

560114

Roselle, Gregory Thomas

Good

From: Sassani, David
Sent: Thursday, May 30, 2013 9:33 AM
To: Roselle, Gregory Thomas
Subject: FW: [EXTERNAL] AW: our discussion on intrinsic Th colloids and Mg-Cl-OH colloids
Attachments: 120329_Discussion Summary_DS_MA.docx

Hi Greg – This email is Marcus Altmaier’s response email and attached Word file. Because he edited the discussion that I included in the email (in addition to his attached Word edited version), I will also forward to you my original request to him that contains the discussion as I drafted it.

Let me know if you get these and need any additional information on it.

Cheers,

David

David Sassani, Ph.D.
Nuclear Waste Disposal Research & Analysis
Organization 06222
Bldg. 823; Off. 3025
Sandia National Laboratories
P.O. Box 5800 MailStop 0747
Albuquerque, NM 87185
dsassan@sandia.gov
Phone: 505-284-8967
Blackberry: 505-917-3765
Fax: 505-844-2348

From: Altmaier, Marcus (INE) [mailto:marcus.altmaier@kit.edu]
Sent: Thursday, March 29, 2012 7:48 AM
To: Sassani, David
Cc: Altmaier, Marcus (INE); Kienzler, Bernhard (INE); Metz, Volker (INE); Gaona Martinez, Javier (INE)
Subject: [EXTERNAL] AW: our discussion on intrinsic Th colloids and Mg-Cl-OH colloids

Dear David,

it took me some time to answer to your email, because I am very busy these days. So this had to wait some days. Sorry for this delay...

Responding to your email, I was carefully re-reading our paper from 2003 (Altmaier, M., Neck, V., Fanghänel, Th. (2004) Solubility and colloid formation of Th(IV) in concentrated NaCl and MgCl₂ solution, Radiochimica Acta, 92, 537-543). And I have to say that I really would “write it again like that” as I have already said during our discussion at INE. Of course I am aware that we may want to ask for more detailed understanding in the future and further develop and validate the models, but for me the presented experimental data and line of argumentation still stands.

I would further like to take this opportunity to remark on this topic that

- Th(IV)coll was investigated both from undersaturation and oversaturation direction in our publication.
- There was strong evidence that Th(IV) or Th(IV)coll is sorbing strongly on Mg-oxychloride phases and maybe get incorporated in the oxychloride phases during a “rapid precipitation” step.

WIPP:1.4.2.2:PHD 560114
Information Only

- We had argued in the paper that Th(IV) is strongly sorbing on the Mg-oxychloride phases and therefore the amount of potentially mobile Th sorbed on these phases should be related to and depend on the available total Mg-oxychloride inventory. And this will be much larger than the suspended Mg-oxy-colloids. We did not say that Mg-oxychloride or Mg-oxychloride colloids can be expected to be instable or irrelevant.
- New and ongoing studies at KIT-INE are focusing on Radionuclide sorption and incorporation on brucite or Mg-oxychlorides. So this hopefully adds more information in the rather near future.
- Regarding all effects possibly related to the “rapid precipitation” step used in some sample preparations from oversaturation, this is surely a scenario that is not to be expected in nature.
- The removal of Mg-oxychlorides from a 4,5 M MgCl₂ obviously fails. Most probably this is due to too small differences in sample density as described in the paper. Therefore, the very high concentrations for [Th] after ultrazentrifugation in 4.5 M MgCl₂ – some at 10-4,5M – do not reflect correct solubility data for Th(IV) after phase separation. These measurements can be regarded as experimental artefacts in respect to repository safety.

I have added a few remarks to clarify my opinion into your text highlighted in yellow below in dark red.

I want to thank you for sending me your email and giving me the opportunity to comment on it. And of course I will be willing and interested to continue our discussions on solubility phenomena and intrinsic colloids in the future, either by email or in Europe or the US.

I add a WORD version of the text as a separate attachment, in case the formatting below fails and copy this mail to some colleagues at INE who are also interested in this topic.

