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Examination of Crystalline Silicotitanate Applicability in Removal of Cesium from SRS High Level Waste (U)

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Summary

The In-Tank Precipitation (ITP) Process decontaminates
radioactive waste by precipitating cesium with tetraphenylborate
(TPB⁻) and adsorbing strontium on monosodium titanate (MST).
Alternative methods for cesium removal may offer improvements
over the ITP process. One method studied is adsorption onto
crystalline silicotitanate (CST), a material developed as a fine
powder by Sandia National Laboratory and Texas A&M University.
The material has recently been made into an engineered form by
UOP. 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
23 °C of 1500 (std. dev. 171) mL/g. Unlike organic-based ion
exchangers, elution is not feasible and the material would likely
need to be disposed directly in glass.

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

Because of the inorganic nature of this material, possible
advantages of CST over the organic resorcinol-formaldehyde or CS-
100 resins are:

o potential for direct compatibility with glass, eliminating the
need for regeneration or alternate disposal of spent resin

o probable lower radiolytic generation rates of hydrogen and
other gases during processing or storage.

The lack of a regeneration step is expected to greatly reduce the
cost of implementing this technology when compared with organic
resins.

Introduction

The ITP Process decontaminates radioactive liquid wastes in Tank
48H by precipitating cesium with tetraphenylborate ion (TPB⁻) and
adsorbing strontium onto monosodium titanate. The radioactive
solids are separated from the salt solution by cross flow
filters. An alternative cesium and strontium removal agent is
crystalline silicotitanate, developed at Sandia National
Laboratory and Texas A&M University.[1,2] The powdered form of this
material was previously studied at SRS[3] for use with High Level

Waste (HLW). The distribution coefficient (Kd) for the powdered material and simulated SRS High Level Waste was 1840 mL/g.[3] Recently the material has become available in an engineered form, where the powdered material is bound in an inorganic matrix. 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, avoiding regeneration common to organic resins.

Prior to proposing use of this material 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 constituents, such as potassium. Understanding of the effectiveness of CST for cesium removal in the presence of other waste components is necessary to evaluate the proposed processing scheme.

The development of this material was funded by the Department of Energy, Office of Science and Technology, Efficient Separations and Processing Crosscutting Program. Testing of this material at SRS was also funded by the Efficient Separations and Processing Crosscutting Program (Technical Task Plan SR1-3-20-07); John Mathur, DOE Headquarters Program Manager.

Experimental Results

Distribution Coefficient Measurements

The batch (lot #07398-38B) of the engineered form of CST, trade name IONSIV IE-911, was prepared by UOP. This batch was a developmental sample available prior to the improved final commercial form. The solid samples of CST (~100 mg) were contacted with 25 mL of simulated salt solution (Table 1). Three replicate samples of the mixtures were shaken with an orbital shaker at ambient temperature (~23 °C). Contact time for these standard measurements was 48 hours. The samples were then filtered through 0.2 micron Nalgene® filters and analyzed by atomic absorption (AA) spectroscopy for cesium content. These tests allow determination of the distribution coefficient (Kd):

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

where $[C]_i$ = initial cesium concentration and $[C]_f$ = final cesium concentration. Table 2 provides these values.

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 quantity (g)	Cs final (mg/L)	Kd (mL/g)
0.1022	5.157	1376
0.1022	5.3348	1322
0.1005	5.2903	1358
0.1026	4.5981	1567
0.0995	4.5338	1642
0.1000	4.3087	1732
	average:	1500
	std.dev.:	171

Capacity Measurements

Capacity measurements were performed to determine how much cesium can be loaded onto the CST, and to subsequently calculate the waste processing rates based on glass compatibility. The Kd was measured in triplicate at increasing initial cesium concentration, using the same simulated salt solution. Results of both the Kd and the capacity (mg Cs/g CST) are shown in Table 3. The results are averages and standard deviations of three replicate samples.

Table 3. 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)
34.16	4.87	1500	171	10.77 7.31	0.19
78.78	9.75	1768	647	17.16	6.64
93.26	15.22	1267	439	19.22	4.90
135.02	30.66	848	321	25.89	8.17
171.77	48.16	628	184	30.25	8.57
195.99	66.09	490	163	32.38	9.45
223.27	90.38	367	125	33.10	9.60

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.

