large amounts of sodium nitrate and sodium hydroxide, and smaller amounts of many compounds. Understanding of the effectiveness of CST at cesium removal in the presence of these compounds is necessary to evaluate the proposed processing scheme.

The assumed configuration of the process incorporating CST is a column, similar to the proposed ion exchange process. In practice, the CST particle size is too fine to support such an operation due to excessively high pressures required to pump solution through a column. Work is underway by a vendor (UOP Inc.) to develop a supporting inorganic matrix to circumvent this problem.

Experimental Results

Distribution Coefficient Measurements

Three batches of CST were tested. The batches were prepared by Sandia National Lab using identical methods. The designations for the batches are: DG-112, DG-113, and DG-114. The solid samples of CST (~50 mg) were contacted with 25 mL of simulated salt solution (Table 1). Four replicate samples of the mixtures were shaken at constant temperature (25 °C) in a water bath. Contact time for these standard measurements was 48 hours (Table 2). The samples were then filtered through 0.2 micron Polyvinylidene difluoride disposable cartridge filters and analyzed by Atomic Absorption. These tests allow determination of the distribution coefficient (Kd):

$$Kd = \left([C]_i / [C]_f - 1 \right) \times (mL\ solution/g\ CST)$$

where $[C]_i$ = initial cesium concentration and $[C]_f$ = final cesium concentration.

To verify that the 48 hour contact time was sufficient, one of each of the three batches was further contacted for an additional 72 hours at room temperature (nominally 23 °C) on an orbital shaker (Table 3).

Table 1. 5.6 M [Na+] aqueous salt solution preparation

Component	Concentration (M)
Na_2SO_4	0.17
$NaNO_2$	0.71
$NaNO_3$	1.2
$NaOH$	2.9
KNO_3	0.015
$Na_2CO_3 \cdot H_2O$	0.2
$Al(NO_3)_3 \cdot 9H_2O$	0.38
$CsNO_3$	0.00024

Table 2. Standard Kd measurements (48 hours)

CST batch	Kd (mL/g)	Standard Dev. (mL/g)
DG-112	1948	113
DG-113	1779	33
DG-114	1780	48

Table 3. Extended Duration Kd measurements (120 hours)

CST batch	Kd (mL/g)
DG-112	2180
DG-113	2041
DG-114	1945

Capacity Measurements

One of the CST batches, DG-112, was selected for cesium
capacity measurements. The purpose of this test was to
determine how much cesium can be loaded onto the CST, and
subsequently calculate the waste processing rates based on
glass compatibility. The Kd was measured in triplicate at
increasingly higher cesium concentration, using the same
simulated salt solution. Results of both the Kd and the
capacity (mg Cs/g·CST) are shown in Table 4. The results are
averages and standard deviations of three replicate samples.

Table 4. Cs Capacity Measurements

$[Cs]i$ (mg/L)	$[Cs]f$ (mg/L)	Kd (mL/g)	Std Dev. (mL/g)	Cs/g CST (mg)	Std Dev. (mg)
28.25	5.86	1948	113	11.59	0.19
48.67	10.01	1971	51	19.73	0.47
63.17	12.49	1980	90	24.70	0.25
74.41	16.02	1796	85	28.76	1.07
117.2	36.92	1094	64	40.31	0.74
139.0	46.32	988	92	45.61	1.39

The capacity of the material as a function of Kd is shown in
Figure 1. The isotherm for the capacity as a function of the
cesium remaining in solution at equilibrium is shown in
Figure 2.

Thermal Decomposition Measurements

The Differential Thermal Analysis (Figure 3) for the CST, in
air, indicates a gradual endotherm centered on ~250 °C, a
subsequent slow exotherm to over 1000 °C, and finally another
gradual endotherm to 1200 °C. The Differential Scanning
Calorimetry (Figure 4) also shows the endotherm at 250 °C.
The Thermal Gravimetric Analysis (Figure 5) indicates a loss
of approximately 11% of the weight up to ~250 °C, and no
further change to 1100 °C. All data were collected with a
DuPont Instruments 2100 Thermal Analyst controller, TGA Model
951, DSC Model 910, and DTA High Temperature Model.

Particle Size Analysis

A scanning electron microscope (ISI-DS-130) was used to
obtain an estimate of the particle sizes of the CST. The

samples were precoated with carbon and placed on the upper
stage of the microscope. The results showed that most of the
particles were below 0.3 microns, with many particles less
than 0.1 micron (Figures 6-7). The Brinkman laser-light
particle size analyzer (Model 2010) was also used to
determine the range of particle sizes of the CST. Results
indicated that all of the particles are less than 2 microns.

