I received today the 44 pages document of comments on the Np/Pu draft by Neck and Fanghänel. I first looked for new piece of information that would require quick action to further update the Np/Pu draft; it appears these comments are not really part of a needed dialogues on specific scientific questions and numbers pointed out in the course of the ongoing discussion; but rather more details on their opinion concerning their own work and a few others. It seems to me, this type of comments on the Np(V) sections have already induced proposal to modify the draft, other comments are clearly for TDB II project. I will continue examining possible new changes in the draft, or performing new calculations and checking if I am asked to, as usually done within our TDB group at this very stage of its duty; but I will not repeat here previous discussion. To this point I am not much interested in the opinion of the authors; but to their arguments: there are not really new ideas, but rather new examples in which they wrote a few errors concerning the description of experimental methodologies used in them.

Typical:
The only point (again not new in this discussion) where I though they should be right, is the activity coefficient of the highly negatively charged Np(V) limiting complex in sodium chloride and perchlorate media. Figures they published and Fig.2.7 in their last comments show differences between both media, they interpret this as specific anion-anion interactions to taken into account in activity coefficient. Actually non of these figures is enough to discuss this point; hence I rather used similar figure for the corresponding K_{s3} values measured in their laboratory... there is no evidence of any difference between both media: I did not really expect this, I was actually expecting to add something about it in the selection of the corresponding interaction coefficient..

This is a typical:
- the problem is not important (just an activity coefficient for a species to be used in media that do not really correspond to conditions for waste disposal),
- it is an interpretation of a global curve fitting exercise, where they did not realised an (other) specific treatment of the data should show direct qualitative evidence of their interpretation. Beside this, if I did not make any error in my figure, it seems the interpretation is finally incorrect: just check it by yourself (see figure below).

An advice to Neck
By working with TDB specialist groups, I (very progressively) learnt to handle problems I found in other's work. I did not write above "a first year student will, at first glance, see your demonstration is, completely stupid beside several errors you made on other problems";
but only: I am just suggesting you to plot a modified SIT figure for K_{s3}, I already plotted it myself; but I prefer you do the same work on your side to check my calculations.
This avoid being ridiculous, otherwise the one who did not think of the special way to perform the calculation, or the one who made an error in the calculation will, and it would be impossible to run a true working team this way.

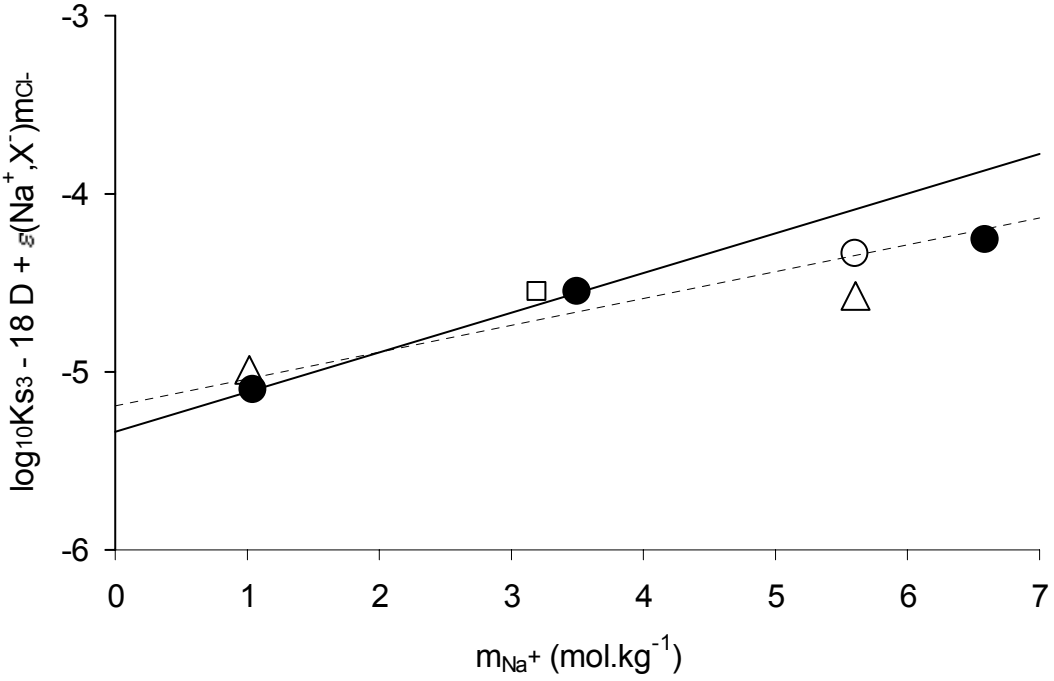
Figure:
For those who are not really familiar with SIT using, the figure to plot is (after corrections to molal units when needed)
$(\log_{10}K_{s3} - 18\ D)$ v.s m_{Na^+}
its theoretical is $\log_{10}K_{s3}^\circ - \Delta\varepsilon\ m$,
where $\Delta\varepsilon\ m = (\varepsilon(NpO_2(CO_3)_3^{5-},Na^+) - 2\ \varepsilon(CO_3^{2-},Na^+))\ m_{Na^+} + \varepsilon(X^-,Na^+))\ m_{X^-} + 3.5\ \log_{10}a(H_2O)$
where X^- is chloride or perchlorate anion,
as a first approximation the major contribution to the slope, $-\Delta\varepsilon$, is $\varepsilon(NpO_2(CO_3)_3^{5-},Na^+)$ and this can show whether it has or not different values in chloride and perchlorate media.

