Powdered Crystalline Silicotitanate (CST) Isotherms for SRS Wastes

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DOE Contract No. **DE-AC09-96SR18500**

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WSRC-RP-98-01051, Rev. 0

Keywords: Cyrstalline silico-
titanate, CST, Equilibrium curves,
Isotherms

Retention: Permanent

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Powdered Crystalline Silicotitanate (CST) Isotherms for SRS Wastes (U)

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Publication Date: September 11, 1998

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Crystalline Silicotitanate (CST) Isotherms for SRS Wastes (U)

SUMMARY

One of the primary inputs for modeling an ion exchange column is the equilibrium driving force for mass transfer between the solution and the solid phase. The equilibrium relationship is typically known as an isotherm. This document contains the predicted isotherms for the various Savannah River Site (SRS) waste types in equilibrium with powdered (*ungranulated*) crystalline silicotitanate (CST). Six isotherms for SRS waste are included: One for each of the three waste types (average, high hydroxide, and high nitrate) and one for each waste type at bounding potassium and cesium. The predictions were made using a proprietary computer program titled CST Ion Exchange Version 5 (CSTIEX5).[1]

WASTE COMPOSITION

A part of modeling an ion exchange column involves evaluating the impact of variations in waste composition. SRS salt waste fall into three categories: average, high hydroxide, and high nitrate. The compositions used for this study are based on Table 5.1-4 of the Salt Team Assumptions and Bases document [2] and are shown in Table 1.

Table 1
SRS WASTE COMPOSITIONS

Component	Average (M)	High OH^- (M)	High NO_3^- (M)
Na^+	5.6	5.6	5.6
Cs^+	0.00014	0.00037	0.00014
K^+	0.015	0.030	0.0041
OH^-	1.91	3.05	1.17
NO_3^-	2.14	1.10	2.84
NO_2^-	0.52	0.74	0.37
AlO_2^-	0.31	0.27	0.32
CO_3^{2-}	0.16	0.17	0.16
SO_4^{2-}	0.15	0.030	0.22
Cl^-	0.025	0.010	0.040
F^-	0.032	0.010	0.050
PO_4^{3-}	0.010	0.008	0.010
$C_2O_4^{2-}$	0.008	0.008	0.008
SiO_3^{2-}	0.004	0.004	0.004
MoO_4^{2-}	0.0002	0.0002	0.0002

These compositions represent the typical values for the three SRS waste types. They represent the extremes of the major components, *e.g.*, hydroxide, nitrite, nitrate. However, they may not be the "worst case" compositions that can be encountered. A comparison of waste compositions and predicted isotherms for wastes from other sites (*e.g.*, Hanford, Oak Ridge) reveals there are two other cations frequently present in other wastes which are low in the three waste types. They are potassium and strontium. High levels of these two cations (0.415 M K^+ and 4.5 E-04 M Sr^{++}) result in an isotherm that has a predicted solid/solution equilibrium ratio almost an order of magnitude lower than for SRS waste. Because of its high pH, SRS waste has very little soluble Sr – and that which is present is removed by treatment with monosodium titanate (MST).

Therefore, it is important to examine the impact of a bounding potassium concentration. Estimates of blended salt solution feeds to an ion exchange system are not available to support preliminary column siting activities performed by SRS engineering and outside consultants. Instead, historical analysis of salt solution supernates was examined to provide a bounding potassium value.[1][3,4] The data are shown in Table 2.

Table 2
SUPERNATE POTASSIUM CONCENTRATIONS

Tank	K^+ (M)	Na^+ (M)	K^+ Adjusted to 5.6 M Na^+ (M)
7F	0.033	5.8	0.032
10H	0.013	9.2	0.008
17 F Batch 3	0.053	6.9	0.043
[redacted]			
Batch 5	0.036	7.5	0.027
20F	0.023	7.7	0.017
29H	0.078	10.9	0.040
30H	0.078	13.3	0.033
41H	0.041	5.0	0.046
43H	0.018	5.8	0.017
44H	0.071	10.6	0.038
24 [3]	0.0068	5.8	0.007
25 [4]	0.17	13.8	0.069
26 [4]	0.18	16.7	0.060
27 [4]	0.14	12.1	0.065
28 [4]	0.13	13.2	0.055
29 [4]	0.086	14.0	0.034
30 [4]	0.039	9.1	0.024
32 [4]	0.019	5.3	0.020
38 [4]	0.083	19.1	0.024
43 [4]	0.085	14.4	0.033

Based on this data, a bounding value of 0.15 M K^+ was chosen for the purposes of this evaluation.