Potassium Effect on Cs Kd

Potassium concentration was varied and the cesium
distribution coefficient measured with CST (DG-112). The
potassium was added as potassium nitrate to a salt solution
containing all reagents as in Table 1, except potassium.
Results of triplicate Kd measurements are shown in Table 5
(average of 3) and Figure 8.

Table 5. Standard Kd measurements

[K] (mM)	Kd (mL/g)	Std. Dev. (mL/g)
6.2	2200	9
10	2100	15
24	1700	57
46	1600	34

Discussion

Distribution Coefficient Measurements

The distribution coefficients indicate the degree to which
CST will extract cesium from salt solution. It is clear from
the data in Table 2 that the CST batches vary only slightly
in cesium absorption. Other cesium-specific ion exchange
materials have been tested using the same simulant
formulation. The Kd of resorcinol-formaldehyde resin[3] is
4400 mL/g. Although the Kd of CST is lower than resorcinol-
formaldehyde resin, use of longer columns (or more in series)
would achieve the required decontamination factor.

Although the single extended contact samples are
statistically different from the 48-hour contact samples, the
48-hour samples are ~90% complete. The temperature was not
controlled on the extended duration samples but the
difference (~2 °C) is probably not significant.

Capacity Measurements

The cesium capacity of ion exchange materials can be used to
estimate the liquid waste processing rate (see "Processing
Impact" below). Cesium capacity will vary with waste
composition.

The cesium capacity of the CST can be calculated from the equation in Figure 2. The maximum capacity for the SRS application is 38 mg Cs/g CST, which is the amount of Cs absorbed on the CST at a final equilibrium of 29 mg/L total Cs in solution. This would be equivalent to the loading to 100% breakthrough on a column of CST using average SRS salt solution. This value permits calculation of the loading of the material in the DWPF glass. Assuming the salt solution is 1.0 Ci/L and 38 atom % Cs-137, this would be 1.3 Ci Cs-137/g CST.

Thermal Decomposition Measurements

In a glass melter, the CST would be exposed to extremely high temperatures. If the thermal decomposition of the material is exothermic, process hazards would increase significantly.

The high temperature thermal decomposition studies indicate that the material is relatively stable. The data indicate that it would not cause thermal-related processing concerns in the DWPF melter. Larger scale experiments are needed to verify that the bulk thermal properties are similar.

Particle Size Analysis

The CST particles are very small and are expected to cause high pressure drops if the material is put into a column configuration. Similarly, high transmembrane pressures would also be expected if filtration is used for separating the liquid from the CST in a batch-type operation. The particle size range (<0.1 micron) extends below the capabilities of the particle size analyzer, so a quantitative distribution of sizes was not feasible. It is evident that a granular form of the material that is supported on an inorganic matrix is needed for column operation.

Potassium Effect on Cs Kd

The effect of potassium on the CST extraction of cesium (i.e., Figure 8 and Table 5) can be important to the operation of a cesium-removal facility. If potassium concentration has a significant impact, salt solution from tanks with high potassium would have to be blended with that from other tanks. Blending salt solutions is expensive and requires adequate tankage to accomplish.

The effect of potassium, over the range expected in SRS waste, is relatively small (Figure 8). A change of 600 mL/g extraction capacity over almost an order of magnitude change in potassium content was observed. By comparison, tetraphenylborate precipitate requires a stoichiometric increase in tetraphenylborate ion for each potassium ion. The impact of increased potassium on a CST-based process

would be similar to that for a resorcinol-formaldehyde resin process. The impact on processing could be minimized by blending salt solutions in the High Level Waste system.

Processing Impact

Among the advantages of using inorganic ion exchange materials for cesium removal is that they may be incorporated directly into the final glass waste form with minimal impact on glass phases or redox chemistry. The solubility of some components of CST are expected to be limited in the DWPF waste glass matrix. To calculate the liquid waste treatment rates, the bounding solubility of components in the glass can be used. Since the DWPF glass production rate is fixed (228 lbs/hr), the rate at which ion exchange material can be incorporated in the glass can be calculated. Assuming full cesium saturation of the ion exchange material and no provision for storage, the liquid waste processing rate can also be calculated. Testing of the solubility of CST in glass has not been done, so process capacities are estimates established with related materials. In addition, there is at least one proprietary component of CST which is unknown to SRS personnel. The impact of this unknown component on the DWPF glass matrix therefore cannot be predicted.

The CST reportedly contains 36 wt % TiO_2, which is limited in DWPF glass to 1 wt %. Assuming a 75% attainment rate for DWPF and 228 lb/hr glass production rate, a CST system usage rate can be calculated. The CST rate is the rate at which CST can be added to the glass and remain at the 1 wt % limit. A CST-based process would allow a corresponding waste processing rate of 2800 L/hr assuming 100% saturated CST (38 mg Cs/g CST). The current overall ITP waste processing rate is 2340 L/hr. This would correspond to 12.3 Ci Cs-137/lb of glass. The current material balance for DWPF Batch 1 is 11.4 Ci/lb of glass,[4] assuming 38 atom % Cs-137.