Potassium Effect on Cs Kd

Potassium concentration was varied and the cesium distribution coefficient measured with the CST. The potassium was added as potassium nitrate to the simulant composition shown in Table 1. Results of triplicate Kd measurements, by atomic absorption spectroscopy, are shown in Table 4 (average of 3) and Figure 3. In four of the five tests, the final potassium concentration was within 5% of the initial concentration. In one test, the potassium concentration dropped from 1077 mg/L to 958 mg/L, a difference of 11% which is attributable to variance in the method and analyses. This indicates that potassium is not appreciably absorbed by CST.

Table 5. Standard Kd measurements

initial [K+] (mg/L)	Kd (mL/g)	Std. Dev. (mL/g)
191	1281	48
535	1500	171
1077	1128	42
1472	972	74
2171	1013	33

Radioactive Waste Decontamination Factor Measurements

A radioactive waste salt solution sample was received from Tank 43H (collected on 5/6/96) and adjusted to a density of 1.24 g/mL with deionized water. The samples were stirred for over 10 hours at room temperature, and filtered with a 0.2 micron Nalgene® filter. The CST (~100 mg) was mixed with a 20 mL aliquot of the salt solution, and the slurry was shaken at ambient temperature (~27 °C) for 48 hours. The samples were then filtered with a 0.2 micron Nalgene® filter with the filtrate removed from the shielded cell and analyzed. An initial untreated sample was diluted (~1000:1) with deionized water and analyzed. An initial, untreated sample was also decontaminated of Cs-137 by acidifying with an equal volume of 8 M nitric acid and mixing with BioRad AMP-1® resin (0.1 g/mL) to remove radioactive cesium. The AMP-1 resin was then removed by filtration (0.45 micron) and washed with water. The decontaminated aqueous sample was then analyzed by counting the radioactive Sr-90 and Sr-85 decay energy, and by measuring the Sr-88 and actinide concentrations using an Inductively Coupled Plasma - Mass Spectrometer (ICP-MS). Atomic absorption spectroscopy, titrations, and ion selective electrodes were also used for further characterization. The results of the analyses are shown in Table 6, and the characterization of the sample is shown in Table 7.

Table 6. Standard DF measurements with Tank 43H Radioactive Waste Sample

Radionuclide	Kd (mL/g)	std. dev.
Cs-137	1100	55
U	87	4
Pu	53	39
Np	>1000	n.a.

Table 7. Initial Composition of Tank 43H Radioactive Waste Sample

Component	Concentration (M)
K^+	0.0326
Na^+	7.85
SO_4^{-2}	0.0118
NO_2^-	1.08
NO_3^-	1.01
OH^- (free)	5.79
CO_3^{-2}	<0.29
Al^{+3}	0.218
Cs^+ (total estimated)	6.4E-5 (8.5 mg/L)

Discussion

Distribution Coefficient Measurements

The distribution coefficients indicate the degree to which CST will extract cesium from salt solution. The Kd is lower for the engineered form of the material (1500 mL/g) versus the powdered form (1840 mL/g) due to "dilution" of the powdered CST in a binder matrix. Other cesium-specific ion exchange materials have been tested using the same SRS simulant formulation. The Kd of resorcinol-formaldehyde resin[4] is 4400 mL/g with the SRS simulant. 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.

Capacity Measurements

The cesium capacity of ion exchange materials can be used to estimate the liquid waste processing treatment rate (see "Processing Impact" below). Cesium capacity will vary with waste composition, depending on the influent cesium concentration (Figure 2). The data suggest that blending high cesium wastes and low cesium wastes would be beneficial to maximizing the loading. Blending the wastes would evenly distribute the titanium and cesium in the DWPF glass and would minimize the size of the IX columns and shielding requirements. The cesium capacity is only slightly dependent on the potassium

concentration (Figure 4), so blending to equalize the potassium is not needed.

The cesium capacity of the CST can be calculated from the equation in Figure 2. The average SRS HLW salt solution contains approximately 29 mg/L of total cesium. The maximum capacity for the SRS application is 25.2 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 capacity measurement 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 final glass waste form. Assuming the salt solution is 1.0 Ci/L and 38 atom % Cs-137, this would be 0.88 Ci Cs-137/g CST.

Potassium Effect on Cs Kd

The effect of potassium on the separation of cesium (i.e., Figures 3 and 4 and Table 5) is important to the operation of a cesium-removal facility. If potassium is found to have a significant impact, salt solution from tanks with high potassium would have to be blended with that from other tanks. Blending salt solutions requires funding and adequate tankage to accomplish.