One other cation is very important – that is the bounding value of Cs itself. This is because the equilibrium ratio between the Cs on the resin and Cs in solution decreases as the [Cs] increases. Therefore, isotherms need to bound the starting Cs concentration. For this study, the highest value of Cs for each waste is ≈ 28 Ci/gal.[2]

RESULTS

The model requires the input of the principal cations and anions. These include the ions that comprise the bulk of the ionic strength as well as those which compete for sites on the CST. The inputs to the model

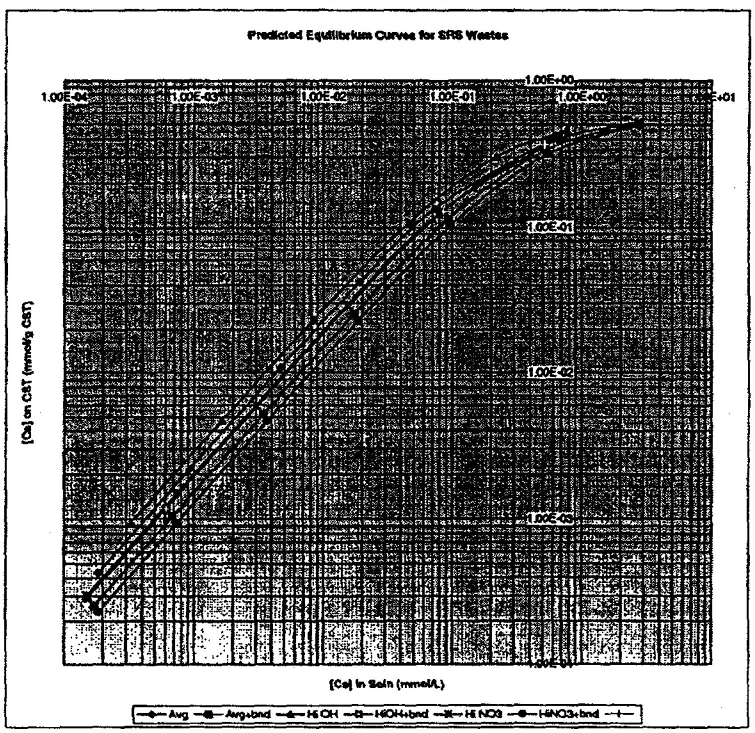
[1] Some of the data in Table 2, provided by D. D. Walker, is not contained in references 3 and 4. The values in Table 2 are used in lieu of projected compositions to be developed from the Tank Farm database and the waste removal schedule. When the projected values are available, the isotherms will be re-developed if necessary to provide bounding estimates.
[2] Based on 22.5 atom percent ^{137}Cs.

are shown in each input table. The additional inputs are the same for each run:

Temperature = 298.15 K
Material = Na form
Liquid = 0.100 L
Solid = 0.050 g
Density = 1258 kg/m^3

The model simulates the results of an experiment to determine the distribution coefficient (K_d). In a K_d experiment, a quantity of solution is placed in contact with a quantity of ion exchange material. After reaching equilibrium, the concentrations of various cations (in the case of a cation resin) are measured. The ending solution concentrations for each cation are used to calculate the K_d for that cation, the loading on the resin, and the equilibrium ratio between the ending solution concentration and the resin. A series of final solution concentrations versus resin concentrations define the equilibrium curve or isotherm. The model predictions of equilibrium solution and solid concentrations are shown for each waste type in each result table as C (the ending concentration of Cs in solution in mmol Cs/L solution) and Q (the ending concentration of Cs on the CST in mmol Cs/g CST). Figure 1 is plot of the results for all six waste types. Samples of the input and output files are in Appendix A.