A significant processing issue is the activity associated with this material. The cesium activity in a fully loaded column would be approximately 4000 Ci/gal, based on the above capacities and the reported bulk density (0.8 g/cm^3). The columns would have to be large enough to support the calculated waste processing rate of ITP (2340 L/hr) and an assumed turnover rate of 3 column volumes/hr, which is typical of ion exchange materials. (Actual turnover rates cannot be determined with this unsupported material.) This calculates to column volumes of 206 gallons each. The average accumulated dose received by the CST for the production would be 300 Mrad over a 14-day cycle.

The thermal heat from a fully saturated column must be examined once a supported material is available. The cesium capacity, thermal conductivity, and packing density of the

supported material must be determined before thermal load data can be estimated. These parameters, coupled with shielding considerations, can then be used to calculate the maximum permissible column diameter.

The achievable decontamination factor for a column must be determined experimentally. The controllable variables which would impact the decontamination factor are column flow rate, temperature, and column size (or number of columns in series).

Conclusions

The CST is an effective extractant for radioactive cesium from SRS HLW salt solution. The average overall Kd at 25 °C for the three batches of CST and the standard simulated salt solution was 1840 (std. dev. 106) mL/g. This may be compared to that for an identical simulant with ion exchange material examined previously.[3] The Kd for SRS-developed resorcinol-formaldehyde resin was 4400 mL/g.

To determine if further experimentation is warranted, calculations were done to estimate waste processing rates. The cesium capacity is estimated to be sufficient to permit inclusion in DWPF glass, based on the TiO_2 concentrations and the assumption that this is the only component limited in the glass. The material would need to be in a column configuration to permit full saturation and sufficient decontamination.

The radiation associated with a fully saturated CST column is extremely high and is expected to be a significant processing concern. Shielding requirements and thermal heating need to be addressed when a supported form is available. Testing of the compatibility of this material with glass to verify the solubility limit is also needed.

Decomposition of the material is expected at the high temperatures in the DWPF melter. The thermal analyses at high temperature did not display significant exothermic reactions. It is concluded that the material would not cause any thermal decomposition problems in the melter, although this remains to be proven experimentally on a larger scale.

The small particle size makes the material unusable in the current form due to the high pressure drops associated with column operation. A "batch and stir" operation, similar to that planned for strontium removal with sodium titanate in ITP, would not be feasible. The CST must be fully saturated with cesium to allow inclusion in the glass or would require more glass for dilution. Also, the material is expected to be very difficult to filter and is not known to be soluble in any common reagent that is compatible with stainless steel,

making filter cleaning impossible. The supported form of the
material is expected to be available within several months.
The new matrix should be evaluated at that time.

Technical Review

J.P Bibler, Interim Waste Technology

Acknowledgements

References

1. Dosch, R.G., Brown, N.E., Stephens, H.P., and Anthony,
R.G., "Treatment of Liquid Nuclear Wstes with Advanced Forms
of Titanate Ion Exchangers", Waste Management 93, p. 1751,
Tucson, AZ.

2. Klavetter, E.A., Brown, N.E., Trudell, D.E., Anthony,
R.G., Gu, D., and Thibaud-Erkey, C., "Ion-Exchange
Performance of Crystalline Silicotitanates for Cesium Removal
from Hanford Tank Waste Simulants", Waste Management 94, P.
709, Tucson, AZ.

