CENTER FOR NUCLEAR WASTE
REGULATORY ANALYSES

This notebook is to document activities by
William M. Murphy in support of the CNWRA.
Pages 1 to 3 contain index information.

WMM 1/1/01

4/4/2006

4/4/2006

Letter of instruction for initial tasks is attached to page 5 and 6.

Comments on "Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier" are attached to pages 7 to 10. The document reviewed was an "information copy" DOE AMR variously labelled Rev 02/2000, ANL-EBS-MD-00001 REV 00 and March 2000

Uel
9/11/00

CNWRA A center of excellence in earth sciences and engineering

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Dr. William M. Murphy
Department of Geosciences
California State University, Chico
400 W. First St.
Chico, CA 95929

August 28, 2000

Dear Bill,

The purpose of this letter is to record and clarify the agreements that we reached during our phone call today, Monday, August 28, 2000. We agreed that you would perform two types of tasks on behalf of the CNWRA are: review DOE AMRs in support of ENFE subissue 2 resolution, and continue collaboration on reactive transport simulations of ambient and thermally perturbed conditions at Yucca Mountain, NV. These tasks are described in more detail below.

1) **Reviews for ENFE subissue 2**:
Tasks: See attached Table listing the AMRs that you have agreed to review, the projected number of hours required for the completion of each AMR, and the due date for completion of the individual AMR reviews.

Initial Guidance: Review of individual AMRs should be focused toward issue resolution. The adequacy of DOE models and data should be determined based on a risk-informed review approach that is explicitly tied to the acceptance criteria (ACs) and review methods (RMs) described in the Yucca Mountain Review Plan (YMRP) Rev. 0. The DOE is expected to demonstrate the importance of a model or data to repository performance. Please provide written statements indicating which DOE models or data are inadequate, why these models or data are inadequate, and how these inadequacies might be repaired. Inadequacies that do not strongly affect repository performance should not be emphasized as heavily as inadequacies that are demonstrated by the DOE to have a greater impact on performance. Any additional guidance received from the NRC will be delivered to you immediately.

2) **Collaboration on Reactive Transport Simulations**:
Tasks: Track progress of reactive transport modeling efforts at the CNWRA, provide comments and suggestions regarding planned and implemented approaches, and help CNWRA staff evaluate and interpret their model results in preparation for conference presentations and the submission of a journal article.

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cwm 9/11/00

Dr. William Murphy
August 28, 2000
Page 2

 Projected Hours for Completion of Task: 0-4 hours/week until project is completed. The projected completion time for this work is March 1, 2000.

Thanks in advance for your continued participation in CNWRA work.

Sincerely,

Lauren Browning
Research Scientist
Geohydrology & Geochemistry

cc: English Pearcy
    Roberto Pabalan

Description	I.D.	Subissue	In Ops Plan?	Availability	Reviewer(s)	Due Date	Time Required
AMR Natural Analogues	U0135	S2	no		Murphy(Browning)	1/15/00	2
AMR (Sepg/Bkfill Intractn)	E0030	S2	no		Murphy(Browning)	1/15/00	8
AMR (Precipitates Salts Analysis)	E0105	S2	no	draft	Murphy(Browning)	1/15/00	20
AMR FEPs for NFE	N0080	S1,S2,S3,S4	Yes		Murphy(Browning)	1/15/00	15
AMR Environ on DS/WP Out Ba Surf	W0070	S2	Yes	draft	Murphy(Browning)	1/15/00	20
AMR Mineralogical Model	I0045	S2	no		Murphy(Browning)	1/15/00	8
Geochemistry Data	U0085	S2	no		Murphy(Browning)	1/15/00	8

Comments on "Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier" AMR version March 2000

William M. Murphy
September 2000

General comments

The range of spatial, temporal, and conceptual conditions considered is limited. (See specific comments 1, 4, 5, 6, 7, 8, 19, 20, 22.)

Aqueous speciation and reaction path (or reactive transport) modeling would beneficially augment the analyses provided in this report and help address NRC acceptance criteria for consideration of alternate models. (See specific comments 9, 11, 15, 21.)

Deliquescence plus surface tension (capillarity) plus sorption (bonding) of water collectively lead to condensation. The AMR tends to treat these phenomena separately. What is their combined effect? (See comment 13.)

The set of criteria in Table 20 seems completely inadequate to establish environmental conditions. (See comment 18.)

Specific comments

1. Many items are deferred to later revisions of the AMR: scale mineralogy (p.12), larger sampling of Yucca Mountain waters (p. 13, 15), microbial effects (p. 15), reactivity of candidate drip shield and waste package materials (p. 17), consequences of solution type for corrosion (p. 20). Is it realistic to expect these issues to be addressed?

2. The assumption is made that limited solubility phases precipitate quickly (p. 12, 44). This assumption is not necessarily valid. Many low solubility phases (e.g., silicates and aluminosilicates) have low nucleation and precipitation rates, and geochemical solutions are commonly supersaturated with respect to these phases.

3. CO_2, SO_2, HCl, O_2 are considered as potential gas phase components. NO_2 could be formed by radiolysis, and could also affect solution chemistry.

4. Generally effects of reaction of EBS materials are not considered in the analysis based on slow reaction rates of metals. (Potential acidification of solutions by metal hydrolysis is noted; p. 46.) However, following breach of the waste containers, alteration of the waste forms may be rapid causing big effects on the waste package environment. The AMR does not address environmental conditions following breach of the waste package (i.e., temporal effects).

5. Effects of backfill on solutions that could interact with the WP are limited to experimental studies using crushed tuff, and qualitative theoretical arguments concerning the buffering capacity of $CaCO_3$ (marble backfill).

6. Primary dilute water compositions: "The primary limitation of the results presented in this AMR relates to the issue of the composition of the 'dilute' water that contacts the EBS components. ... the two types of water considered characteristic of Yucca Mountain were considered" (p. 13). The AMR classifies Yucca Mountain waters in two categories: saturated zone/perched and pore waters from upper strata (p. 43, 46, 62). This is a reasonable first order classification. However, Browning et al. (2000) in a figure of bicarbonate fraction of anions vs. Ca fraction of cations shows another water chemistry classification scheme, which should be considered. Do Browning et al. concur (do their data support the contention) that Calico Hills pore water is a mixture of the perched and pore type waters as stated on p. 62?

7. In response to the NRC acceptance criterion concerning temporal and spatial variations: "The AMR considered the range of water chemistries sampled at Yucca Mountain ... This can be construed as considering the spatial variation across the repository. Temporal variations are manifested as variation in T and RH." However, "No attempt has been made to understand how this [spatial[chemistry variation in terms of specific composition or ionic strengths of the solutions would affect the solutions that develop on the EBS components" (p. 74). In general, the NRC acceptance criterion concerning uncertainty due to temporal and spatial variations was not addressed, except to note that it "should be considered" (p. 16).

8. Numerous NRC acceptance criteria were noted to be unaddressed or beyond the scope of the AMR. The AMR is written to address specific topics, not specifically sets of NRC acceptance criteria. Abstracted models and performance assessments analyses are explicitly beyond the scope of the AMR. Modes of corrosion and irregular wet and dry cycles (EBS acceptance criteria topics) are not addressed.

9. Alternate modeling approaches were not really considered or evaluated as specified by NRC acceptance criteria. Reaction path modeling would be an appropriate alternate modeling approach to the problems addressed in the AMR.

10. Vadose gas at Yucca Mountain is enriched in CO_2 relative to the atmosphere and devoid of CH_4. However, the AMR regards atmospheric CO_2 and CH_4 contents as its baseline (p. 23, 40, 44). This cornerstone of conceptual modeling is basically wrong.

11. Solubilities reported in Table 9 seem to be correct but are applied inappropriately to interpretations of multicomponent solutions for which solubility products, rather than dissolved mass concentration is the appropriate measure of solubility. For example, judging K_2SO_4 solubility by its total mg/L dissolved in pure water (p. 67) is not a valid approach to multicomponent solutions. K is squared in the solubility product, which should be calculated to determine solubility. EQ3 type calculations would be appropriate.

12. Relative humidity is defined as the water partial pressure divided by the partial pressure of water vapor in liquid water saturated gas at the same temperature. This is a proper definition. Because of Randy Manteufel, some CNWRA documents use a different definition (maximum vapor pressure of water at the given T and p, not the saturated water vapor pressure at the same T), which I think is less useful (and adds confusion) for Yucca Mountain applications. This distinction is probably unclear to many people.

13. Figures 1 and 2 show water sorption on nickel. The label on the left axis is undefined. The label on the right axis is probably mass per surface area (not mass grain as written). I am skeptical about the general applicability of these data because of the potentially strong dependence of water sorption on surface characteristics, e.g., roughness and degree of oxidation/passivation. The crossing of the curves or data trends in figures 1 and 2 for different temperatures implies considerable uncertainty/inaccuracy in the data and data regression curves. It is also odd that sorption increases with increasing T for a given RH. This result is counter-intuitive. I am dubious of these data and their applications. The discussion of condensation on p. 55 is based on surface tension of water. There are additional forces related to water bonding to surfaces that augment capillary forces, which should be taken into consideration. These sorption like forces seem to be neglected in eq. 19.

14. The Henry's law constant is defined on page 51. It would be nice to present the definition where the constant is introduced on page 37. I assume the definitions are the same as units would suggest. The temperature range of the usefulness of the Henry's law constant regression (eq. 6) would be informative.

15. It would be useful to know the controls on the CO_2 pressure in the evaporation experiments summarized in section 4.1.20. If the pressure was atmospheric (as I suspect) then what are the implications for applicability to conditions at Yucca Mountain? The Si content of J-13 is given a s 28.5 mg/L in Table 14. The initial 100x J-13 water composition in Table 18 has Si content of 13 mg/L, which seems contradictory. Control on the initial water in these experiments is unclear and the rationale for them is unclear. Was the initial water a consequence of reaction with tuff? Is there really 0 fluoride in two evaporated solutions and 0 Ca in two others as indicated in Table 18? Measurements of pH after dilution (with what) by 10 to 1000 times are of questionable meaningfulness. Evaporation experiments described in section 6.7 were apparently conducted in the presence of crushed tuff. Reaction with tuff are likely the cause (at least in part) of apparent mass balance discrepancies, e.g. silica gains greater than gains in conservative anions. All the evaporation experiments should be tested for reasonableness with EQ3 type calculations. Critical review of the source of these data would be valuable.

16. Attention to salt dust is a good idea.

17. Future work is listed in section 4.1.23. Among kinds of future work that would be valuable are effects of rate of evaporation on mineral precipitation and solution composition.

18. System environment criteria in Table 20 include only microbes, pH, and colloids. This AMR concludes that the pH range listed is insufficient (p. 76). How about chloride, oxygen, fluoride, carbonate, nitrate, silica, …?

19. The assumption on page 43 that waters "can be bounded by the types of concentrated solutions (brines) that would evolve because of evaporative concentration of waters sample at Yucca Mountain" ignores the potentially important effects of backfill, air circulation, dust deposition, and reactions with waste package (including waste form) materials.