All the best regards,
Marcus Altmaier

*Karlsruher Institut für Technologie (KIT)
Institut für Nukleare Entsorgung (INE)*

Dr. Marcus Altmaier

Aquatic Chemistry and Thermodynamics

*Hermann-von-Helmholtz-Platz 1
76344 Eggenstein-Leopoldshafen
Phone: +49 721 608-22592
Fax: +49 721 608-24308*

E-Mail: marcus.altmaier@kit.edu

<http://www.kit.edu>

KIT -Universität des Landes Baden-Württemberg und
nationales Forschungszentrum in der Helmholtz-Gemeinschaft

Von: Sassani, David [mailto:dsassan@sandia.gov]
Gesendet: Donnerstag, 22. März 2012 19:23
An: Altmaier, Marcus (INE)
Betreff: our discussion on intrinsic Th colloids and Mg-Cl-OH colloids

Dear Marcus,

Information Only

Thank you for the wonderful tour of your experimental facilities within KIT-INE, I very much enjoyed the discussions we had also.

I am in the process of finalizing my trip report and wanted to send you the portion that covers the discussion we had on the Th colloid work – both the intrinsic colloids and the Mg-Cl-OH colloids (see below). Would you please review this and let me know if this accurately reflects the discussion or if you see anything that should be corrected in it?

I appreciate your time to look at this and look forward to seeing you again, either here in the US or perhaps once more in Europe!

Thank you very much,

David

Discussion Summary:

First, I asked about MA his opinion of how the work performed at KIT-INE on the intrinsic Th colloids and the experimental work done at LANL on intrinsic Th colloids (presented in the November 2011 ABC-Salt meeting at KIT-INE) could be interpreted consistently, or if they did not mesh in his mind, if he had any rationale regarding the inconsistencies. MA indicated that for his work, he felt that the band of concentrations at high pH ($\log[\text{Th}]$ concentration (M) about -6.3 ± 0.5) that delineated the Th intrinsic colloids was sufficiently defined that he did not have any reason to doubt that this was a real phenomenon that should be expected (the values are very reproducible). MA said that when he applied ultracentrifugation or 10kD (2-3 nm) ultrafiltration followed by (ultra)centrifugation, the concentration of Th that is left is comparable to the solubility of $\text{Th}(\text{OH})_4$ at the expected $\sim 10^{-8.5}$ M concentration level, which argues strongly that the additional Th was colloidal in the solutions. He agreed with the facts that LANL had slightly lower overall values of total Th compared to the $10^{-6.3}$ concentration level found in his experiments for $\text{Th}(\text{IV})$ coll and did not see intrinsic colloids (i.e., no difference in Th concentrations in solution after filtering at this concentration level. He finds this result puzzling and he was not certain of why that might be. He did volunteer a possible difference that may contribute is that his experiments were done in simple solutions Na-Mg-Cl and that the LANL work in synthetic WIPP brines (solutions with other cations and anions present) may create a difference in the colloid stability from the $\text{Th}(\text{OH})_4$ polymerization or even in total Th solubility.

Second, we also discussed the mineral fragment colloid aspects of the KIT-INE tests in 4.5 M MgCl_2 which are responsible for about a further two order of magnitude increase in total Th up to $\sim 10^{-4.5}$ M. He confirmed that the formation of the Mg-Cl-OH mineral fragment colloids in this study is an artifact of the experiment, stated that they formed when he mixed two disequilibrium solutions (concentrated MgCl_2 brine containing dissolved Th-nitrate and NaOH solution $\text{Mg}(\text{OH})_2$ and NaCl brine) because of the drastic pH shift. This “rapid precipitation” process, and that they would not be expected to form within an actual system. MA also stated that he thought they had stated this in their paper, and I agreed with this position and indicated that by my reading they had said this clearly. The paper states “The high solubility observed in 4.5M MgCl_2 due to the formation of pseudocolloids $\text{Th}(\text{IV})\text{-Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$ (coll) has not to be expected in real systems...” “The high solubility observed in 4.5M MgCl_2 due to the formation of pseudocolloids $\text{Th}(\text{IV})\text{-Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$ (coll) has not to be expected in real systems where, contrary to the present laboratory experiments, the ratio of solution volume and solid magnesium hydroxide/hydroxychloride is very small so that sorption of Th(IV) onto solid (immobile) magnesium hydroxychloride will prevail over sorption onto (mobile) colloids”. Given the fact that Th sorbed onto those colloids, separation via UCF was not possible because they were about the same density as the solution (i.e., no density difference), so they could not determine directly the dissolved concentrations of Th. He again commented spontaneously that he stated in his paper that these experimental artifacts leading to total Th concentrations above $\sim 10^{-6}$ M are not well defined solubility data or expected to form in a real system. I agreed with him, and I discussed the reaction path of the actual waste forms with him in a repository setting, and he restated that he did not feel that these measurements colloids were anything more than an artifact of the experimental approach.