3. Bibler, J.P., Wallace, R.M., "Proceedings from Waste
Management '90", R.G. Post and M.E. Wacks, eds., p. 747,
1990.

4. WSRC-TR-92-211, Revision 1, "Material Balance Tables for
the DWPF Radioactive Runs with Batch 1 Sludge/Supernate Feed
(U)", November, 1992.
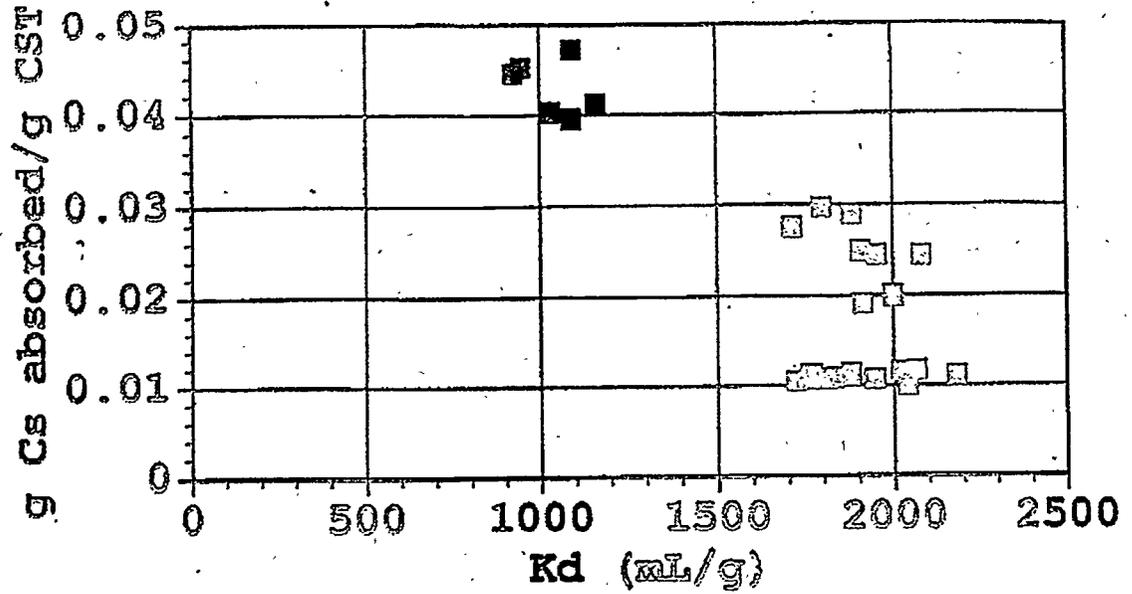
Figure 1. Cesium capacity vs. Kd
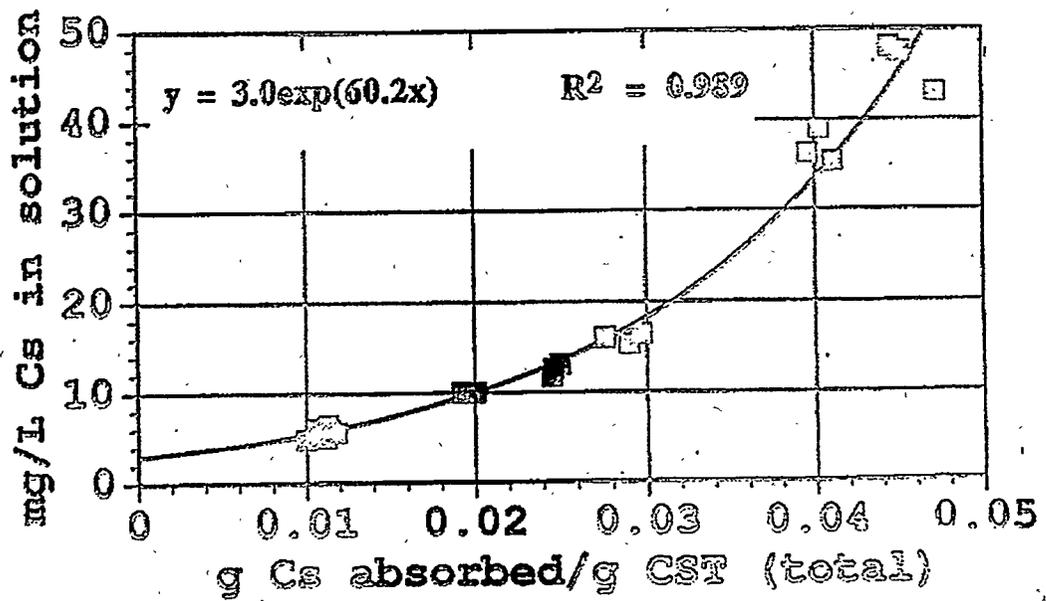
Figure 2. Cesium capacity vs. [Cs] final