20. In general the AMR focuses on worst case conditions of extreme evaporation and deliquescence due to salts. Such conditions may occur and should be examined. However, study of the environment should also consider that such solutions and salts can be easily washed away and may exist for only a short time if at all. The predominant environments may be much closer to ambient conditions, or ambient conditions slightly modified by heating and backfill. The AMR should examine how long extreme conditions may persist, i.e., temporal variations in the context of NRC acceptance criteria.

21. Consideration of deliquescence point of $NaNO_3$ as a limiting value for liquid water is probably fairly conservative. However, in multicomponent systems the water chemistry will include a little bit of all the salts and the deliquescence point of the system will be less than that of any individual salt. For example, a little $CaCO_3$ in solution in addition to $NaNO_3$ will stabilize that solution to a lower RH than a pure $NaNO_3$ solution. I don't know how big an effect this would be, but it should be checked, e.g., with multicomponent speciation calculations.

22. The discussion of RH on the drift wall and WP surface on p. 49 is correct for a static system. However, the gas phase will circulate water vapor, and other effects may lead to variations in RH in the gas phase. For example, Vidal and Murphy (1999) showed that thermogravitation for certain geometries can lead to large RH gradients. Simple binary mixing of air and water vapor can greatly reduce the O_2 and CO_2 purging effects of evaporation as illustrated in figures 4 and 5. Binary diffusion is normally considered in thermohydrologic models. The statement that "Above 100 C there is no partial pressure of oxygen – therefore there is no dissolved oxygen in any of the solutions" (p. 52) is an extreme case neglecting mixing by flow or diffusion. Also, total pressure can increase above the ambient value due to boiling. This effect may be inconsequential for chemistry, but if it is neglected, as it is in the AMR, its negligible effects should be justified.

23. Units should be given in eq. 17.

24. The chemical divide theory is based on closed system behavior. How is the chemical divide evolution of water chemistry affected by loss of CO_2 by open system volatilization?

Leon 9/14/00

Lauren,

Based on the table you sent previously I judge the most important reviews to be DS/WP Outer Barrier (which I completed although I only submitted the "draft" report), Precipitates/Salts (which I can complete within a few days), and FEPs for NFE (which I will attack next and complete by early November). In addition I'll look at Natural Analogues briefly. I do not believe I can commit to other reviews by November 15. I know that the solubility AMRs are not in your subissue, but I think review of those is particularly important. Perhaps I could provide a review of the reviews for Bobby at some later date.

Here is my view on the AMR schedule and reviews: The harder the push to do fast reviews, the more critical and less constructive they must be. The best reviews identify problems and offer solutions. Quick reviews can only identify possible problems. There will be a legitimate role for constructive reviews after any organizational deadline; the problems won't go away although the specific documents of focus may shift.

I don't have copies of the FEPs for NFE AMR or analogs AMR in my office here. (Perhaps I have them buried in boxes at home.) Would you please send me copies of these AMRs?

Two more weeks till GSA. Yikes.

Bill

Hi Bill,

Bret asked me to contact you about AMR reviews. He wants to know which AMRs you can commit to reviewing by what date. We have to complete the AMR reviews by the third week of November now, at the very latest, because we have to give the DOE a list of concerns at that time. Telecoms between us and the DOE are scheduled for the last week of November. Aaaahhh.

This memo is corrected from the original email.

Wm 10/25/00

Comments on "In-Drift Precipitates/Salts Analysis" AMR version April 2000

William M. Murphy
November 2000

Following a brief description of the DOE approach, AMR review comments are organized on the following subjects: scope of study; critique of model assumptions; calibration with laboratory data; model usefulness; and limits of validation. In general, models in this AMR are based on many assumptions, which are mostly reasonable and reasonably documented, but many are loosely constrained by data or theory. The models constitute a reasonable speculative exercise, illustrating the complexity and difficulty of the problem and the limited ability to describe precisely the details of near-field chemistry. However, the AMR falls far short of presenting results of certainty sufficient to provide confidence in their use in affirming repository safety.

Description of DOE Approach

DOE used a geochemical modeling approach to evaluate the chemical effects of evaporation of groundwater and precipitation of salts with particular focus on variations in solution pH, chloride concentration, ionic strength, and maximum relative humidity for dry conditions to exist. For calculations at ionic strength less than about 10, the high relative humidity (HRH) model, a new Pitzer model data base was developed which has estimated values for essential aqueous species and estimated values for temperature dependence parameters. The EQ3/6 aqueous speciation and reaction path modeling code was used for the HRH model. The HRH model invoked chemical equilibrium except for selected suppression of precipitation of some minerals. For ionic strengths greater than 10, the low relative humidity (LRH) model employed a mass balance approach. Nitrate salt deliquescence was assumed at 50 percent relative humidity. An arbitrary dependence on time (and increasing relative humidity) was assumed for dissolution of other salts. The LRH model was merged with HRH model results at 85 percent relative humidity. Reactions of groundwaters with rock and engineered materials are beyond the scope of the models in this AMR. Model results were compared to laboratory results on evaporation of synthetic groundwaters with correspondence deemed to be acceptable within very loose criteria for model validity.

Scope of Study

The objective of the study is limited to provide models for pH, chloride, and ionic strength, which are important parameters in PA. Additional chemistry is noted as potentially important: "Although the list of output variables is short, the entire major ion chemistry of seepage water must be modeled to determine these outputs. Interactions between ions in solution, gas-phase carbon dioxide, and mineral precipitates are critical or are potentially critical to the Precipitates/Salts analysis" (p. 85). Despite this reasonable assertion, the existing models neglect much chemistry and presently make no use of input seepage compositions. In contrast, "The Precipitates/Salts Model is intended to incorporate seepage composition data from thermohydrological-chemical (THC)

modeling when they become available" (p. 16). Many additional components of the near-field system are neglected: "The Precipitates/Salts model does not simulate interaction with potential materials within the drift, such as tuff, grout, or waste package materials" (p. 21).

According to Table 8, few FEPs are addressed by the precipitates/salts AMR. Three of the four FEPs in this table deal with backfill, and it is stated in Table 22 that two of these three are not addressed in this AMR. This AMR is relevant to the FEP on redissolution of precipitates. An additional primary FEP in the DOE data base named thermo-chemical alteration (2.2.10.06.00) encompasses a secondary entry named precipitates from dissolved constituents of tuff and repository materials form by evaporation during the thermal period (2.2.10.06.07), which appears to be addressed by this AMR, but is not listed in Table 8.

Critique of Model Assumptions

It is difficult to accept that "The assumption of equilibrium conditions will not affect the uncertainty in the model and is therefore not designated TBV" (p. 22). Equilibrium is an appropriate vantage point, but kinetics can have a big effect, too. The report notes that some "slow-forming minerals are not allowed to precipitate" which is acknowledgement of the role of kinetics. Indeed certain discrepancies between the model and experimental data examined in an effort to validate the model are ascribed to kinetic effects. In addition, lack of interaction with drift materials is basically a kinetic assumption, which is probably unrealistic.

Limitations exist in the HMW and PIT (Pitzer) data bases, and it is reasonable to attempt provisional extrapolations from these data bases for the purposes of exploratory modeling. It would be reasonable to review the work of Reardon (1990) cited in the AMR to evaluate approximations used to generate the extended Pitzer data base. Some data in Table 14 were vaguely "added to improve solubility calculation" with no other justification.

The assumption that SiO_2 is an insignificant component in the LRH model (p. 32) is questionable. It's assumed in the HRH model that silica phases do not precipitate, so aqueous silica concentrations should increase. Also, it's possible that dissolved silica may play a role in buffering pH at elevated pH, which is one of the variables of primary focus of the study. High silica contents are noted as a characteristic of natural brines described on p. 36, but neglected in the LRH model.

Dissolution of salts as an arbitrary function of time in the LRH model (p. 32) is not a chemically based assumption. "The dissolved fractions of chloride, sulfate, and carbonate salts increase with increasing relative humidity such at complete dissolution of these accumulated salts does not occur until the relative humidity reaches 85 percent" (p. 86). Use of this model to justify estimates of variations in water chemistry parameters has questionable legitimacy. The unrealistic increase in chloride concentration as the relative humidity rises and the ionic strength decreases is a consequence of this arbitrary

assumption. In contrast, it is stated "These approximations are presented as reasonable upper bounds on the chloride concentrations…" (p. 86), and "…assumptions tended to err on the side of conservatism. In particular, they tended to result in a shorter dry period, … and higher chloride concentrations at lower relative humidities." These conclusions are unjustified because chloride is lowest at low humidity in the LRH model.

In contrast to the statement in section 6.3.1.3, the most likely location for evaporation is in the rock, either in the matrix or at fracture surfaces. This process is specifically neglected in the salts/precipitates AMR.

The theoretical meaning of pH for the LRH solutions is unclear, and its value for PA is unclear. For example, are corrosion rates (or anything else) known as a function of pH in solutions of ionic strength greater than 10?

The assumption that salts behave independently in the LRH model could lead to nonconservative results. Nitrate salts are allowed to dissolve as soon as the RH reaches 50 percent (p. 32). However, as soon as an aqueous phase exists, it will incorporate some amount of all components, e.g. some Cl^-, SO_4^{2-}, etc., which will stabilize the solution at RH lower than that stabilized by the pure nitrate salt.

Calibration with Laboratory Data

Rosenberg et al. lab data are noted to be "used only as a reference for model validation" (p. 12). — not for calibration ? AMY 1/5/01

There is uncertainty in the pH of the waters in the Rosenburg et al. experiments. They're reported as 7.84 in Table 3 of the AMR and 8.46 and 8.65 in Table 4. The control on CO_2 pressure in these experiments is uncertain.

Results shown in Table 3 for the Rosenberg et al. 1999a evaporation experiments (evap1) are questionable. The concentration factor is 956, and Na increased by a factor of 958, which is an indication of conservative behavior of Na and good chemical analysis. However, Cl increased by a factor of only 700, which seems most likely to indicate bad chemical analysis. Aqueous SiO_2 increased by a factor of 1600, which is impossible unless there was a silicate reactant like tuff. Variations in pH were not reported. Given these uncertainties, the use of these data to validate models, the primary goal of which is to predict ionic strength, Cl, and pH, is unreasonable.

Although it is reasonable to limit the LRH model components, the rationale that "other components are almost entirely precipitated at lower ionic strength in evaporated J-13 well water" (p. 32) is inconsistent with the experimental data in Table 3 showing elevated F^- and SiO_2 concentrations in evaporated J-13 water.