Instead of this approximation you can plot a figure similar to the above (classical SIT) one:
$(\log_{10}K_{s3} - 18\ D + \varepsilon(X^-,Na^+)\ m_{Cl^-} + 3.5\log_{10}a(H_2O))$ v.s m_{Na^+}

Figures added later to this file. They evidence no difference between Cl^- and ClO_4^- media for equilibrium constants written with negatively charged aqueous complexes (typically $NpO_2(CO_3)_3^{5}$), as determined by the authors, while they used different empirical coefficients for anions in these two media.

Ks_3 for

$NaNpO_2CO_3(s,hyd) + 2\ CO_3^{2-} \rightarrow Na^+ + NpO_2(CO_3)_3^{5-}$



● NaClO4 [91KIM/KLE, 94NEC/RUN, 95NEC/FAN]

○ NaCl [94NEC/KIM]

△ NaCl [94RUN/KIM]?

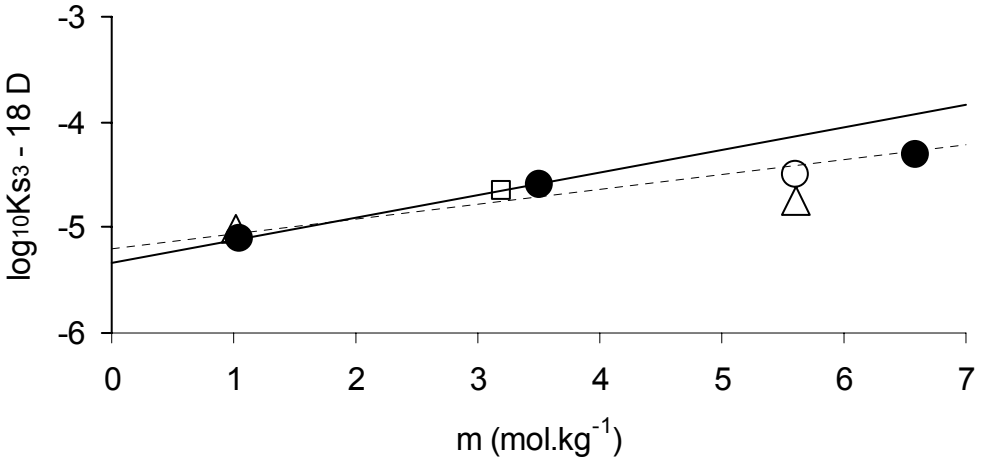
------ 1 to 5 M NaClO4

——— 1 and 3 M NaClO4

□ [96RUN/NEU]

Ks_3 for

$NaNpO_2CO_3(s,hyd) + 2\ CO_3^{2-} \rightarrow Na^+ + NpO_2(CO_3)_3^{5-}$



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