Figure 3. Crystalline Silico Titanate Differential Thermal Analysis

DTA

File: DG112DTA.001
Operator: JCM

Sample: DG-112 (CST)
Size: 5.0000 mg
Method: DTA SI-TITANATE
Comment: DTA RUN 1
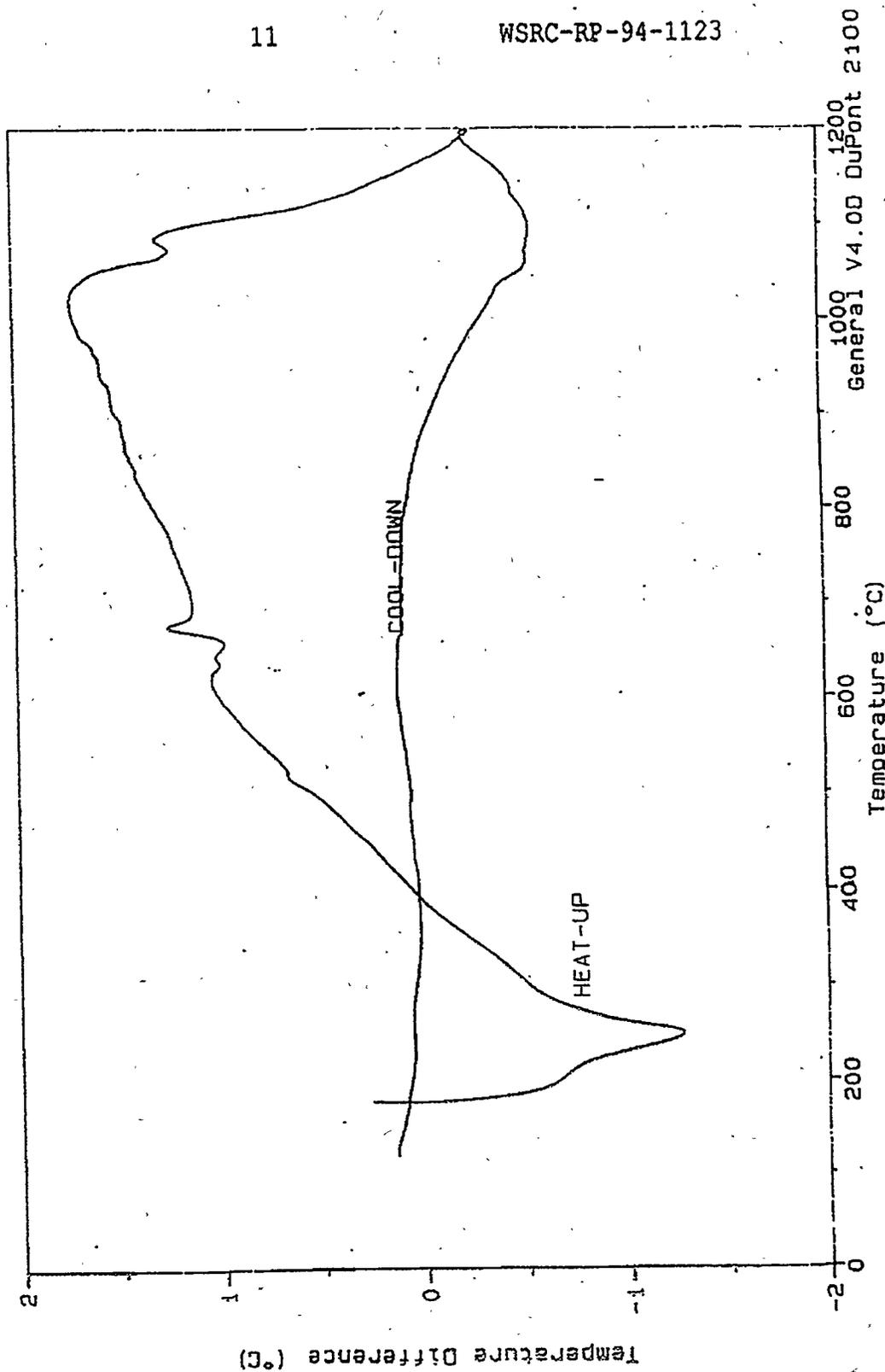
Figure 4. Crystalline Silico Titanate Differential Scanning Calorimetry
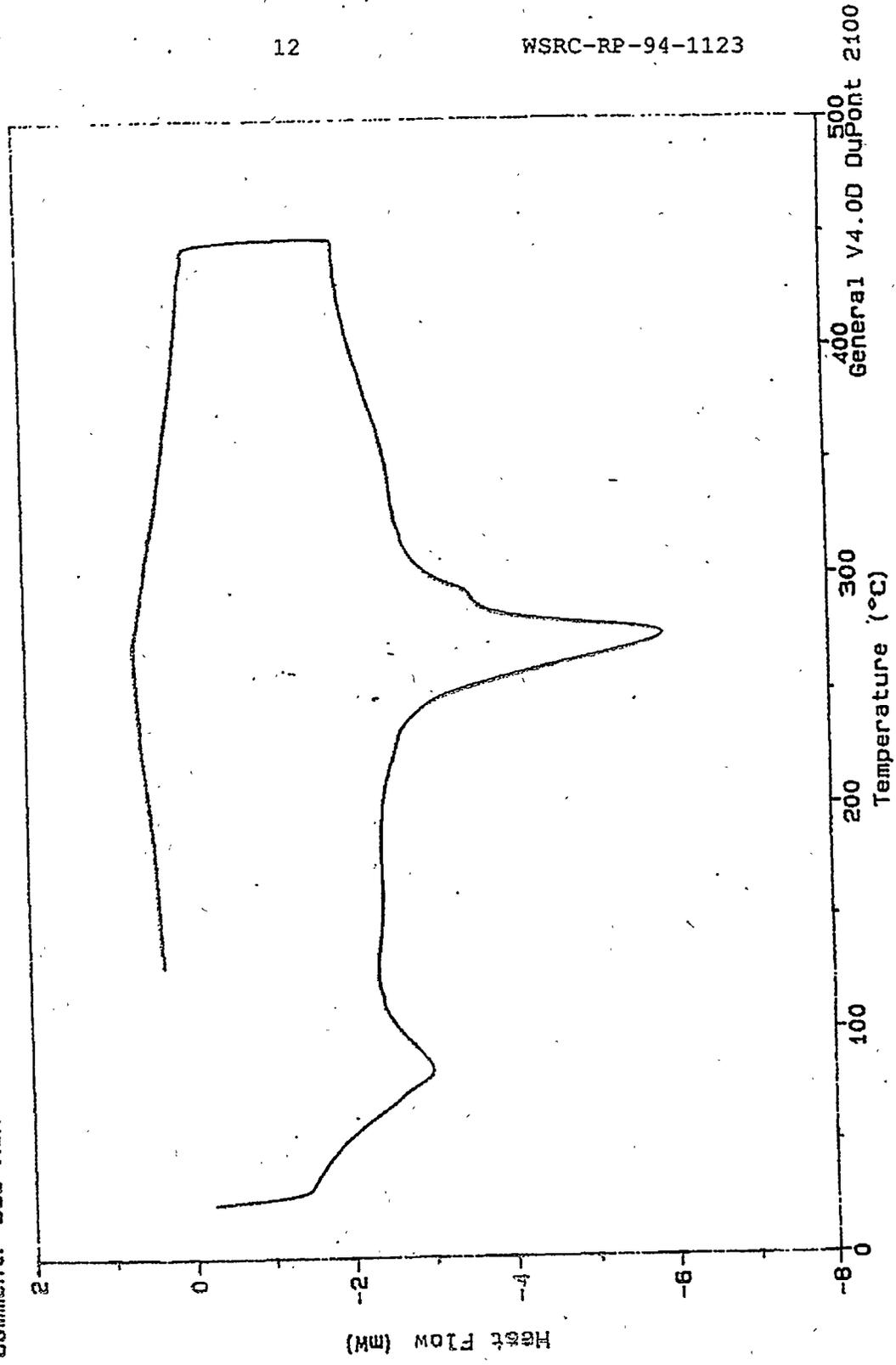
Figure 5. Crystalline Silico Titanate Thermal Gravimetric Analysis