Model Usefulness

The HRH model underestimates Si and Ca in the Rosenberg experiments by an order of magnitude and underestimates Mg by two orders of magnitude (p. 51). The model is nevertheless "validated" because the concern is only pH, Cl, and ionic strength. However, the value of developing a complicated multicomponent model is questionable. The HRH model reasonably predicts Na, Cl, etc., concentrations in experiments when there is no precipitation of phases containing these species, and the concentration ratio is based on the nitrate concentration. This is a trivial result, and this comparison is not a test of the model except that it accurately represents conservation of mass. In contrast, for species that precipitate (e.g., Ca and Mg) the model prediction fails by orders of magnitude (p. 56). There is limited value of a detailed multicomponent model when the model results are wrong and deemed to be irrelevant anyway.

Similarly, the ionic strength approximation in the HRH model appears to be good only to within a factor of about 2 relative to experimental results (p. 59), and is consistently low. Given the arbitrarity of the approximation and the consistency in the discrepancy, it seems that a simpler and more accurate approach could be adopted. It's difficult to accept the conclusion that "HRH model results for pH, chloride concentration, and ionic strength strongly agree with the laboratory results…."

Limits of Validation

Broad ranges are accepted for model validation recognizing large model uncertainties (p. 42). The claim that model validation criteria are met in every case is based more on loose criteria than on valid models. The AMR reasonably notes major discrepancies between model results and data used to judge "validity."

Agreement of the LRH model with the HRH model where the two models are joined (p. 63) no measure of validity; it's a simple assumption. Furthermore, validation of LRH model results by comparison to HRH model results is risky because the HRH model is imperfect.

The validation criterion that Cl, ionic strength, and pH are conservative or within an order of magnitude (p. 63) is also risky because conservatism is difficult to determine. For example, low ionic strength may be conservative for colloid transport, but high ionic strength may be conservative for corrosion.

The LRH model is packed with provisional arbitrary assumptions, some of which have no physical chemical basis. The notion that the LRH model can be "validated" is unrealistic and unreasonable.

The statement "The LRH model uses no data that are TBV" (p. 89) is a tautology because the LRH model uses no data. It is stated in the AMR that there are no data available for validation of the LRH model.

Comments on December 1, 2000 teleconference concerning ENFE Subissue 2

Incomplete design is a problem for characterizing the chemical environment. The emphasis in the discussion on trace components may obscure more important questions of uncertain major chemistry. Are there trace components (e.g., lead) of particular concern? It's reasonable that the DOE reference design is the best they have to offer. The big and likely risk is that a license will be granted based on one reference design, then the design will change, but the licensing hurdle will be passed. It's reasonable to allow advances in design, but a system is necessary to assure that changes are reviewed and acceptable. For example, design changes to accommodate engineering requirements must be examined for their effects on the near field geochemical environment.

Numerous relevant AMRs were noted as in progress or in revision. Many rev. 1 versions of AMRs acknowledge incompleteness. When are AMRs to be complete? Is it prior to a site suitability determination or prior to licensing?

It will be necessary to accept that all couplings cannot be addressed explicitly. Couplings are recognized as important in the AMRs. The challenge is to keep up with the evolving AMRs to determine if coupling is addressed. For example, there is no chemistry in the THC processes AMR rev. 0. The salts/precipitates AMR states it will use results from the THC processes AMR when they are available. The physical and chemical environment abstraction AMR noted in the discussion and its review may be the places where questions of the adequacy of coupling are addressed.

The PC4 database is poorly justified. (See review of salts/precipitates AMR.) Wolery is purported to be using this database to develop in-drift chemistry models. Wolery should be seriously questioned about the validity of the database. Wolery should also be questioned on kinetics/equilibrium aspects of the models. I suspect that he'll provide legitimate and insightful responses.

The discussion of FEPs in the teleconference focused on the hydrothermal flooding issue (which I think DOE and NRC would willingly put to bed). However, the discussion of FEPs in general should not stop here with this FEP. What are others and are they addressed? Also, in the context of the near-field environment, the relevance of studies of hydrothermalism is greatest in helping to predict future conditions due to repository heating.

Model validation is particularly important for the near field because of the complexity of models. Discussion of model validation should not be put off to a separate meeting among PA folks on validation methods. The salts/precipitates AMR is a good case for focus. The models there are speculative and potentially useful but weakly justified. Nevertheless, arguments are made that they are validated. Although it's admirable that the question of validation is raised, this AMR sets a very weak standard for validation. Should NRC accept it?

12/1/00

Correspondence from L. Browning re: work 12/12/00

Also, my time is pretty booked up next year, and I was wondering if you might be interested in a couple of other collaborations. First, helping me plan a silica mobilization experiment, and second, being the primary editor for a special journal issue on reactive transport (with me as the second editor). The first will definitely fly, but the second possibility is contingent on my getting Debra's agreement.

Murphy's response 12/12/00

3. Yes, on the experiment. I will assume for now that some work on that subject falls in the category of transport modeling assistance, which I'm tasked to provide, and I'll write a summary of my ideas on theoretical basis for appropriate experimentation on silica transport in the next few days.

Murphy, William

From:	English Pearcy [epearcy@swri.edu]
Sent:	Wednesday, December 13, 2000 12:08 PM
To:	Murphy, William; Lauren Browning (lbrowning); Roseanne Ard (rard); Roberto Pabalan (rpabalan)
Subject:	Re: notes from Chico

Hi Bill!

Yes, I would like you to participate in the ENFE technical exchange. Please coordinate with Lauren on the schedule and logistics. This note will serve to document my request for this task under your general contract. I will copy Roseanne Ard on this email so that she can add it to your file.

Teaching is difficult work. Be encouraged! You are by nature and experience an exceptionally talented instructor. I am sure that your lectures are both thoughtful and engaging. You are doing a good thing.

English

cc: Ard, Browning, Pabalan
****

"Murphy, William" wrote:

> English,
>
> Lauren proposed that my participation in the ENFE technical exchange in
> January would be useful and suggested that I contact you directly about it.
> At this point I'm available to participate. Please let me and/or Lauren know
> your recommendations.
>
> Classes are over for the semester and I feel relieved. I put a large effort
> into them, like giving two or three original talks each week. Student
> reactions to tests were the toughest issue. I'm sure I influenced many of
> the students, but I'm not sure they're all happy about it now as they study
> (or neglect to study) for their final.
>
> Bill

1/1/01

Observations on silica at Yucca Mountain and silica redistribution experimentation

William M. Murphy
December 2000

Silica redistribution is an important near-field issue because of its potential effects on permeability, porosity, and sorption properties of rocks.

Comments on distribution of silica at Yucca Mountain

Volcanic glass is silica rich and thermodynamically unstable. Glass metastability is a practical modeling approximation, but theoretically it's a difficult concept because of the implausibility of a glass precipitation reaction. Glass may become armored by a silica rich phase at metastable equilibrium with groundwater. White et al. (USGS, 1985) proposed glass as the source of aqueous silica at Rainier Mesa.

Silicate dust is deposited at the ground surface. Unsaturated zone groundwaters have high aqueous silica concentrations from the ground surface down, indicating that the primary silica source is near the surface. Dust is clearly a source for Ca and Mg, and, together with rain, is an important source of Cl, SO4, and HCO3 in unsaturated zone waters and secondary minerals. Reactive silicate dust is probably an important initial source of aqueous silica.

Alkali feldspars are abundant and silica rich. Volcanic alkali feldspars are unstable in acidic recharging water, which is initially poor in K and Na.

Silica occurs as primary (quartz, cristobalite, tridymite) and secondary (opal, moganite (?)) phases. Groundwaters tend to be supersaturated or highly supersaturated with respect to primary silica phases at Yucca Mountain, proving that their dissolution cannot generate observed aqueous silica concentrations under isothermal conditions.

Secondary aluminosilicates (e.g., zeolites, clays, analcime, alkali feldspars) may control silica concentrations. A predominant diagenetic progression at Yucca Mountain relevant to silica distribution is from clinoptilolite as a glass alteration product to analcime with depth. Clinoptilolite is silica rich, and analcime is silica poor. Yucca Mountain analcime is enriched in silica relative to stoichiometric analcime, but analcime is a silica poor phase relative to clinoptilolite as exemplified by the reaction, Na-clinoptilolite -> analcime + silica. The clinoptilolite – analcime transition with depth at Yucca Mountain corresponds to a decrease in aqueous silica concentrations in coexisting waters (see early research report for NRC by Murphy. There is probably also a decrease in aqueous silica concentrations corresponding to the glass – clinoptilolite transition based on unsaturated zone water chemistry data.

Aqueous silica in the saturated zone at Yucca Mountain is approximately buffered at 1 millimolar, but the buffering reaction(s) is(are) uncertain.

Experimental system considerations

Silica colloid effects could be important, possibly in nature, more possibly in the near field, and most possibly in experiments. Colloid formation is a way that apparently supersaturated solutions can be generated by interactions with silica phases.

Glassware was a complicating source of aqueous silica in experiments at 25 C and pH 9 in our lab.

Experimental studies on this subject would be remiss unless they include detailed attention to solid phase characterization, colloids, accurate and complete aqueous solution analysis, and control of gas pressures (particularly CO2). Mineral phases including opal-CT should be characterized by the best possible optical microscopy and XRD (and possibly other techniques such as IR spectroscopy). Colloids need to be tested by ultrafiltrations. Solutions analyses must be confirmed by aqueous speciation calculations demonstrating charge balance and other aspects of internal consistency, such as pH-carbonate relations and mineral saturation states.

Theoretical considerations

Variations in pH and temperature affect aqueous silica. Silicate phase solubilities increase at low pH, silica and silicate phase solubilities increase at high pH. Dissolution rates tend to follow the same pattern with pH. Rates increase with increasing temperature, and silica phase solubilities increase with increasing temperature. Silicate solubilities are more complicated functions of temperature.

Some basic questions possibly to be addressed by experimentation

In the near field are aluminosilicate reactions important in silica redistribution or do silica phases alone control the effects? What are the important phases responsible for silica redistribution effects in transient nonisothermal systems, and do they change as a function of temperature, pH, or ionic strength?

How do reaction kinetics (and silica phase solubilities) vary with ionic strength? Evaporation leads to high ionic strength solutions and is coupled with silica redistribution as a function of temperature and pH variations and fluid flow. Effects of coupled ionic strength and temperature variations on kinetics could be examined theoretically to help define experimental studies.

Details of aqueous speciation remain to be resolved. Are silica complexes important (e.g., NaSiO3- or polynuclear silica speicies)?

Experimental precedents (both good and bad examples)

Moore et al.: High temperature-pressure gradient experiments with low permeability granite showed strong changes in permeability interpreted to be due to silica redistribution.

Rimstidt et al.: Boiling rock soup experiments were naively designed and provided data that were impossible to interpret.

Lin et al.: Strong effects on fracture permeability were observed due to silica redistribution in saturated tuff at elevated temperature. These are the best and most relevant studies. What questions were prompted by these studies?

Matyskiela et al.: Large effects were purported, but data must be regarded with strong skepticism. In general details of experimentation were not provided and results appear to systematic to be real.

Numerous other experimental studies have been conducted. (Some are noted in Murphy's Evans Conference poster of the mid 90's.) The risk of experimentation in this field is the possibility of acquiring ambiguous or useless results. Experimental design to address theoretically based questions is the route of good science.

