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Title:	Comparison of the calculated thorium solubility (concentration) using the constants from the FMT_050405 Database with the experimental data published in Altmaier, M., Neck, V., Müller, R. and Fanghänel, T. Radiochimica Acta, 93(2), 83-92 (2005).
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COMPARISON OF THE CALCULATED THORIUM SOLUBILITY (CONCENTRATION) USING THE CONSTANTS FROM THE FMT_050405 Database WITH THE EXPERIMENTAL DATA PUBLISHED IN Altmaier, M., Neck, V., Müller, R. and Fanghänel, T. *Radiochimica Acta*, 93(2), 83-92 (2005).

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To: Don Reed
From: Michael Richmann

Subject: Comparison of the calculated thorium solubility (concentration) using the constants
         from the FMT_050405 Database with the experimental data published in Altmaier, M.,
         Neck, V., Müller, R. and Fanghänel, T. *Radiochimica Acta*, 93(2), 83-92 (2005).

To this letter are attached the details of a calculational exercise using the Geochemist's
Workbench geochemical modeling program (see Attachment A) where the FMT speciation
scheme for thorium is compared with the speciation scheme used by Altmaier *et al*[1]. This was
done as a partial response to the overall issues regarding thorium speciation in the WIPP that
were raised in the recent EPA visit (February 24 2010) and documented in EPA comments 1-23-
3 and 4-C-35.

In these calculations, the FMT thorium speciation scheme was used to calculate the thorium
solubility under the conditions of the thorium solubility studies in the Altmaier *et al*. paper. This
was done in lieu of using their experimental data/speciation scheme to calculate WIPP-relevant
thorium concentrations since the needed Pitzer data for some species proposed by Altmaier *et al*.
are not available. The calculations, within the limitations of this exercise, provide a direct but
qualitative comparison of the predictions of the two speciation schemes for a common
experimental system.

The most important result of this exercise is our conclusion that the FMT speciation scheme is
conservatively high in its prediction of the solubility of thorium when compared directly to the
Altmaier *et al*. data set.

ATTACHMENT A

To: Don Reed
From: Michael Richmann

Subject: Comparison of the calculated thorium solubility (concentration) using the constants
         from the FMT_050405 Database with the experimental data published in Altmaier *et al.*[1]

In Altmaier *et al.*[1], the thorium speciation was described using the following general reaction:

$$Th(OH)_4(am) + zCO_3^{2-} \leftrightarrow Th_x(OH)_y(CO_3)_z^{4-y-2z} + (4-y)OH^- \qquad (1)$$
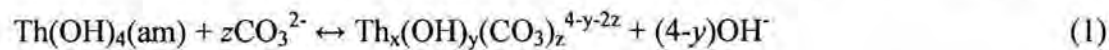
For reaction (1) the stability constants for species having significant impact on thorium
speciation as determined in [1] over certain ranges of carbonate concentration and designated as
(x,y,z) are as follows:

For (1,4,0) $\log \beta^0 = 39.0 \pm 0.5$
For (1,3,1) $\log \beta^0 = 38.5 \pm 0.6$
For (1,2,2) $\log \beta^0 = 37.0 \pm 0.4$
For (1,1,4) $\log \beta^0 = 35.8 \pm 0.3$
For (1,0,5) $\log \beta^0 = 31.4 \pm 0.5$

As it turns out, the stability constants for these species could not be directly compared with the
stability constants for the corresponding species present in FMT database because the standard
chemical potential for the key species, $Th(OH)_4$,(am), is not a part of the FMT database.

Therefore, for comparison of the experimentally determined solubility of thorium reported in [1],
the Geochemist's Workbench thermodynamic code (V6.0.5) was used for calculating thorium
concentrations using the stability constants from FMT database. In the FMT_050405 database,
the standard chemical potentials for $Th(OH)_4(aq)$, $Th(OH)_3(CO_3)^-$ and $Th(CO_3)_5^{6-}$ are given.
With these standard potentials, it is possible to calculate stability constants for the general
reaction 2:

$$xTh^{4+} + yOH^- + zHCO_3^- \leftrightarrow Th_x(OH)_y(CO_3)_z^{4-y-2z} + (y+z)H^+ \qquad (2)$$
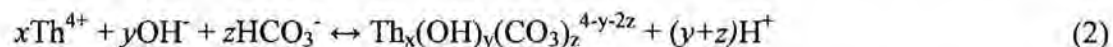
These stability constants for the species designated as (x,y,z) are as follows:

For (1,4,0) $\log K^0 = -17.5002$
For (1,3,1) $\log K^0 = -14.0457$
For (1,0,5) $\log K^0 = -24.5828$

Since there is no sulfate in the Altmaier work and therefore none in this test case, the solid-state
species equilibrated against in the FMT set is amorphous ThO_2.