TGA

File: C: DG112TGA.001
Operator: JCM

Sample: DG-112 CST
Size: 9.1480 mg
Method: TGA SI-TITANATE
Comment: TGA RUN 1

TGA V5.1A DuPont 2100
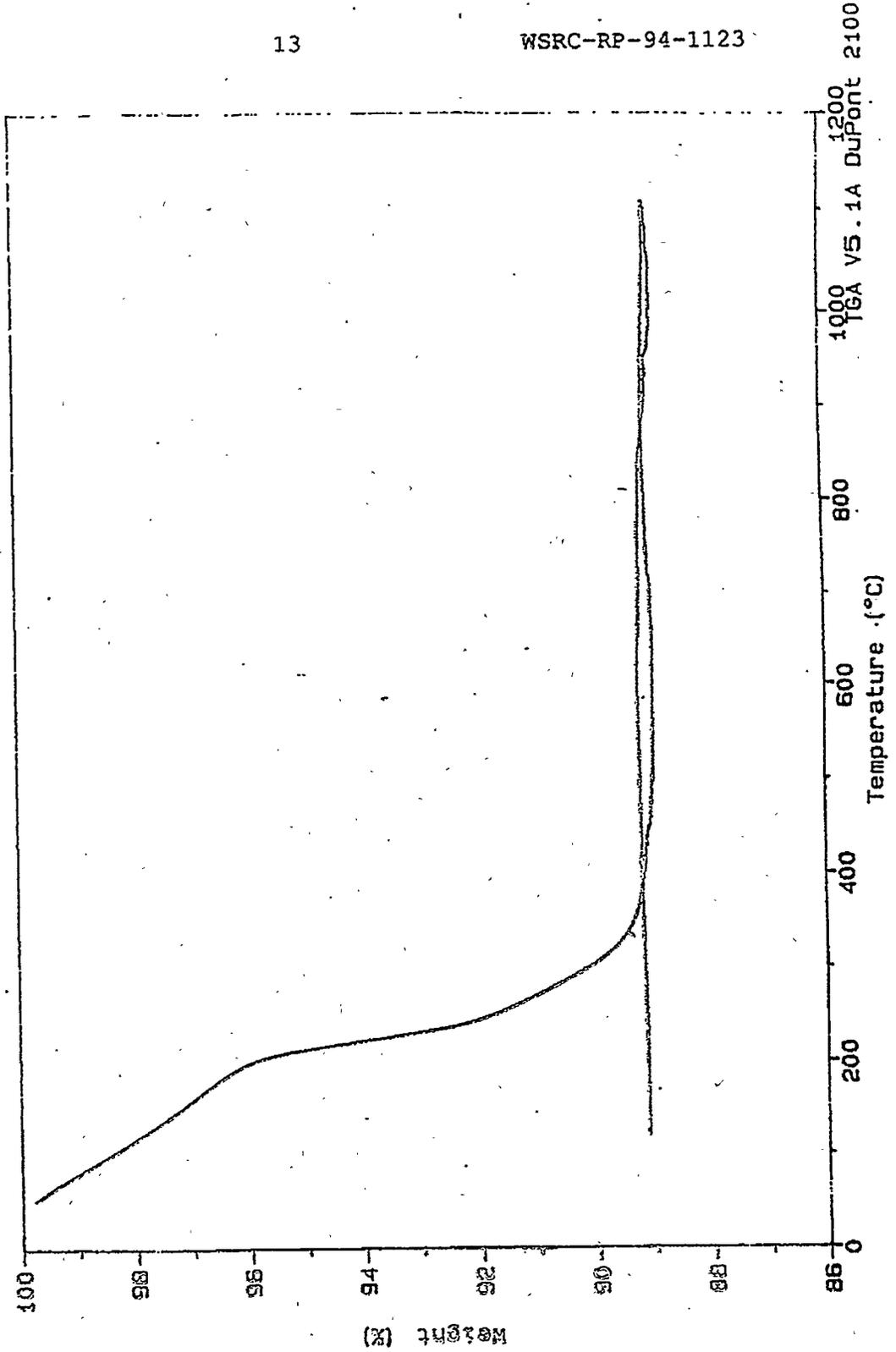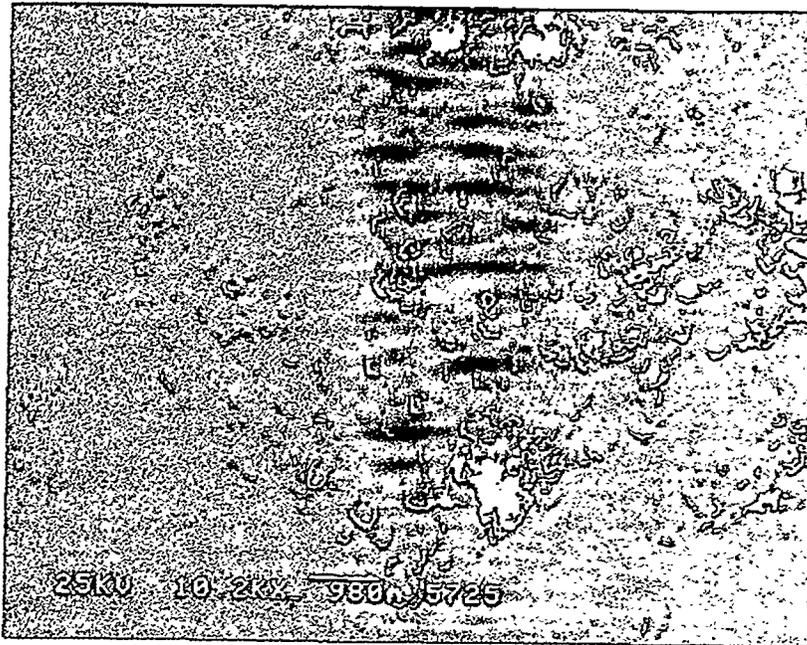