The role of modeling

Big system, multicomponent, reactive transport modeling is not much help for experimental design because of difficulties and uncertainties in thermodynamic data for aluminosilicates, kinetics, surface area, theoretical porosity-permeability relations, etc. Models have tended to be simplistic, model results have tended to depend primarily on assumptions, and models have shown almost every imaginable effect. However, theoretical questions, e.g., in kinetics and thermodynamics, and theoretical examinations of those questions should provide a basis for experiments.

The role of natural analogs

Natural analog data and Yucca Mountain characterization data provide guidance and an essential basis for validation.

Paiute Ridge is an important site, which DOE (or NRC) should investigate further. Trenching and detailed mapping, sampling, and petrographic characterization are warranted.

Green advocates field experiments at Pena Blanca. The best justifications for this site for field experiments are access (e.g., surface and drift) and possible variations in hydraulic properties of rocks around the ore deposit. Experimental field studies at Yucca Mountain appear to be more directly applicable.

Proposed inclusion of analcime in reactive transport modeling

Analcime is a common alteration phase at Yucca Mountain forming at relatively advanced stages of alteration (e.g., Bish and Chipera, 1989). This alteration may be indicative of repository induced changes. Inclusion of analcime in reactive transport modeling for the perturbed system at Yucca Mountain requires thermodynamic and kinetic data for analcime dissolution and precipitation as a function of temperature.

Thermodynamic and kinetic data for analcime dissolution and precipitation at 25.C are available from Murphy et al. (1996). Application of these thermodynamic data provided plausible interpretations of detailed groundwater chemistry data from the vicinity of Yucca Mountain (Murphy et al., 1996).

The idealized reaction of interest is

$$NaAlSi_2O_6.H_2O + 4\,H^+ \Leftrightarrow Na^+ + Al^{3+} + 2\,SiO_2(aq) + 3\,H_2O \qquad (1)$$
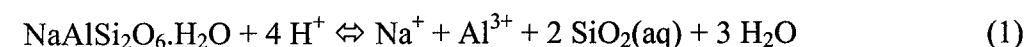
The base 10 logarithm of the equilibrium constant is 7.92 for analcime dissolution at 25.C from Murphy et al. (1996), which is applicable to reaction (1). Thermodynamic data from Murphy et al. (1996) are based on studies with analcime of slightly silica poor composition. Other experimental thermodynamic data are available for analcime of slightly silica rich composition (e.g., Johnson et al., 1982). Analcime from the vicinity of Yucca Mountain generally is enriched in silica relative to the stoichiometry indicated in reaction (1). However, the equilibrium constant for the dissolution reaction (1) is insensitive to these small differences in composition. For applications to large scale multicomponent reactive transport modeling small differences in analcime composition can be neglected, and the idealized reaction (1) can be adopted for convenience. (If model predictions of variations in analcime compositions are of interest then another approach would be necessary. Unlike the equilibrium constant or the standard state free energy of the reaction, standard state free energies of formation depend strongly on the detailed reaction stoichiometry. Caution is required in using standard state free energies of formation of mineral phases derived from mineral solubility studies to determine reaction equilibrium constants for use in geochemical modeling.)

The temperature dependence of the equilibrium constant is given by

$$(d \ln K / d\,(1/T)) = -DHr / R \qquad (2)$$

which for constant DHr can be integrated yielding

$$\ln K(T) - \ln K(T0) = -DH\,r/ R\,(1/T - 1/T0) \qquad (3)$$

where K represents the equilibrium constant, T and T0 denote temperature and reference temperature in K, DHr stands for the standard state enthalpy of reaction, and R is the gas constant. Reported standard state enthalpies of formation for analcime summarized in Murphy et al. (1996) range from –3297 to –3310 kJ/mole; -3300 kJ/mole is adopted for

this study. Standard state enthalpies of formation at 25.C for H^+, Na^+, Al^{3+}, $SiO_2(aq)$, and H_2O given in SUPCRT92 (and consistent with the EQ3/6 data base) are 0 kJ/mole, −240.3 kJ/mole (−57.433 kcal/mole), −538.4 kJ/mole (−128.681 kcal/mole), −877.7 kJ/mole (−209.775 kcal/mole), and −285.8 (−68.317 kcal/mole), respectively. Using these values, the standard state enthalpy of reaction (1) at 25.C is 446.8 kJ/mole. For purposes of calculating equilibrium constants for reaction (1) at elevated temperatures up to about 100.C, it is assumed that the standard state enthalpy of reaction (1) is constant. From equation (3), equilibrium constants are given as

T(.C)	Log K
0	9.39
25	7.92
60	6.23
100	4.69
150	3.18
200	1.98
250	1.02
300	0.22

(Values above 100 C are provided to permit smooth interpolations of values at lower temperatures.)
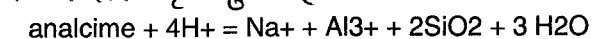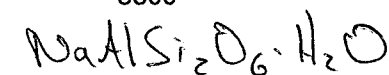
Murphy et al. (1996) provided alternate interpretations of the dissolution kinetics of analcime and provided no kinetic interpretation for precipitation experiments. Experiments were conducted with a relatively high water-rock ratio compared to natural systems, and precipitation experiments closely approached equilibrium within less than one year. For reactive transport modeling of Yucca Mountain, a reasonable assumption is that analcime precipitation kinetics would not be a rate-limiting process once analcime exists in the system. This assumption is reasonable based on the kinetics experiments and based on the apparent equilibrium between analcime and low temperature waters in the vicinity of Yucca Mountain. Analcime nucleation kinetics and analcime growth kinetics under circumstances when there is little analcime in the system could be rate limiting. It is recommended to set a threshold supersaturation for precipitation, then to allow analcime to remain at equilibrium, or to set rate constants so that equilibrium is approached. In other words, the details of the rate constants for analcime dissolution and precipitation are neither easy to evaluate or particularly important.

---

species	DHf (kcal) suprcrt92	DHf (kJ)
		cal = 4.184 J
Al3+	-128.681	-538.4013
SiO2(aq)	-209.775	-877.6986
Na+	-57.433	-240.300
H2O	-68.317	-285.8383
analcime		-3300

$DHf = DHf \times 4.184 \frac{J}{cal}$
(kJ) (kcal)

$NaAlSi_2O_6 \cdot H_2O$

analcime + 4H+ = Na+ + Al3+ + 2SiO2 + 3 H2O

DHr kJ/mole
-91.61316

$= DH_{Na} + DH_{Al} + 2DH_{SiO_2} + 3DH_{SiO_2} - DH_{Analcime}$

InK = ln K0 - DH/R (1/T - 1/T0)

T C	log K	ln K	T K	ln K	log K
0			273.15	21.6192	9.389039
25	7.92	18.23659	298.15	18.23659	7.92
60			333.15	14.35383	6.233747
100			373.15	10.80827	4.693941
150			423.15	7.318954	3.178561
200			473.15	4.567104	1.983455
250			523.15	2.34127	1.016794
300			573.15	0.503787	0.218791

$R = 0.008314 \frac{kJ}{K \, mole}$

This page gives a tabulation of data used in the analcime solubility calculations described on the previous pages.

1/3/01

Murphy, William

From:	English Pearcy [epearcy@swri.edu]
Sent:	Wednesday, February 28, 2001 6:17 AM
To:	Murphy, William; Arturo Ramos (aramos)
Subject:	re: Bill Murphy update

Bill,

Thanks for the update. I sent you the Pena Blanca web material the week after the ENFE tech exchange for you to review. Did you not receive it?

Art, please confirm that the review package for the Pena Blanca web material went out to Bill Murphy. It was a regular set of review forms, plus paper copies of the web pages for Bill to review, plus a CD with an electronic version of the files.

English

****

"Murphy, William" wrote:

> English,
>
> Some particular questions prompt this message today, but I've been intending
> to give you an update of some activities for a while.
>
> Jim Prikryl and I have been working on an abstract for Migration 01. I guess
> it's in review there now. The lab data are ambiguous, but we teased out some
> systematics that warrant an abstract in my opinion, and we'll do more work
> before the presentation and paper.
>
> I was invited to give a talk at the GEOTRAP meeting in May and asked David
> Pickett if he would coauthor it (and the short accompanying paper). David is
> willing and has been helpful already. The topic was assigned, isotope
> fractionation in radionuclide transport.
>
> I'm interested to do the review of the Pena Blanca web material as we
> discussed previously. I still have nothing new from Russell Alexander, and
> I'd like to have something to offer him.
>
> I was asked to give a presentation at a TRB meeting in April on multiple
> lines of evidence for the Yucca Mountain case. I believe that this activity
> would pose no conflict of interest with CNWRA/NRC work because the TRB is
> independent of the DOE.
>
> I hope you're doing well.
>
> Bill

The Peña Blanca web page material was subsequently
sent, and reviewed according to CNWRA procedure.
(to Murphy
                           [signature] 3/17/01

1

Page 1 de 1

Murphy

De :	English Pearcy <epearcy@swri.edu>
À :	<murphy@geologie.ens.fr>; Roseanne Ard (rard) <rard@gargol.cnwra.swri.edu>; James Prikryl (jprikryl) <jprikryl@gargol.cnwra.swri.edu>; Roberto Pabalan (rpabalan) <rpabalan@gargol.cnwra.swri.edu>
Envoyé :	jeudi 5 juillet 2001 08:16
Objet :	additional task for Bill Murphy

Roseanne,

The purpose of this email is to document additional scope for Bill Murphy's consulting work.

New task: Interpretation of uranophane solubility data and preparation of an associated conference paper

Time allocated: 50 hours

Duration: Through September 30, 2001

Please add this email to Bill Murphy's consulting file.

Thanks,

English

cc: J. Prikryl, B. Pabalan, W. Murphy

Statement of Work
William Murphy
June 5, 2001

Tasks anticipated to be conducted by Dr. Murphy under this consulting contract include:

1) Review DOE documents related to geology and geochemistry of the Yucca Mountain system.

2) Conduct geochemical modeling of portions of the Yucca Mountain system.

3) Interpret geochemical data from Yucca Mountain.

More specific tasking will be established as needs become evident. Specific work tasks will be established by letter, email, or memorandum from CNWRA management staff. Each such task will provide a scope, a completion date, and the maximum number of hours allowed. No work is to be undertaken in the absence of such direction. Work products will be documented in reports or memoranda submitted to the CNWRA.

                                 [signature] 10/6/01

The following task is added to the SOW for Dr. W. Murphy:

(i) review the DOE Supplemental Science and Performance Analyses report section pertaining to thorium, technetium, neptunium, and plutonium solubility limits using the five YMRP generic acceptance criteria.

(ii) determine acceptability of DOE abstraction of solubility limits for the four radioelements or provide rationale for unacceptability of DOE approach

Estimated number of hours required: 20 hours

Expected date of completion of review and submission of report: September 5, 2001

Charge number 20.01402.561

English Pearcy
August 21, 2001

On 9/4/01 an electronic file was delivered to CNWRA fulfilling the SSPA review task described above.