The effect of potassium on cesium uptake, over the range expected in SRS waste, was found to be relatively small (Figure 3). A change of 35% (530 mL/g) extraction capacity over more than an order of magnitude change in potassium content was observed, although the results were not linear. 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.

Radioactive Waste Decontamination Factor Measurements

A radioactive waste sample was used in standard decontamination factor tests in the SRTC Shielded Cells. The results (Table 6) indicate that the resin was very effective for cesium removal. The sodium and potassium concentrations of the Tank 43H sample were higher than in the standard simulant formulation (Table 7), and the total cesium concentration was slightly lower. Allowing for these differences, the cesium distribution coefficient is in relatively good agreement with the simulant results. Also, the CST was found effective for removal of actinides from HLW. The results for uranium are consistent with those observed previously with powdered CST and simulated Hanford alkaline supernate.[7] Further work is needed to determine the maximum loading capacity of actinides on CST to establish if the material is intrinsically safe from criticality. The measurement of the neptunium was below the detection limit of the instrument after treatment. The measurement of the Sr-90 on the treated samples was at or below the detection limit of the instrument. Due to sample dilution

requirements, calculation of an accurate distribution coefficient for Sr-90 was not feasible. Further work is needed to verify the results of Np and Sr removal.

Processing Impact

Among the advantages of using inorganic ion exchange materials for cesium removal is that, in principal, 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, primarily titanium, are expected to be limited in the waste glass matrix. To calculate the liquid waste treatment rates in a theoretical processing plant, the bounding solubility of components in the Defense Waste Processing Facility (DWPF) 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 a variety of glass formulations is being done by the Vitrification Technology Section of SRTC, but estimates of the processing rate can be calculated based on the current glass formulation. In addition, there is at least one proprietary component of CST which is unknown to Waste Processing Technology personnel. The impact of this unknown component on the DWPF glass matrix, therefore, cannot be predicted.

The engineered form of CST reportedly contains 20 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 limiting 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 maximum corresponding waste processing rate of 3350 L/hr assuming 100% saturated CST (25 mg Cs/g CST). This significantly exceeds the current overall ITP waste processing rate of 2340 L/hr (i.e., the work off rate for disposal of loaded CST in glass exceeds current flow sheet requirements). This CST processing rate would correspond to 18 Ci Cs-137/lb of glass. The current material balance for DWPF Batch 1 is 11.4 Ci/lb of glass, assuming 38 atom % Cs-137.[5] This suggests that the TiO2 limit in glass will not be the limiting factor in loading the material in glass.

A significant processing issue is the activity associated with this material. The cesium activity in a fully loaded column would be approximately 3400 Ci/gal, based on the above capacities and the reported bulk density (63 lb/ft^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 6 column volumes/hr, which is typical of recent testing with CST.[6] (Actual turnover rates have not been determined with SRS waste.)

This equates to a minimum column volume of 130 gallons each,
assuming a 75% attainment rate.

An initial engineering design is needed to estimate the thermal
heat load of the cesium saturated resin. Actinide loading
studies are also needed for input to the heat load calculations.
These parameters, coupled with shielding considerations, can then
be used to calculate the maximum permissible column diameter and
potential location for the columns.

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, column size, and number of columns in series.

Organic resins, such as resorcinol-formaldehyde and CS-100 are
known to generate hydrogen, nitrogen oxides, and other gases
during radiolysis.[8] Due to the absence of organic compounds in
CST, the gas generation rates are expected to be significantly
lower. Radiolysis of water is likely to be the only source of
gases during processing.

Conclusions

The CST is an effective extractant for radioactive cesium from
SRS HLW salt solution. The average overall Kd at 23 °C for the
three batches of CST and the standard simulated salt solution was
1500 (std. dev. 171) mL/g. This may be compared to that for an
identical simulant with resorcinol-formaldehyde ion exchange
material examined previously.[4] The Kd for SRS-developed
resorcinol-formaldehyde resin was 4400 mL/g. Although the CST
exhibits a lower distribution coefficient, it is expected that an
adequate decontamination could be achieved by using longer ion
exchange columns.

Unlike resorcinol-formaldehyde resin, CST is not amenable to
elution and would be disposed by vitrification in the DWPF. To
determine if further experimentation is warranted, calculations
were done to estimate waste processing rates. The cesium
capacity is estimated as sufficient to permit inclusion in the
current DWPF glass formulation, 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.
Further work on the maximum loading capacity of actinides is
needed to examine the potential for criticality.