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With these log K^o values and the standard chemical potentials for other needed species, e.g. OH⁻, HCO$_3$⁻, etc., supplied in the FMT database, it was possible to modify the supplied Geochemist's Workbench thermodynamic database to perform low ionic-strength calculations. Subsequently, thorium concentrations were modeled for a variety of species for I = 0.5 M and total carbonate concentration = 0.015 M, i.e. for the experimental conditions in which data were generated and presented in Figure 2 of reference [1]. The concentrations of relevant thorium species were calculated for four pC_{H+} values, where pC_{H+} is defined as $-\log[H^+]$, and are listed in Table 1.

Table 1

pC_{H+}	$[Th(OH)_3(CO_3)^-]$	$[Th(OH)_4(aq)]$	$[Th(CO_3)_5^{6-}]$	$[Th]_{total}$
9	3.44e-6	9.39e-8	2.42e-9	3.53e-6
9.5	2.68e-6	9.39e-8	2.24e-9	2.77e-6
10	1.58e-6	9.39e-8	5.10e-10	1.67e-6
10.5	6.81e-7	9.38e-8	2.51e-11	7.75e-7

The comparison of the experimental data from [1] with the ones calculated in this work is presented in Figure 1. The concentration of the most prevalent Th species, the (1,3,1) complex, in the pC_{H+} range from 9 to 10.5 calculated using the above FMT derived log K^o values is, at a minimum, a factor of 3 higher than the total thorium concentration determined by Altmaier et al[1] at pC_{H+} = 9 and becomes even more conservative as the pC_{H+} increases to 10.5. As is also evident, the FMT calculation also reproduces the general behavior of the total thorium concentration in this pC_{H+} region as well. The thorium pentacarbonato (1,0,5) complex does not play a significant role in this range of pC_{H+}.

These calculations suggest that the (1,4,0) and (1,3,1) species used in the FMT calculations are sufficient to model thorium solubility in total carbonate concentrations of 0.015 M and lower, and that the constants used in the FMT database provide conservative estimates of the thorium concentrations.
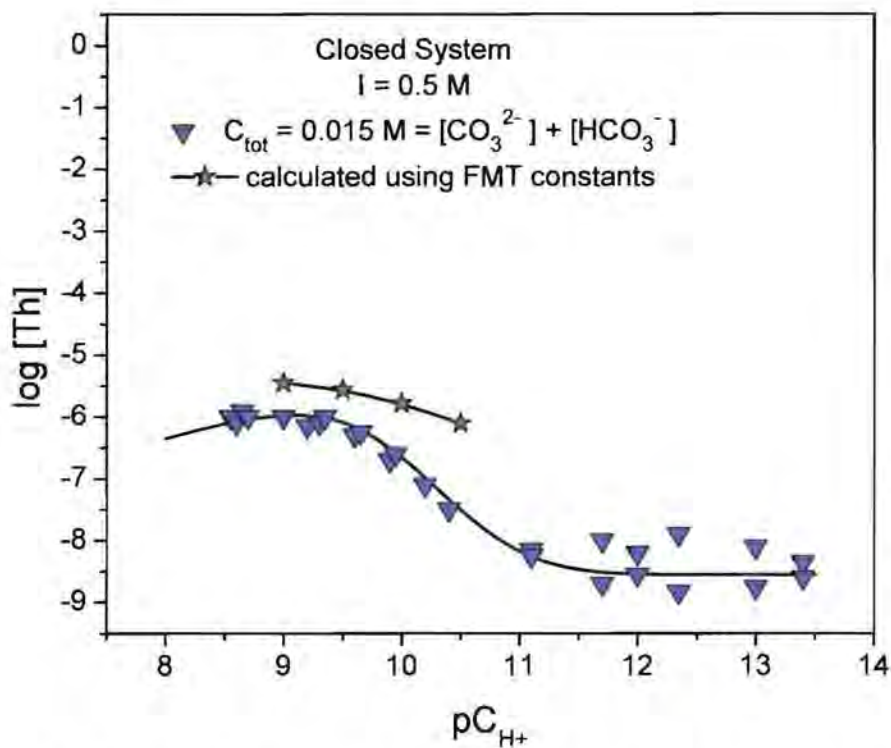
Figure 1. Log[Th]$_{total}$ as a function of pC$_{H+}$ from the Altmaier work. The total thorium concentration determined from the FMT set is plotted for comparison from pC$_{H+}$ = 9 to 10.5.

References
[1] Altmaier, M., Neck, V., Müller, R. and Fanghänel, T., Radiochimica Acta, 93(2), 83-92 (2005).