As of early October 2001 the poster on uranoplane studies in collaboration with Jim Prikryl was presented at Migration '01, and the corresponding paper is in review.

_W_ 10/6/01

June 2003

The following statement of work initiated an examination of concentration limits for the source term in performance assessment.

Murphy, William

From:	English Pearcy [epearcy@cnwra.swri.edu]
Sent:	Thursday, May 29, 2003 1:57 PM
To:	Murphy, William
Cc:	Roberto Pabalan
Subject:	statement of work

Bill,

At your earliest convenience, please undertake the work described below. These activities need to be completed by September 15, 2003. The maximum number of hours we have for this work is 400.

1. Review of DOE TSPA and NRC TPA abstractions of radionuclide concentration limits.

2. Search and review recent literature on solubilities of radionuclides that are considered in TSPA and TPA calculations.

3. Develop probability distributions (types and parameter values) of radionuclide concentration limits for use in TPA Version 5.0 calculations.

4. Write a report providing technical basis for selected probability distribution type and parameter values.

Best regards,

English

cc: Bobby Pabalan

_W_ 6/2/03

In comparisons of concentration limits a consistent set of units was required and values of $\log_{10}$ concentration were chosen with concentration in $kg\ m^{-3}$. These are units used in CNWRA/NRC PA documents.

For SKI data, which are reported in moles m^{-3} in Andersson (1988) SKI Technical Report 91:21, the conversion is

$$\frac{moles}{m^3} \times \frac{g}{mole} \times \frac{kg}{1000g} = \frac{kg}{m^3}$$

molecular/atomic weight

For DOE Data from the AMR on dissolved concentration limits (ANL-WIS-MD-000010 rev 02) data are reported in mg/liter (or $\log_{10}$ (mg/liter))

The conversion is

$$\frac{mg}{liter} \cdot \frac{liter}{1000 cm^3} \cdot \frac{100^3 cm^3}{m^3} \cdot \frac{kg}{10^6 mg} = \frac{kg}{m^3}$$

9/18/03

These conversions were implemented in an excel spreadsheet and the results are shown of the following pages, with some clarifying notes. First the final table presented in the report submitted to CNWRA on 9/15/03 is presented. This report provides the primary documentation of the analysis. Footnotes to this final table are given below and the table is given on page 30.

Footnotes for Table 1.

1. High applies to elements that were deemed not to be controlled by concentration limits because of their high solubilities. For NRC/CNWRA entries, default "high" values are reported in Table 1 corresponding to concentrations of 1 molar.
2. Neptunium concentration limits are represented as a log triangular distribution by CNWRA/NRC. The midpoint of the distribution is reported in the Estimated/Fixed Value column of the Table.
3. DOE uses two fixed values for radium solubility applicable to conditions above (higher solubility) and below (lower solubility) pH 7.75.

9/18/03

Table 1. Concentration Limits for Radioactive Elements ($\log_{10}$ kg/m^3)

Element	Source	Minimum	Estimated/Fixed Value	Maximum
Am	NRC	-7.62		-3.62
	SKi	-8.31	-4.01	-0.61
	DOE	-5.12		-2.96
C	NRC		1.15 (high[1])	
	SKi		high	
	DOE		high	
Cl	NRC		1.56 (high)[1]	
	SKi		high	
Cm	NRC		-3.62	
	SKi	-8.31	-4.01	-0.61
Cs	NRC		2.13 (high)	
	SKi		high	
	DOE		high	
I	NRC		2.11 (high)	
	SKi		high	
	DOE		high	
Nb	NRC		-6.03	
	SKi	-7.03	-6.03	-5.03
Ni	NRC		-0.96	
	SKi	-4.23	-1.23	-0.77
Np	NRC	-2.92	-1.47[2]	-0.62
	SKi	-5.63	-0.45	-0.45
	DOE	-3.75		-0.97
Pb	NRC		-4.18	
	SKi	-5.68	-3.68	-1.68
	DOE	-6.00		-4.00
Pu	NRC	-5.62		-3.62
	SKi	-9.14.	-6.01	-4.83
	DOE	-4.75		-3.69
Ra	NRC		-4.64	
	SKi	-5.65	-4.04	-1.65
	DOE		-4.70, -2.92[3]	
Se	NRC		1.90 (high)	
	SKi	-0.10	0.90	1.60
Tc	NRC		2.00 (high)	
	SKi		high	
	DOE		high	
Th	NRC		-3.64	
	SKi	-7.22	-6.40	-5.29
	DOE	-5.40		-2.37
U	NRC		-2.12	
	SKi	-4.45	-0.45	-0.45
	DOE	-2.79		-0.73

[signature] 9/18/03

Results of concentration limit conversions for SKi data are presented in the table attached to this page

Element	Estimate mole/m^3	Minimum mole/m^3	Maximum mole/m^3	Estimate kg/m*3	Minimum kg/m*3	Maximum kg/m^3	log estim. log kg/m^3	log min. log kg/m^3	log max log kg/m^3	Source Ski
Am	4.00E-04	2.00E-08	1.00E+00	9.72E-05	4.86E-09	2.43E-01	-4.01E+00	-8.31E+00	-6.14E-01	Ski
C	High									Ski
Cl	High									Ski
Cm	4.00E-04	2.00E-08	1.00E+00	9.88E-05	4.94E-09	2.47E-01	-4.01E+00	-8.31E+00	-6.07E-01	Ski
Cs	High									Ski
I	High									Ski
Nb	1.00E-05	1.00E-06	1.00E-04	9.29E-07	9.29E-08	9.29E-06	-6.03E+00	-7.03E+00	-5.03E+00	Ski
Ni	1.00E+00	1.00E-03	2.90E+00	5.87E-02	5.87E-05	1.70E-01	-1.23E+00	-4.23E+00	-7.69E-01	Ski
Np	1.50E+00	1.00E-05	1.50E+00	3.56E-01	2.37E-06	3.56E-01	-4.49E-01	-5.63E+00	-4.49E-01	Ski
Pb	1.00E-03	1.00E-05	1.00E-01	2.07E-04	2.07E-06	2.07E-02	-3.68E+00	-5.68E+00	-1.68E+00	Ski
Pu	4.00E-06	3.00E-09	6.00E-05	9.76E-07	7.32E-10	1.46E-05	-6.01E+00	-9.14E+00	-4.83E+00	Ski
Ra	4.00E-04	1.00E-05	1.00E-01	9.04E-05	2.26E-06	2.26E-02	-4.04E+00	-5.65E+00	-1.65E+00	Ski
Se	1.00E+02	1.00E+01	5.00E+02	7.90E+00	7.90E-01	3.95E+01	8.97E-01	-1.03E-01	1.60E+00	Ski
Tc	High									Ski
Th	1.70E-06	2.60E-07	2.20E-05	3.94E-07	6.03E-08	5.10E-06	-6.40E+00	-7.22E+00	-5.29E+00	Ski
U	1.50E+00	1.50E-04	1.50E+00	3.57E-01	3.57E-05	3.57E-01	-4.47E-01	-4.45E+00	-4.47E-01	Ski

[signature] 9/18/03

Element	Minimum mg/L	Maximum mg/L mg/L/1000 = kg/m3	log min log kg/m^3	log max log kg/m^3	Distribution	Minimum mole/L	Maximum mole/L	minimum kg/m^3	maximum kg/m^3	log min log kg/m^3	log max log kg/m^3
Am	7.63E-03	1.10E+00	-5.12E+00	-2.96E+00							
C	High										
Cl	not considered										
Cm	not considered										
Cs	high										
I	high										
Nb	not considered										
Ni	not considered										
Np	1.78E-01	1.07E+02	-3.75E+00	-9.71E-01	log normal	4.80E-09	4.80E-07	9.95E-07	9.95E-05	-6.00E+00	-4.00E+00
Pb											
Pu	1.78E-02	2.05E-01	-4.75E+00	-3.69E+00							
Ra	2.00E-02	1.2	-4.70E+00	-2.92E+00	fixed depending on pH						
Se	not considered										
Tc	high										
Th	4.01E-03	4.25	-5.40E+00	-2.37E+00							
U	1.62	185	-2.79E+00	-7.33E-01							
Ac											
Pc	High										
Sr	High										

Results for conversions of DOE concentration limits are given on this page.

(signature) 9/18/03

Additional commentary from the 9/15/03 report to CNWRA is attached to this page.

A first order evaluation of CNWRA/NRC concentration limits is provided by comparison to values determined in different studies. A summary is provided in Table 1 of concentration limits from the CNWRA/NRC TPA 4.0 (CNWRA, 2002a), the SKi Project-90 (Andersson, 1988), and the DOE concentration limits AMR rev. 02 (OCRWM, 2003), which are largely independent. The SKi compilation is for oxidizing conditions in generic crystalline rocks. SKi reported estimated values as well as upper and lower limits, and these are also reported in Table 1. DOE values were extracted from tables of solubilities provided as functions of pH and log CO_2 pressure. As discussed in section V, the ranges of these parameters considered by DOE are very broad. For the comparison presented in Table 1, maximum and minimum solubility values were selected from the DOE tables for reasonably realistic conditions of pH between 7 and 9 and of log CO_2 pressure (bars) between −2.5 and −3.5. In some cases, DOE models failed to achieve calculated solubilities for all conditions even within these ranges. DOE concentration ranges reported in Table 1 only reflect solubilities that were calculated. Also, stochastic variations applied by DOE to accommodate uncertainties in solid phase identities or properties or fluoride complexation are not included in the values represented in Table 1. No values were reported for DOE for several elements that were screened out of their analyses because of small predicted effects on performance.

(signature) 9/18/03

Concentration limits studies continued in 2004 focusing on appropriate distribution functions. Results of this study were published in the Materials Research Society Proceedings v. 824 of the Scientific Basis for Nuclear Waste Management Symposium XXVIII. This paper went through formal CNWRA reviews, and the technical content of the paper is primarily documented in the paper.

For this paper natural system data were taken from the USGS data base cited in the paper and found at http://water.usgs.gov/owq/data.html.

Data for Ca concentrations were evaluated for population density and found to be bimodal. The statistical analysis was described in the paper and is reproduced on the following page of this notebook. These calculations were conducted by Colin Gallagher, who was a coauthor of the paper.