Figure 1
ISOTHERMS



General comments regarding the model runs:

1) In the bounding wastes, the increase in potassium is offset by decreasing the sodium to maintain a constant ionic strength.

2) In each case, one of the ions is increased to force the ionic balance. This is noted by the nominal + the increment. For example, in the nominal SRS average salt waste, the hydroxide is increased by 0.00414 M as noted; that is, 1.91 + 0.00414.

3) In all SRS cases, the molybdate was excluded and the ionic strengths due to silicate and oxalate were included with the nitrate ion.

<u>Average SRS Salt Waste</u>

Table 3
INPUT

Component	Nominal (M)	Bounding (M)
Na^+	5.6	5.465
Cs^+	1.4E-04	7.0E-04
H^+	5.24E-15	5.24E-15
K^+	0.015	0.150
OH^-	1.91+0.00414	1.91+0.00470
NO_3^-	2.164*	2.164*
NO_2^-	0.52	0.52
$Al(OH)_4^-$	0.31	0.31
$CO_3^=$	0.16	0.16
$SO_4^=$	0.15	0.15
Cl^-	0.025	0.025
F^-	0.032	0.032
PO_4^{-3}	0.010	0.010

*includes $C_2O_4^=$ and $SiO_3^= = 2*(0.008 + 0.004)$

Table 4
RESULTS

Nominal		Bounding	
C (mmol Cs/L)	Q (mmol Cs/g CST)	C (mmol Cs/L)	Q (mmol Cs/g CST)
6.31E-01	4.19E-01	2.75	5.10E-01
7.30E-02	1.34E-01	5.31E-01	3.38E-01
1.90E-02	4.20E-02	9.29E-02	1.14E-01
4.61E-03	1.08E-02	1.73E-02	2.54E-02
9.14E-04	2.17E-03	3.41E-03	5.18E-03
1.82E-04	4.35E-04	6.80E-04	1.04E-03
3.65E-05	8.71E-05	1.70E-04	2.60E-04
9.12E-06	2.18E-05	3.40E-05	5.20E-05
1.82E-06	4.35E-06	6.80E-06	1.04E-05

High Hydroxide SRS Waste

Table 5
INPUT

Component	Nominal (M)	Bounding (M)
Na^+	5.6	5.48
Cs^+	3.7E-04	7.0E-04
H^+	3.25E-15	3.25E-15
K^+	0.030	0.150
OH^-	3.05+0.00237	3.05+.00270
NO_3^-	1.124	1.124
NO_2^-	0.74	0.74
$Al(OH)_4^-$	0.27	0.27
$CO_3^=$	0.17	0.17
$SO_4^=$	0.030	0.030
Cl^-	0.010	0.010
F^-	0.010	0.010
PO_4^{-3}	0.008	0.008

includes $C_2O_4^=$ and $SiO_3^=$ = 2(0.008 + 0.004)

Table 6
RESULTS

Nominal		Bounding	
C (mmol Cs/L)	Q (mmol Cs/g CST)	C (mmol Cs/L)	Q (mmol Cs/g CST)
7.70E-01	4.60E-01	2.74	5.23E-01
2.19E-01	3.03E-01	5.16E-01	3.68E-01
4.60E-02	1.08E-01	8.53E-02	1.29E-01
8.38E-03	2.32E-02	1.56E-02	2.89E-02
1.64E-03	4.71E-03	3.05E-03	5.90E-03
3.27E-04	9.45E-04	6.08E-04	1.18E-03
8.18E-05	2.36E-04	1.52E-04	2.96E-04
1.64E-05	4.73E-05	3.04E-05	5.93E-05
4.09E-06	1.18E-05	7.59E-06	1.48E-05