Figure 6. Scanning Electron Microscope Image, DG-114
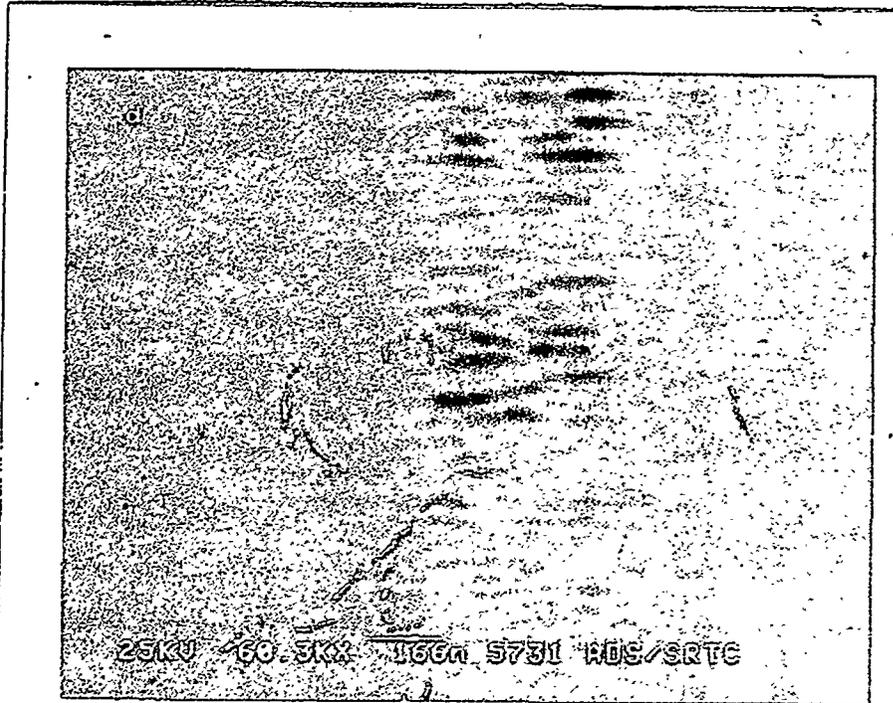
Figure 7. Scanning Electron Microscope Image, DG-114
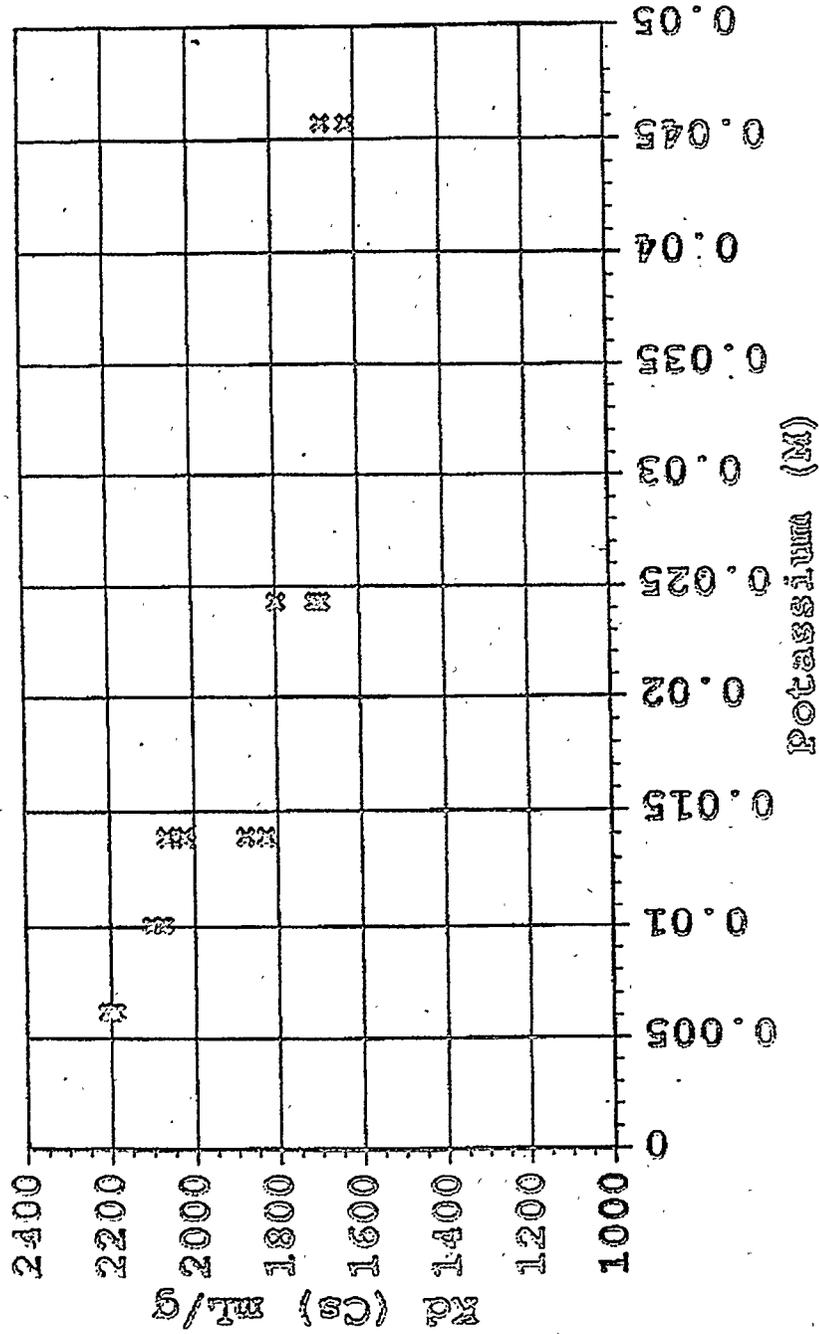
Figure 9. Kd (Cs) vs. Potassium concentration