[signature] 10/5/04

Maximum Concentration Limits for Yucca Mountain Source Term Performance Assessment

Element	Mol.Weight	Constant kg/m^3	log const. log kg/m^3	Minimum kg/m^3	log min. log kg/m^3	Peak	log peak log (kg/m^3)	Maximum kg/m^3	log max log kg/m^3	Distribution Source NRC
Am	243	1.40E+01	1.15E+00	2.40E-08	-7.62E+00			2.40E-04	-3.62E+00	uniform
C	12.011	3.60E+01	1.56E+00							
Cl	35.453	2.40E-04	-3.62E+00							
Cm	247	1.35E+02	2.13E+00							
Cs	132.91	1.29E+02	2.11E+00							
I	126.9	9.30E-07	-6.03E+00							
Nb	92.91									
Ni	58.7	1.10E-01	-9.59E-01							
Np	237.05			1.20E-03	-2.92E+00	3.40E-02	-1.47E+00	2.40E-01	-6.20E-01	log triangular
Pb	207.2	6.60E-05	-4.18E+00							
Pu	244	2.30E-05	-4.64E+00							
Ra	226.03			2.40E-06	-5.62E+00			2.40E-04	-3.62E+00	uniform
Se	78.96	7.90E+01	1.90E+00							
Tc	99	9.93E+01	2.00E+00							
Th	232.04	2.30E-04	-3.64E+00							
U	238.03	7.60E-03	-2.12E+00							

units->

Summary of concentration limits from 9/15/03 report to CNWRA.

[signature] 9/15/03

TO CREATE THE PICTURE (using recommended bandwidth; see below)
```
>lines(density(logCa,width=4*1.06*sqrt(var(logCa))*n^(-1/5)))
> 4*1.06*sqrt(var(logCa))*n^(-1/5) #SPLUS uses width ¼ the standard definition
[1] 0.9288613
>for(w in seq(.9275, 2, by=.025)) plot(density(logCa,w))) #TO find the cut off for unimodality
```

Non-parametric density estimates can be used to estimate a population density from observed data without assuming a specific family, e.g., normal, lognormal, etc…, for the population. These methods assume only that the population has some density function and let the data determine the shape of the estimate, while a bandwidth parameter controls the smoothness of the resulting estimated density. For an overview of the standard statistical methods see the monograph by Silverman (1986). Figure _____ was created from log-scale Ca concentrations using the *density* function available in the S-Plus software package, which uses a kernel density estimation procedure (Venables and Ripley, 1996). Kernel density estimates depend on a bandwidth parameter, which following the rule of thumb given in Silverman (1986) was taken to be $1.06sn^{-1/5}$, where s is the sample standard deviation. The kernel distribution was taken to be normal (the default). The bump in the figure near the mode indicates a possible bimodality in the distribution. Since bimodal distributions are indicative of a mixture of two distributions, we are interested in performing a hypothesis test for bimodality. Following Silverman (1986, section 6.3) we vary the bandwidth (smoothness) parameter, b, until we find a critical value (b_{crit}) for which larger values of b result in a unimodal estimate and smaller values of b result in a bimodal estimate; b_{crit} is used as a test statistic to test the null hypothesis of a unimodal population against the alternative hypothesis that the population is bimodal. Using the S-Plus density procedure b_{crit} was found to be 0.3075. Jones (1983, section 5.4) indicates that only about 5% of samples drawn from normal distributions will have $b_{crit} > 1.25\,\sigma n^{-1/5} \approx 1.25 sn^{-1/5}$. In this case we would reject the null hypothesis of a unimodal population in favor of the alternative hypothesis of bimodality, since $.3075 > 1.25 sn^{-1/5} = 0.2738$. There is significant evidence that the natural distribution of Ca concentrations is bimodal at the .05 level of significance. For more on this test for multimodality see Silverman (1983).

References
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Silverman, B.W. (1983). Some properties of a test for multimodality based on kernel density estimates. In Kingman, J.F. C. and Reuter, G.E.H. (eds.), *Probability, Statistics and Analysis*. Cambridge: Cambridge University Press, pp. 248-259.
Silverman, B.W. (1986). *Density Estimation for Statistics and Data Analysis*. London: Chapman & Hall.
Venables, W.N. and Ripley, B.D. (1996). *Modern Applied Statistics with S-Plus*. New York: Springer.

10/5/04

July   auu 7/30/05
August 30, 2005

The objective of this exercise is to compile thermodynamic data for uranyl minerals to evaluate their relative stabilities as a function of temperature. This work supports preparation of a talk accepted at the 2005 Geological Society of America meeting: Thermodynamics of hydrothermal uranyl mineral formation at Nopal I, by Murphy, Prikryl, and Pickett.

A primary source of reviewed data is Chemical Thermodynamics V. 5: Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium, and Technetium, published by the NEA in 2003. (Guillaumont et al. 2003)

(G. et al. 2003)

Previously Murphy (1997) (Retrograde Solubilities of Source Term Phases) (MRS Proc. 465) focused on "schoepite" which may more currently be called metaschoepite, with a formula $UO_3 \cdot 2H_2O$ or $\cancel{UO_2(OH)_2}$ or $(UO_2)_8 O_2 (OH)_{12} \cdot 10H_2O$.

auu 8/24/05 - not metaschoepite auu 8/24/05

G. et al. 2003 give these values for ~~metaschoepite~~ ($\beta - UO_2(OH)_2$):

auu 8/24/05 not metaschoepite auu 8/24/05

$\Delta G_f^\circ = -1398.683 \pm 1.765$ $\Delta H_f^\circ = -1533.800 \pm 1.500$
kJ/mole   kJ/mole

auu 8/30/05

7/30/05

Soddyite:

Guillaumont et al., 2003 (G. et al. 2003) review soddyite solubility studies by Moll et al. (1996) and Nguyen et al. (1992), which yield notably different values for the equilibrium constant for the dissolution reaction.

Uranophane

G. et al. 2003 reject the data from Nguyen et al. 1992 and Pérez et al. 2000 for uranophane solubility. Note that Murphy and Pabalan (CNWRA 95-014) also rejected the Nguyen et al. uranophane data on a similar basis – non stoichiometric solids, assumed reactions inconsistent with data – etc.

Chen, Ewing, and Clark (American Mineralogist, v. 84, p. 650-664, 1999) conclude that the Nguyen et al. solubility data are "plausible approximations."

7/31/05

Chen et al. 1999 adopt standard state Gibbs free energies of formation for soddyite and uranophane based on a collective view of available experimental data, but they do not provide enthalpies for these phases.

To explore the temperature dependent phase relations, it's necessary to have standard state enthalpies of formation. Chen et al. 1999 use sums of structural components to estimate free energies and enthalpies for uranium minerals (excluding enthalpies for uranophane and soddyite). The uranophane components are

$$CaO_{(1)} + H_2O_{(s)} + 2UrO_5 + 2SiO_{2(IV)} + 5H_2O_{(H)}$$
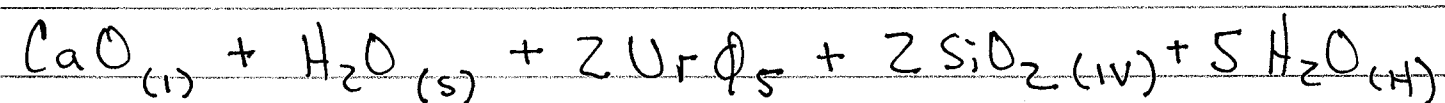
The same components apply to α and β uranophane. Structural component enthalpies derived by Chen et al. '99 are: (kJ/mole)

$CaO_{(1)}$: -726.57 $H_2O_{(s)}$: -299.93

UO_3: -1233.75 $H_2O_{(H)}$: -295.58
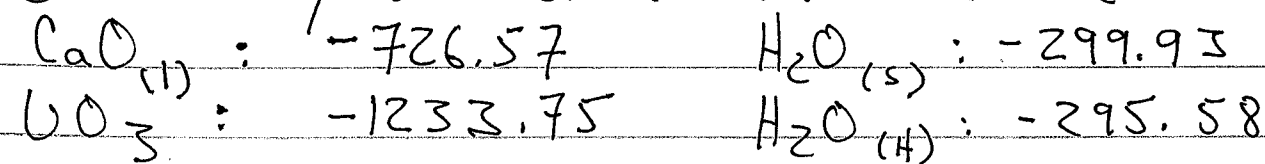
UrO_5 is UO_3 type O_5, but Chen et al. determine a single value for all UO_3 types.

7/31/05

Chen et al. provide no enthalpy values for the SiO_2 (IV) component.

Chermak and Rimstidt (American Mineralogist, v. 74, p. 1023-1031; 1989) preceded Chen et al. in using this approach to estimating data, and Chen et al. state: "this method is similar to that developed by Chermak and Rimstidt ... for silicate minerals."

The structural enthalpy value for (4) SiO_2 from Chermak and Rimstidt is −910.97 kJ/mole.

This value is based on a different set of regressions than the Chen et al. data, so it's not perfectly consistent. There could possibly be theoretical or empirical (e.g., standard state data) differences between the approaches. However, in the context of the present study, this value for SiO_2 seems to be reasonable. Some indication of consistency is given by the values of enthalpies for the CaO component from C + Rimstidt: [6]CaO: −696.65 kJ/mole; [8-z]CaO: −736.04 kJ/mole.

7/31/05

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These CaO enthalpies from Chermak + R bracket the value from Chen et al.: −726.57 kJ/mole.

Hence, summing the enthalpies of the uranophane components yields

$$\Delta H_f^0 = -726.57 - 299.93 - 2(1233.75) - 2(910.97) - 5(295.58)$$

$$= -6793.84 \text{ kJ/mole} \quad \text{⚡ uranophane}$$

The Chen et al. structural components of soddyite are $2 \, UrO_5 + SiO_2 \text{(IV)} + 2H_2O \text{(s)}$

By the method used above for uranophane, the enthalpy of soddyite is estimated to be
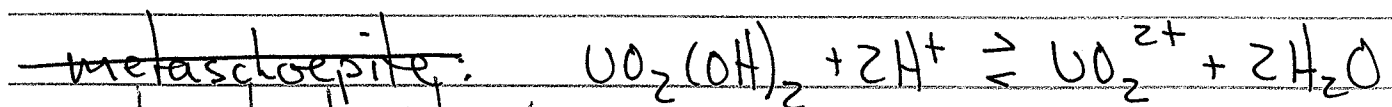
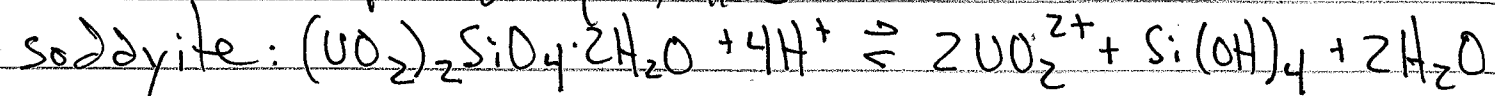$$\Delta H_f^0 = 2(-1233.75) - 910.97 - 2(299.93)$$

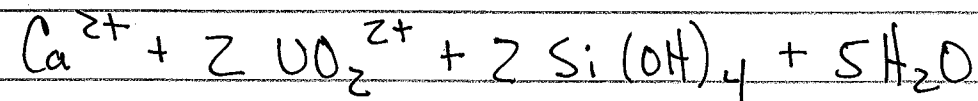$$= -3978.33 \text{ kJ/mole} \quad \text{⚡ soddyite}$$

7/31/05

7/31/05

Dissolution reactions are:

~~metaschoepite:~~ $UO_2(OH)_2 + 2H^+ \rightleftharpoons UO_2^{2+} + 2H_2O$

not metaschoepite /MM/ 8/24/05

soddyite: $(UO_2)_2SiO_4 \cdot 2H_2O + 4H^+ \rightleftharpoons 2UO_2^{2+} + Si(OH)_4 + 2H_2O$

uranophane:
$Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O + 6H^+ \rightleftharpoons$

$Ca^{2+} + 2UO_2^{2+} + 2Si(OH)_4 + 5H_2O$
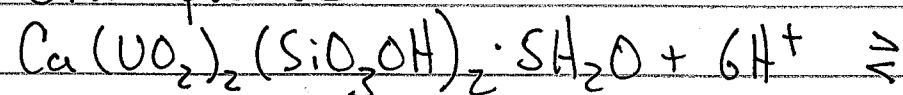
Standard state enthalpy data from Guillaumont et al. (2003) are: (kJ/mole)

$UO_2(OH)_2$: -1533.8
UO_2^{2+} : -1019.0
H_2O : -285.83
$Si(OH)_4$: -1456.96
Ca^{2+} : -543.0
H^+ : 0

/MM/ 7/31/05

7/31/05

Standard state enthalpies of the dissolution reactions are:

~~metaschoepite:~~ $-1019.0 - 2(285.83) + 1533.8$

not metaschoepite /MM/ 8/24/05 $= -56.86$ kJ/mole

see page 46 /MM/ 8/24/05

soddyite: $2(-1019.0) - 1456.96 - 2(285.83) + 3978.33$
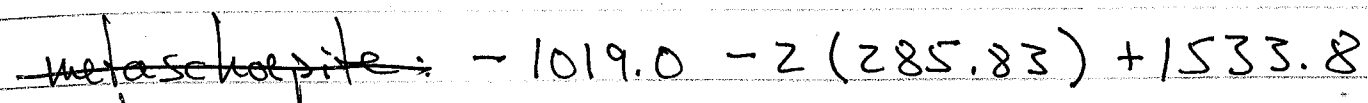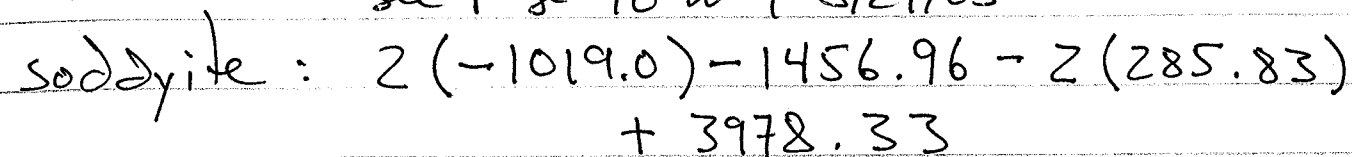
$= -88.29$ kJ/mole

uranophane:
$-543.0 - 2(1019.0) - 2(1456.96) - 5(285.83) + 6793.84$

$= -130.23$ kJ/mole

According to van't Hoff: $\dfrac{d\ln K}{dT} = \dfrac{\Delta H_r^0}{RT^2}$

Negative standard enthalpies of reaction indicate decreasing solubility (ln K) with increasing temperature. Uranyl minerals have retrograde solubilities.   (Murphy, 1997)

/MM/ 7/31/05

7/31/05

Murphy (1997) generated a temperature dependent equation for the heat capacity for the (meta)schoepite dissolution reaction. The heat capacity characterizes the temperature dependence of the enthalpy of reaction, which can be used in integration of the van't Hoff equation to obtain equilibrium constants at elevated temperatures. Considering the uncertainties in the heat capacity of reaction, and the very slight effect that a temperature dependent enthalpy has on the equilibrium constant between 25°C and 125°C for (meta)schoepite solubility, as shown by Murphy (1997), it is reasonable to neglect deviations of the heat capacity of reaction from zero for the present study. It's reasonable to assume that the enthalpies of reaction are constant.   as a function of temperature

Relative stabilities of minerals are likely to be even less sensitive to small heat capacities of dissolution reactions than the solubilities because the small effects are likely to be in the same direction for each mineral.

7/31/05

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7/31/05
for the record:

July 31, 2005

TDB project coordinator
OECD Nuclear Energy Agency, Data Bank
Le Seine-St. Germain
12, boulevard de Iles
F-92130 Issy-les-Moulineaux
France

Cher Coordinator:

The Chemical Thermodynamics series is an outstanding resource and provides a cornerstone for thermodynamic studies related to geologic disposal of nuclear waste.

On page 555 of the recent volume 5 there is a discussion of 97MUR (Retrograde Solubilities of Source Term Phases, Materials Research Society Symposium Proceedings, v. 465, p. 713-720; 1997), which I wrote. It is stated in this discussion of 97MUR that "The calculated solubility of schoepite decreases from $10^{-3.1}$ to $10^{-4.8}$ M when T decreases from 100 to 25°C." This statement is incorrect and implies the opposite of the correct conclusion of the paper. The paper states "the equilibrium solubility constant of schoepite increases with decreasing temperature from $10^{3.1}$ to $10^{4.8}$ between 100° and 25°C." In context, the equilibrium solubility constant refers to the equilibrium constant for the schoepite dissolution reaction, not molarity, and the exponents are positive.

Thank you for recognizing this error in Chemical Thermodynamics, volume 5.

Respectfully,

William M. Murphy

7/31/05

8/24/05

$UO_2(OH)_2$ is a uranyl hydroxide that is not metaschoepite, which can be written $UO_3 \cdot 2H_2O$ and is represented by $UO_3 \cdot 2H_2O_{(cr)}$ in Guillaumont et al. (2003). This is the same as the "schoepite" addressed in Murphy (1997). Standard state free energy of formation and enthalpy of formation from Guillaumont are:

$$\Delta G_f^\circ = -1636.506 \ kJ/mole$$
$$\Delta H_f^\circ = -1826.100 \ kJ/mole$$

The reaction (to replace that on top of p. 42 is

$$UO_3 \cdot 2H_2O + 2H^+ \rightleftharpoons UO_2^{2+} + 3H_2O$$
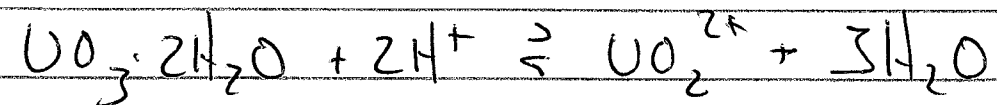
The standard state enthalpy of this reaction (replacing that on top of p. 43) is.

$$-1019.0 - 3(285.83) + 1826.100 = -50.39 \ kJ/mole$$

This correction changes no conclusions discussed on p. 43 and p. 44.

8/24/05

8/24/05

ΔG_r° for the metaschoepite dissolution reaction is

$$\Delta G_r^\circ = \Delta G_{f, UO_2^{2+}}^\circ + 3\Delta G_{f, H_2O}^\circ - \Delta G_{f, UO_3 \cdot 2H_2O}^\circ$$

$$= -952.551 - 3(237.140) + 1636.506 \ kJ/mole$$

$$= -27.465 \ kJ/mole$$
(data from G et al. 2003)

$$\log K_{r, metaschoepite} = \frac{-\Delta G_r^\circ}{(2.302585) RT}$$

$$= \frac{27.465 \frac{kJ}{mole} \cdot \frac{1000J}{kJ}}{(2.302585) \cdot 8.31451 \frac{J}{K \ mole} \cdot 298.15 \ K} = 4.8116$$

Summarizing essential data: at 25°C

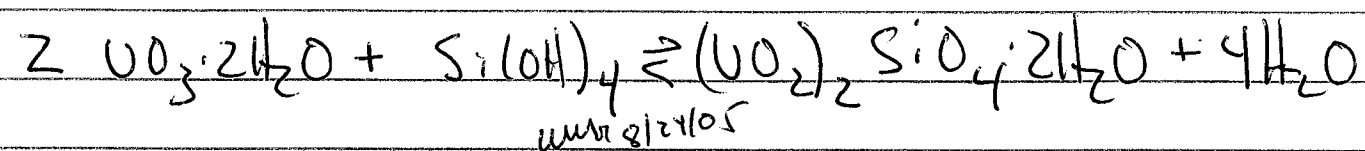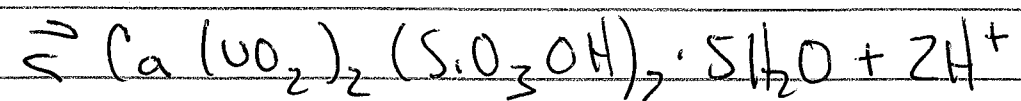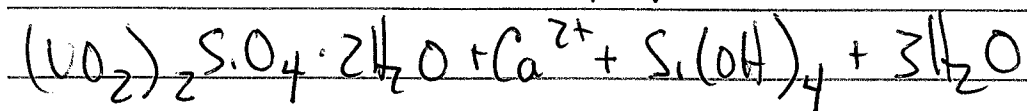| Dissolution reaction	log K	ΔH_r°
metaschoepite	4.81	-50.39 kJ/mole
soddyite	5.35	-88.29 kJ/mole
uranophane	10.93	-130.23 kJ/mole

8/24/05

48

8/24/05

The equilibrium constant for soddyite dissolution given in the table on p.47 is from the Grammar and Hering (Geochimica et Cosmochimica Acta, v. 66, p 3235-3245) (2002) reinterpretation of Nguyen et al. (1992; Journal of Chemical Thermodynamics, v.24, p 359-376.)

The equilibrium constant for uranophane is from the current interpretation of uranophane reversal by Jim Prikryl at CNWRA – see his contemporary scientific notes.

