WPO 30930

Sandia National Laboratories
MANAGED BY MARTIN MARIETTA CORPORATION
FOR THE U. S. DEPARTMENT OF ENERGY

P. O. BOX 5800
ALBUQUERQUE, NEW MEXICO 87185-1320

date: 19 January 1996

to: E. James Nowak, Org. 6831, MS 1320

Craig F Novak

from: Craig F. Novak, Dept. 6748, MS 1320, 848-0619

subject: Preliminary Inorganic Model for Thorium Solubility in WIPP Brines, in database file HMW_3TH5_960119.CHEMDAT

A preliminary model for Th(IV) interactions with carbonate in $NaHCO_3$, Na_2CO_3, and $NaClO_4/CO_2(g)$ media has been developed by Andy Felmy and Dhan Rai of PNL and transmitted to SNL. This memorandum contains the parameters of this model along with the parameters for the Th^{4+}-Na^+-Mg^{2+}-Cl^- system developed earlier. All parameters not explicitly listed here are the same as in Harvie et al. (1984). The parameters for the Th^{4+}-HSO_4^--SO_4^{2-} system are given in Felmy and Rai (1992), and not reproduced here, although they are included in the FMT database named below.

The parameters given here are preliminary for several reasons. The value of $\theta_{Na^+,Th^{4+}}$ given below was not used in fitting the Th-$NaHCO_3$, Th-Na_2CO_3, and Th-$NaClO_4$-$CO_2(g)$ systems. Thus, the Th-Na^+-Mg^{2+}-Cl^- and the Th-$NaHCO_3$/Th-Na_2CO_3/Th-$NaClO_4$-$CO_2(g)$ systems are not quite consistent in their parameter values. Also, the values for Th^{4+}-ClO_4^- ion interaction parameters were estimated to be the same as those for Th^{4+}-Cl^- interactions because the values listed below were unavailable. These differences in model assumptions and fitting need to be checked before the model will become final.

The CHEMDAT data base file is available on the WIPP Dec Alphas as U1:[CFNOVAK.FD.CHEMDAT]HMW_3TH5_960119.CHEMDAT, although official QA'd versions should be obtained through the Configuration Management System.

Dimensionless Standard Chemical Potentials

Species	μ°/RT	Source
Th^{4+}	–284.227	Felmy et al., 1991
CO_3^{2-}	–212.944	Harvie et al., 1984
H^+	0.0	Harvie et al., 1984
OH^-	–63.435	Harvie et al., 1984
$H_2O(l)$	–95.6635	Harvie et al., 1984
$Th(OH)_3CO_3^-$	–775.627	new work by PNL
$Th(CO_3)_5^{6-}$	–1411.364	new work by PNL
$Th(OH)_4(aq)$	–622.840	new work by PNL

Ion Interaction Parameters

i	j	$\beta_{ij}^{(0)}$	$\beta_{ij}^{(1)}$	$\beta_{ij}^{(2)}$	C_{ij}^{ϕ}	Source
H^+	$Th(OH)_3CO_3^-$	0.0	0.0	0.0	0.0	new work, PNL
H^+	$Th(CO_3)_5^{6-}$	0.0	0.0	0.0	0.0	new work, PNL
H^+	ClO_4^-	0.1747	0.2931	0.0	0.00819	Pitzer, 1992
Na^+	$Th(OH)_3CO_3^-$	0.0	0.0	0.0	0.0	new work, PNL
Na^+	$Th(CO_3)_5^{6-}$	2.0	1.31	0.0	0.0	new work, PNL
Na^+	ClO_4^-	0.0554	0.2755	0.0	–0.00118	Pitzer, 1992
Th^{4+}	$Th(OH)_3CO_3^-$	0.0	0.0	0.0	0.0	new work, PNL
Th^{4+}	$Th(CO_3)_5^{6-}$	0.0	0.0	0.0	0.0	new work, PNL
Th^{4+}	Cl^-/ClO_4^-	1.092	13.7	–160.0	-0.112	Roy et al., 1992
Th^{4+}	ClO_4^-	1.19	27.3	0.0	–-0.0566	new work, SNL/FSU

i	j	θ_{ij}	Source
ClO_4^-	$Th(OH)_3CO_3^-$	0.0	new work, PNL
ClO_4^-	$Th(CO_3)_5^{6-}$	5.54	new work, PNL
Na^+	Th^{4+}	0.421	new work, PNL
Mg^{2+}	Th^{4+}	0.600	new work, PNL

i	j	k	Ψ_{ijk}	Source
Na^+	Th^{4+}	Cl^-	0.208	new work, PNL
Mg^{2+}	Th^{4+}	Cl^-	0.214	new work, PNL

References

Felmy, A.R., and D. Rai. 1992. "An Aqueous Thermodynamic Model for a High Valence 4:2 Electrolyte Th^{4+}-SO_4^{2-} in the System Na^+-K^+-Li^+-NH_4^+-SO_4^{2-}-HSO_4^--H_2O to High Concentration." *Journal of Solution Chemistry* vol. 21 #5: 407-423.

Felmy, A.R., D. Rai, and M.J. Mason. 1991. "The Solubility of Hydrous Thorium(IV) Oxide in Chloride Media: Development of an Aqueous Ion-Interaction Model." *Radiochimica Acta* vol. 55: 177-185.

Harvie, C.E., N. Møller, and J.H. Weare. 1984. "The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O System to High Ionic Strength at 25°C." *Geochimica et Cosmochimica Acta* vol. 48: 723-751.

Pitzer, K.S. 1991. *Activity Coefficients in Electrolyte Solutions*. Boca Raton, Florida: CRC Press.

Roy, R.N., K.M. Vogel, C.E. Good, W.B. Davis, L.N. Roy, D.A. Johnson, A.R. Felmy, and K.S. Pitzer. 1992. "Activity Coefficients in Electrolyte Mixtures: HCl + $ThCl_4$ + H_2O for 5°–55°C." *Journal of Physical Chemistry* vol. 96: 11065-11072.

Copies to:

6831	R.V. Bynum, MS 1320	6748	J.T. Holmes, MS 1341
6747	R.F. Weiner, MS 1341	6748	R.C. Moore, MS 1341
6748	S.C. Babb, MS 1341	6748	C.F. Novak, MS 1320
6748	C.C. Crafts, MS 1341	6748	M.D. Siegel, MS 1320

SWCF WBS 1.1.10.1: ~~RNC~~ (2 copies)

TD 2/12/96

Information Only