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 heat loads may limit
the size of resin columns that can be used. Testing of the
compatibility of this material with glass to verify the

solubility limit is underway by the Defense Waste Processing
Technology section of SRTC.

Design Check

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D.T. Hobbs, Waste Processing Technology   date

Acknowledgments

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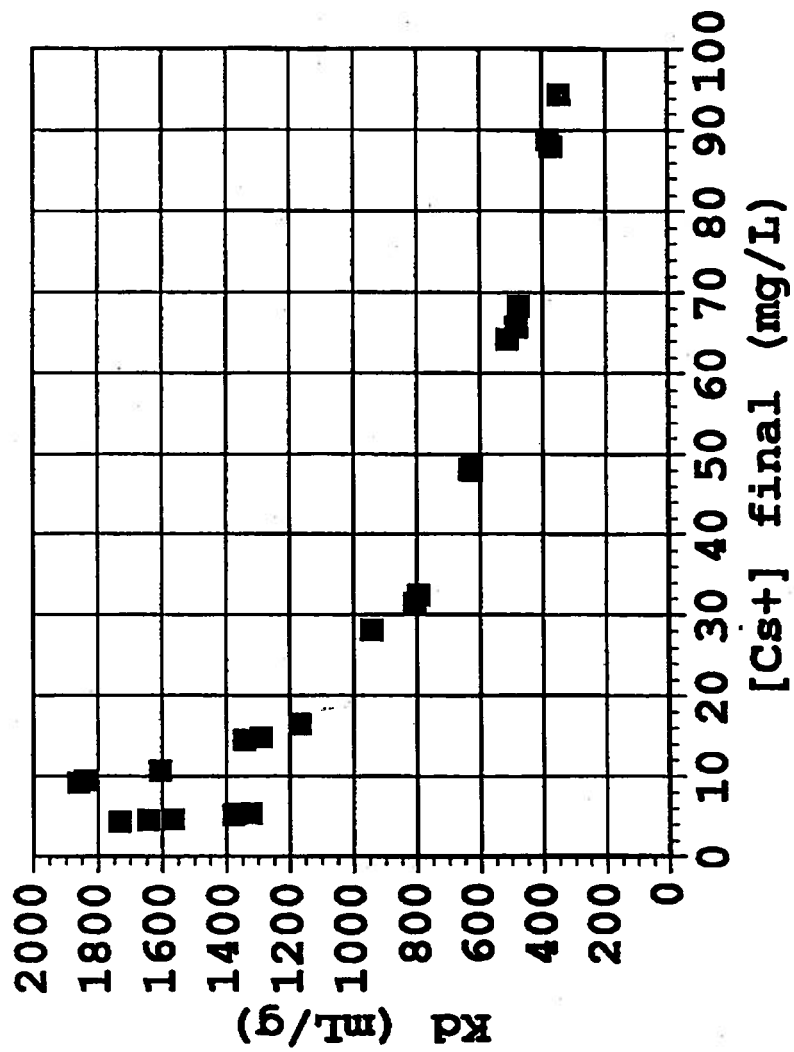10772, September, 1995.