High Nitrate SRS Waste

Table 7
INPUT

Component	Nominal (M)	Bounding (M)
Na^+	5.6	5.4541
Cs^+	1.4E-04	7.0E-04
H^+	8.55E-15	5.24E-15
K^+	0.0041	0.150
OH^-	1.17+0.00024	1.17+0.00080
NO_3^-	2.864	2.864
NO_2^-	0.37	0.37
$Al(OH)_4^-$	0.32	0.32
$CO_3^=$	0.16	0.16
$SO_4^{=*}$	0.22	0.22
Cl^-	0.040	0.040
F^-	0.050	0.050
PO_4^{-3}	0.010	0.010

includes $C_2O_4^=$ and $SiO_3^=$ = 2(0.008 + 0.004)

Table 8
RESULTS

Nominal		Bounding	
C (mmol Cs/L)	Q (mmol Cs/g CST)	C (mmol Cs/L)	Q (mmol Cs/g CST)
6.39E-01	4.01E-01	2.75	4.98E-01
7.78E-02	1.24E-01	5.42E-01	3.16E-01
1.53E-02	2.95E-02	9.82E-02	1.04E-01
2.99E-03	6.02E-03	1.86E-02	2.29E-02
7.44E-04	1.51E-03	3.66E-03	4.67E-03
1.49E-04	3.03E-04	7.31E-04	9.38E-04
2.97E-05	6.05E-05	1.83E-04	2.35E-04
4.96E-06	1.01E-05	3.65E-05	4.69E-05
		7.31E-06	9.39E-06

REFERENCES

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2. P. L. Rutland, et al, *Bases, Assumptions, and Results of the Flowsheet Calculations for the Initial Eighteen Salt Disposition Alternatives (U)*, WSRC-RP-98-00166, June 15, 1998.

3. J. R. Fowler and L. M. Lee, *Projected Composition of Decontaminated Salt from Tank 24*, DPST-82-404, March 1982.

4. D. D. Walker, *et al.*, *Composition of Tank Farm Supernate Samples (U)*, WSRC-RP-93-1009, July 1993.

APPENDIX A

CSTIEX5 input file

```
1, 298.15                                            Activity Coeff. Model, Temperature
Avg SRS salt waste                                   Title
7,9                                                  Number of Cations & Anions
1258                                                 Density(kg/m3)
3, 6, 1, 5, 4, 40, 13                                Names of Cations
13, 9, 27, 28, 19, 15, 2, 1, 20                      Names of Anions
5.6,1.4e-4,5.24e-15,0.0,0.015,0.0,0.0                Concentrations of Cations
1.91414,2.164,0.52,0.31,0.16,0.15,0.025,0.032,0.010  Concentrations of Anions
0.100, 0.050                                         Liquid(L), Solid(g)
0                                                    Initial solid Form
0.05                                                 Calculation Adjustment
```

CSTIEX5 output file

```
Solution:  Avg SRS salt waste                                  Title
  ***********************INPUT***********************

   Density=  .1258E+04 kg/m3

                   Molecular Wt.    Valance    Molarity(mol/L)
  Na+.....           22.9898           1.        .5600E+01
  Cs+.....          132.9054           1.        .1400E-03
  H+......            1.0079           1.        .5240E-14
  Rb+.....           85.4678           1.        .0000E+00
  K+......           39.0983           1.        .1500E-01
  SrOH+...          105.0000           1.        .0000E+00
  Sr++....           87.6200           2.        .0000E+00
  OH-.....           17.0073          -1.        .1914E+01
  NO3-....           62.0049          -1.        .2164E+01
  NO2-....           46.0000          -1.        .5200E+00
  Al(OH)4-           95.0000          -1.        .3100E+00
  CO3--...           60.0092          -2.        .1600E+00
  SO4--...           96.0636          -2.        .1500E+00
  Cl-.....           35.4527          -1.        .2500E-01
  F-......           18.9984          -1.        .3200E-01
  PO4---..           94.9712          -3.        .1000E-01

 Material: Na Form


  **********************OUTPUT***********************

 Ionic Strength=          .698E+01 mol/kg
 Equilibrium pH=          14.6

          Q (mmol/gCST)    C (mmol/L)     Kd (ml/gCST)
  Cs        .134E+00        .730E-01        .184E+04
  Rb        .000E+00        .000E+00        .000E+00
  SrOH      .000E+00        .000E+00        .000E+00
  K         .878E-01        .150E+02        .587E+01
```

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