David Sassani, Ph.D.
Applied Systems Analysis & Research
Organization 06224
Bldg. 823; Off. 3025
Sandia National Laboratories
P.O. Box 5800 MailStop 0736
Albuquerque, NM 87185
dsassan@sandia.gov
Phone: 505-284-8967
Cell/Blackberry: 505-917-3765
Fax: 505-844-0955
Fax: 505-844-2348

Information Only

Discussion Summary:

First, I asked about MA his opinion of how the work performed at KIT-INE on the intrinsic Th colloids and the experimental work done at LANL on intrinsic Th colloids (presented in the November 2011 ABC-Salt meeting at KIT-INE) could be interpreted consistently, or if they did not mesh in his mind, if he had any rationale regarding the inconsistencies. MA indicated that for his work, he felt that the band of concentrations at high pH ($\log[\text{Th}]$ concentration (M) about -6.3 ± 0.5) that delineated the Th intrinsic colloids was sufficiently defined that he did not have any reason to doubt that this was a real phenomenon that should be expected (the values are very reproducible). MA said that when he applied **ultracentrifugation or 10kD (2-3 nm) ultrafiltration** ~~followed by (ultra)centrifugation~~, the concentration of Th that is left is comparable to the solubility of $\text{Th}(\text{OH})_4$ **at the expected $\sim 10\text{-}8.5$ M concentration level**, which argues strongly that the additional Th was colloidal in the solutions. He agreed with the facts that LANL had slightly lower overall values of total Th **compared to the $10\text{-}6.3$ concentration level found in his experiments for $\text{Th}(\text{IV})\text{coll}$** and did not see intrinsic colloids (i.e., no difference in Th concentrations in solution after filtering **at this concentration level**). He finds this result puzzling and he was not certain of why that might be. He did volunteer a possible difference that may contribute is that his experiments were done in simple solutions Na-Mg-Cl and that the LANL work in synthetic WIPP brines (solutions with other cations **and anions present**) may create a difference in the colloid stability from the $\text{Th}(\text{OH})_4$ polymerization **or even in total Th solubility**.

Second, we also discussed the mineral fragment colloid aspects of the KIT-INE tests **in 4.5 M MgCl_2** which are responsible for about a **further** two order of magnitude increase in total Th **up to $\sim 10\text{-}4.5$ M**. He confirmed that the formation of the Mg-Cl-OH mineral fragment colloids **in this study** is an artifact of the experiment, stated that they formed when he mixed two disequilibrium solutions (concentrated **MgCl_2 brine containing dissolved Th-nitrate and NaOH solution $\text{Mg}(\text{OH})_2$ and NaCl brine**) because of the drastic pH shift. **This “rapid precipitation” process** ~~—and that they~~ would not be expected to form within an actual system. MA also stated that he thought they had stated this in their paper, and I agreed with this position and indicated that by my reading they had said this clearly. The paper states ~~“The high solubility observed in 4.5M MgCl_2 due to the formation of pseudocolloids $\text{Th}(\text{IV})\text{-Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$ (coll) has not to be expected in real systems.”~~ **“The high solubility observed in 4.5M MgCl_2 due to the formation of pseudocolloids $\text{Th}(\text{IV})\text{-Mg}_2(\text{OH})_3\text{Cl}\cdot 4\text{H}_2\text{O}$ (coll) has not to be expected in real systems where, contrary to the present laboratory experiments, the ratio of solution volume and solid magnesium hydroxide/hydroxychloride is very small so that sorption of Th(IV) onto solid (immobile) magnesium hydroxychloride will prevail over sorption onto (mobile) colloids”.**

Given the fact that Th sorbed onto those colloids, separation via UCF was not possible because they were about the same density as the solution (i.e., no density difference), so they could not determine directly the dissolved concentrations of Th. He again commented spontaneously that he stated in his paper that these **experimental artifacts leading to total Th concentrations above $\sim 10\text{-}6$ M** are not **well defined solubility data** or expected to form in a real system. I agreed with him, and I discussed the reaction path of the actual waste forms with him in a repository setting, and he restated that he did not feel that these **measurements** ~~colloids~~ were anything more than an artifact of the experimental approach.

Information Only