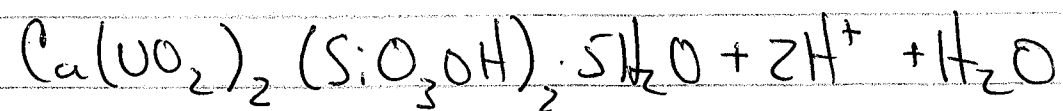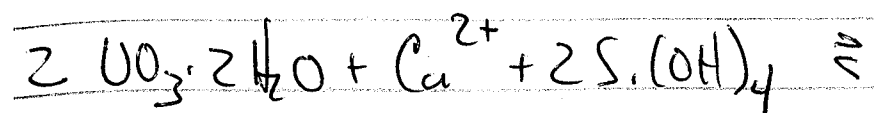The reactions between the uranyl minerals, conserving uranium are:

$$2\ UO_3 \cdot 2H_2O + Si(OH)_4 \rightleftharpoons (UO_2)_2 SiO_4 \cdot 2H_2O + 4H_2O$$

uwr 8/24/05

$$\log K_{SC-SO} = 2(5.35) - 5.35 = 4.27 \quad at\ 25°C$$
4.81

$$(UO_2)_2 SiO_4 \cdot 2H_2O + Ca^{2+} + Si(OH)_4 + 3H_2O$$

$$\rightleftharpoons Ca(UO_2)_2 (SiO_3OH)_2 \cdot 5H_2O + 2H^+$$

$$\log K_{SO-UR} = 5.35 - 10.93 = -5.58 \quad at\ 25°C$$

uwr 8/24/05

49

8/25/05

$$2\ UO_3 \cdot 2H_2O + Ca^{2+} + 2Si(OH)_4 \rightleftharpoons$$

$$Ca(UO_2)_2 (SiO_3OH)_2 \cdot 5H_2O + 2H^+ + H_2O$$

$$\log K = 2(4.81) - 10.93 = -1.31 \quad at\ 25°C$$
SC-UR

To find $\log K$ at elevated T

$$\frac{d\ln K}{d(1/T)} = \frac{-\Delta H_r^°}{R}$$

$$\log K_T - \log K_{25°C} = \frac{-\Delta H_r^° (kJ/mole) 1000J/kJ}{2.302585 \cdot 8.31451\ J/K\ mole} \left(\frac{1}{T} - \frac{1}{298.15} \right)$$

Using this equation:

Dissolution reaction	$\log K_{100°C\ (373.15K)}$	$\log K_{200°C\ (473.15K)}$
metaschoepite	3.04	1.545
soddyite	2.24	-0.371
uranophane	6.34	2.49

uwr 8/25/05

8/25/05

Equilibrium constants for reactions among these minerals, conserving uranyl, as written on p. 48 and p. 49 can be expressed:

	25°C	100°C	200°C
$\log K_{SC-SO} =$	4.27	3.84	3.46
$\log K_{SO-UR} =$	-5.58	-4.10	-2.86
$\log K_{SC-UR} =$	-1.31	-0.26	0.60

———— 8/25/05 ————

———— 8/26/05 ————

Here are some reflections on these results:

The 100°C equilibrium constant for metaschoepite, $\log K = 4.84$ [3.04 inserted] is very similar to that reported by Murphy (1997) [WM 8/26/05] who used the same free energy and enthalpy data, but also applied a heat capacity correction. The 100°C $\log K$ from Murphy (1997) was 3.1. Given uncertainties in the heat capacities, their neglect is acceptable in this temperature range.

WM 8/26/05

The reciprocal of the equilibrium constant for the metaschoepite – soddyite reaction gives the buffered aqueous silica activity (for unit activity of H_2O). At 25°C the aqueous silica activity buffered by metaschoepite – soddyite is $10^{-4.27}$, which is less than quartz solubility ($10^{-4.00}$). With increasing temperature the schoepite – soddyite silica buffer is farther and farther below quartz solubility. — Silica Activity

	25°C	100°C	200°C
metaschoepite – soddyite silica buffer	$10^{-4.27}$	$10^{-3.84}$	$10^{-3.46}$
quartz solubility	$10^{-4.00}$	$10^{-3.08}$	$10^{-2.44}$

(quartz data from the EQ 3/6 data base.

Under silicic environmental conditions soddyite should always be stable relative to schoepite.

Uranophane stability increases enormously relative to schoepite and soddyite with increasing temperature. This result was predicted by Murphy (1997).

WM 8/26/05

9/10/05

Increasing uranyl carbonate complex
stability with increasing temperature
mitigates (in part) the retrograde
solubilities of uranyl minerals.
Two predominant uranyl carbonate complexes
are formed by the reactions

$$UO_2^{2+} + 2HCO_3^- \rightleftharpoons UO_2(CO_3)_2^{2-} + 2H^+$$

$$UO_2^{2+} + 3HCO_3^- \rightleftharpoons UO_2(CO_3)_3^{4-} + 3H^+$$
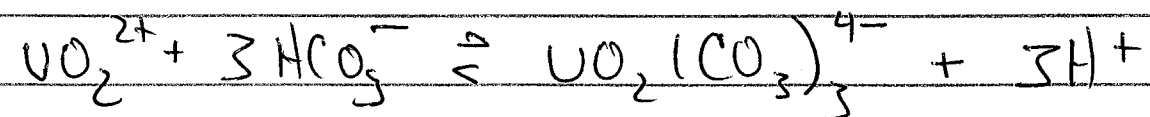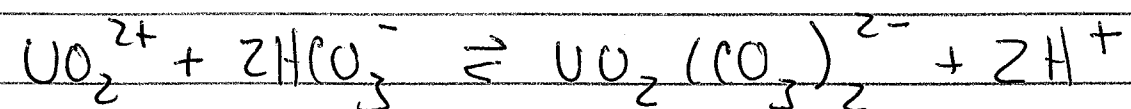
Equilibrium constants for these reactions taken
from the EQ3/6 data base and consistent
with the NEA data base of Grenthe et al.
1992 are

reaction	$\log K_{25°C}$	$\log K_{100°C}$	$\log K_{200°C}$
$\rightarrow UO_2(CO_3)_2^{2-}$	-3.75	-1.83	0.483
$\rightarrow UO_2(CO_3)_3^{4-}$	-9.43	-9.00	-7.65

9/10/05

Metaschoepite dissolution can be written to form
$UO_2(CO_3)_2^{2-}$ as

$$UO_3 \cdot 2H_2O + 2HCO_3^- \rightleftharpoons UO_2(CO_3)_2^{2-} + 3H_2O$$
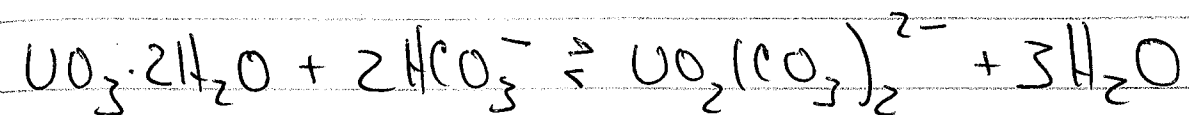
Combining the equilibrium constants for
metaschoepite dissolution on pages 47 and 49
with those for uranyl carbonate complex formation
on p. 52 yields for the reaction above

$$\log K_{25°C} = 1.06$$
$$\log K_{100°C} = 1.21$$
$$\log K_{200°C} = 2.03$$

Thus the ratio of $(a_{UO_2(CO_3)_2^{2-}})/(a_{HCO_3^-})^2$

increases by an order of magnitude between
$25°$ and $200°C$ at equilibrium with
metaschoepite. The retrograde solubility
of metaschoepite is effectively mitigated
by the increasing stability of the
uranyl carbonate complex.

9/10/05

For uranophane the reaction is

$$Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O + 4HCO_3^- + 2H^+$$

$$\rightleftharpoons Ca^{2+} + 2 Si(OH)_4 + 2 UO_2(CO_3)_2^{2-} + 5H_2O$$
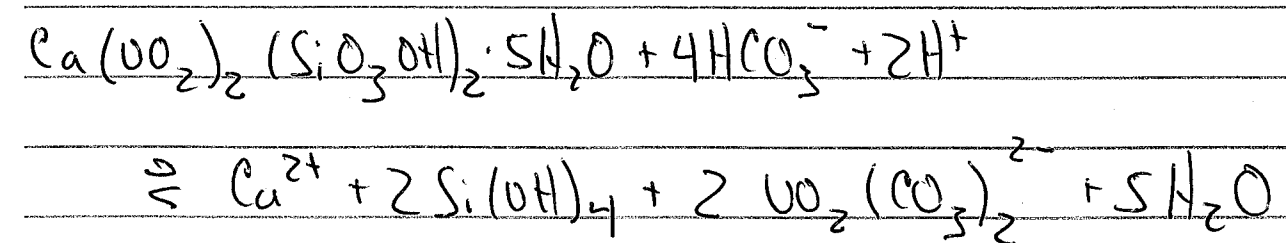
and $\log K_{25} = 10.93 + 2(-3.75) = 3.43$

$\log K_{100} = 6.34 + 2(-1.83) = 2.68$

$\log K_{200} = 2.49 + 2(+0.483) = 3.46$

Whether or not the uranium concentration increases or decreases with increasing temperature depends on silica, bicarbonate, Ca^{2+}, and pH, at equilibrium with uranophane, but the log K for this reaction doesn't vary unilaterally with increasing temperature.

3/9/06

Principal records of my contributions to the CNWRA are publications. A bibliography of the papers I authored or coauthored with support of the CNWRA is attached on the following pages.

William M. Murphy: Bibliography

CNWRA Publications (chronological)

Murphy, W.M. (1991) The high-level nuclear waste repository near-field environment: Performance assessment perspectives with reference to the proposed repository at Yucca Mountain, Nevada. Proceedings from the Technical Workshop on Near-Field Performance Assessment for High-Level Waste Held in Madrid October 15-17, 1990, Sellin, P., Apted, M., and Gago, J. (eds.) SKB (Swedish Nuclear Power Inspectorate) Technical Report 91-59, p. 11-22.

Murphy, W.M., Pearcy, E.C., and Goodell, P.C. (1991) Possible analog research sites for the proposed high-level nuclear waste repository in hydrologically unsaturated tuff at Yucca Mountain, Nevada. Fourth Natural Analogue Working Group Meeting and Poços de Caldas Project Final Workshop, Commission of European Communities, EUR 13014 EN, p. 267-276.

Murphy, W.M., and Pearcy, E.C. (1992) Source-term constraints for the proposed repository at Yucca Mountain, Nevada, derived from the natural analog at Peña Blanca, Mexico. Scientific Basis for Nuclear Waste Management XV, Sombret, C. (ed.) Materials Research Society Symposium Proceedings, v. 257, p. 521-527.

Codell, R.B., and Murphy, W.M. (1992) Geochemical model for ^{14}C transport in unsaturated rock. High-Level Radioactive Waste Management Proceedings of the Third International Conference, American Nuclear Society, p. 1959-1965.

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Murphy, W.M. (1992) Natural analog studies for geologic disposal of nuclear waste. Technology Today. Southwest Research Institute, San Antonio, Texas, June, p. 16-21.

Murphy, W.M. (1993) Technical issues related to groundwater flow and radionuclide transport in unsaturated fractured rock. In Evans, D.D., and Nicholson, T.J. (eds.) Proceedings of Workshop V: Flow and Transport Through Unsaturated Fractured Rock-Related to High-Level Radioactive Waste Disposal. NUREG/CP-0040, Nuclear Regulatory Commission, p. 230-232.

Murphy, W.M., and Pearcy, E.C. (1994) Performance assessment significance of natural analog studies at Peña Blanca, Mexico, and at Santorini, Greece. In von Maravic, H., and Smellie, J. (eds.) Fifth Natural Analogue Working Group Meeting and Alligator River Analogue Project (ARAP) Project Final Workshop, Commission of European Communities, EUR 15176 EN, p. 219-224.

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The work recorded in this notebook was terminated at the Direction of NRC upon the appointment of W. Murphy to the NWTRB.

E. C. Pearcy 4/4/2006

I have reviewed this scientific notebook and find it in agreement with QAP-001.

E. C. Pe
4/4/2006