Figure 1. Cesium Capacity

Figure 2. Cesium Loading

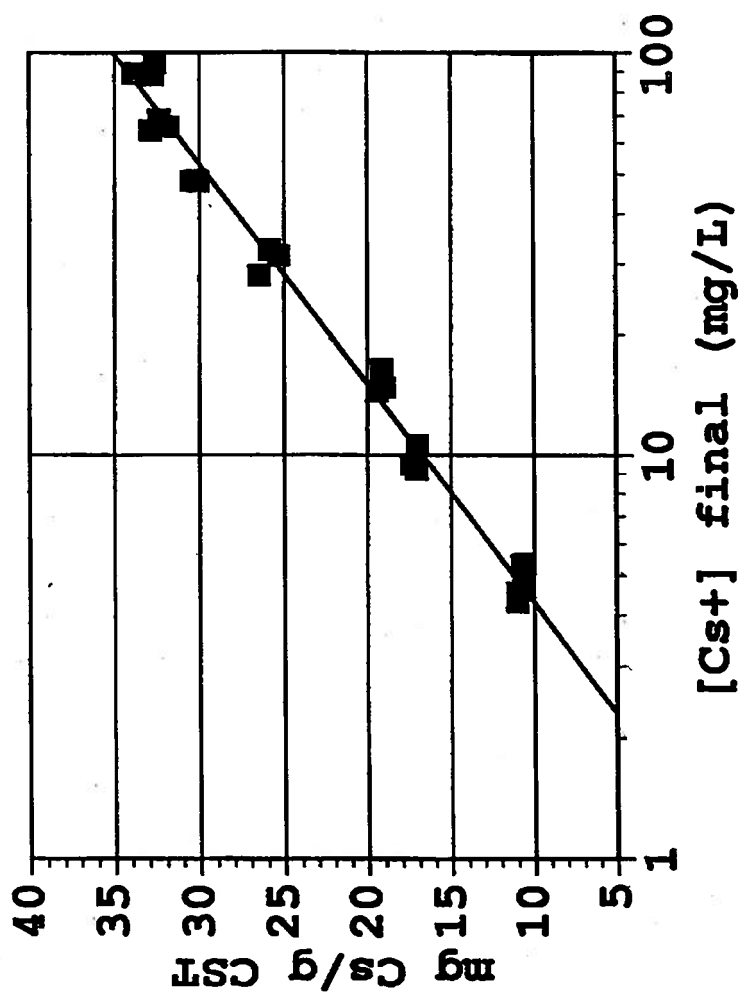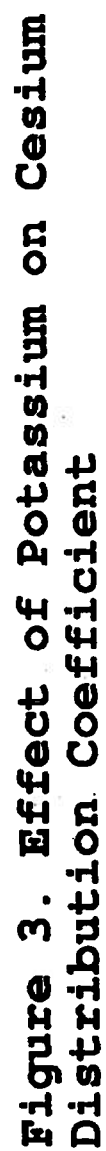mg Cs/g CST = 7.97E+0 * ln(Cs$_f$) + -1.61E+0

R^2 = 9.87E-1

Figure 3. Effect of Potassium on Cesium
Distribution Coefficient
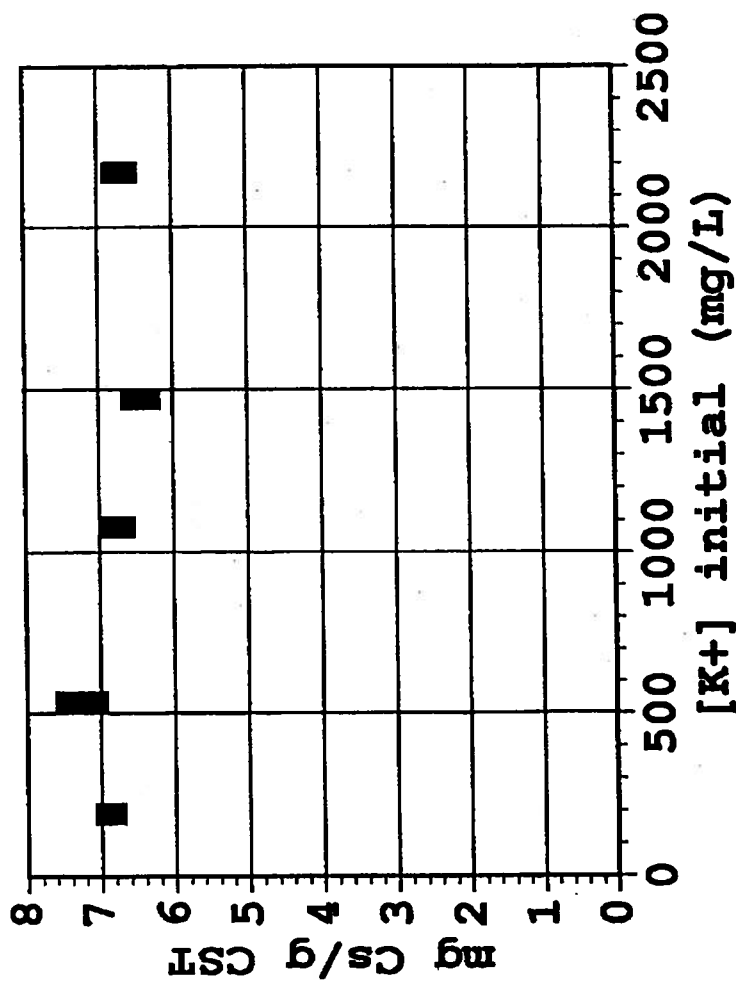
Figure 4. Effect of Potassium on Cesium Capacity