David Pickett
CNWRA - Southwest Research Institute
Near Field Environment KT1
20-5708-563

"DAP" = David Pickett
"BAW" = Bradley Wesling - Bradley Wesling

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This notebook documents work performed under the following projects:
20-5708-563
20.01402.561
20.01402.871
20.06002.01.071
20.06002.01.222

7/24/96 DAP

Yucca Mountain Region Water Chemistry

This effort is being conducted under the Near-Field KTI (20-5708-563), and deals with the use of hydrothermal and paleohydrothermal conditions in the Yucca Mountain (YM) region as an analog for possible effects of the heated repository on conditions in the repository near field. (See also book 121/54 for a discussion of field work addressing similar issues.)

Specifically, we are looking for data on ground waters which show a range of temperatures and which have data reported on major elements and aluminum (Al). Al is of particular interest because of its possible effect on equilibria involving zeolite minerals. We will look for patterns in chemistry and temperature which may yield clues to mineralogic effects on chemistry (and vice versa).

In March and April of 1996, DAP searched available groundwater data from the YM region for records containing both temperature and Al data. I started with the Database of Perfect et al. (USGS Open-File Report 94-305). I created two data sets based on geography — i.e., I edited the data to include records only from two boxes surrounding YM — one large and one small. Other editing was performed, as noted on the next page.

The resulting Excel spreadsheets: ym_lg_ed.xls and ym_sm_ed.xls are included on the diskette in the inside back cover of this notebook.

Attached are new versions of the two data sheets of YM area water chem. The lat-long areas are the same as before:

ym_lg_ed.xls 36.6 to 37.2, 116.1 to 116.8
ym_sm_ed.xls 36.67 to 37, 116.37 to 116.6

I edited the data in the following ways:

1. Entries with little or no chemical data were excluded.

2. Entries with no temperature were excluded. This is because I want to do EQ3 modelling.

3. Redundancies were excluded; Perfect et al. didn't catch them all. These often took the form of one record having rounded-off values compared to another. There are still some very suspicious possible redundancies; if data were very similar with only a few differences, I nevertheless kept them separate.

4. Where it was clear that separate lines contained major and trace-element data from the same water sample, I combined them.

5. I added aluminum values from Young (1972) and White (1979). I added one entire entry from White (Upper Indian Spring; 11S/46-26bbb) that had been omitted.

6. I added analyses from Daniels et al. (1982) for J-13, UE25b-1, UE29a-2, and USW H-1. For all of these, I had to estimate temperatures, either from other analyses or from the gradients shown in the SCP, Figure 4-13. All the added entries are so noted with my name in the Comments column.

Refs.
Daniels et al. (1982) Summary Report..., LA-9328-MS
White (1979) Geochem...Oasis Valley, USGS Prof Pap 712-E
Young (1972) Water Supply...NTS, USGS Water-Supply Paper 1938

DAP 7/24/96

YM Tuff Alteration 1996 Sampler

7/30/96 DAP This documents subsampling of rock samples obtained during the June 1996 field trip with Bill Murphy.
The field work is described in CNWRA notebooks #121 (DAP) and 180 (WMM).
Rationale for the trip is in #121.
Initial sample handling and preparation is in #121.

Today, I will make subsamples of the whole-rock powders prepared by Jim Brikerd (121/50). These will be used for XRD analysis by Jim Spencer here at SwRI.
Will include two replicates - one tuff, one caliche.

Sample Prefix is "NFA96-".

~~Sample~~ DAP 7/30/96 Weights of XRD subsamples will be determined by taring the small snap-cap vials, then weighing after sampling.
Use OHAUS Precision Standard balance (serial no. 2883 on calibration sticker; calibration due 11/2/96) in Room L102, Bldg 57.
Transfer powder from large vial to small using stainless steel "scoop." Rinse with acetone between samples.

New samples are numbered "NFA96-__-WR_-XRD"

See table on next page.

DAP 7/30/96

New sample	wt. of XRD	total (vial + powder) wt. of parent after	Notes
NFA96-01-WR1-XRD	1.12 g	33.01 g	
NFA96-01-WR2-XRD	1.15	30.82	
NFA96-02-WR1-XRD	1.01	32.54	
NFA96-07-WR1-XRD	1.09	34.96	
NFA96-09-WR1-XRD	1.06	40.16	
NFA96-10-WR1-XRD	1.09	34.47	
NFA96-11-WR1-XRD	0.91	32.81	
NFA96-12-WR1-XRD	1.01	30.82	
NFA96-13-WR1-XRD	0.73	32.38	
NFA96-14-WR1-XRD	0.95	33.44	
NFA96-15-WR1-XRD	0.82	32.59	
NFA96-16-WR1-XRD	0.82	33.11	
NFA96-17-WR1-XRD	0.81	29.76	
NFA96-17-WR2-XRD	0.75		← Actually a replicate sub-
NFA96-18-WR1-XRD	1.06	32.28	sample of NFA96-17-WR1.
NFA96-19-WR1-XRD	1.03	24.16	
NFA96-19-WR2-XRD	1.07		← Actually a replicate sub-
NFA96-20-WR1-XRD	0.96	32.01	sample of NFA96-19-WR1.
NFA96-21-WR1-XRD	1.28	36.93	
NFA96-22-WR1-XRD	0.88	29.79	
NFA96-23-WR1-XRD	1.09	36.39	
NFA96-24-WR1-XRD	1.26	37.05	
NFA96-26-WR1-XRD	1.13	35.74	
NFA96-27-WR1-XRD	0.88	23.42	
NFA96-28-WR1-XRD	0.99	32.53	
NFA96-29-WR1-XRD	0.88	31.27	

Note: the above weights are not quality-affecting. These are recorded merely to keep track of usage of the powders.

7/31/96 Took samples to Jim Spencer, SwRI Div. 6, for XRD analysis. Objective is to learn what alteration minerals are present in samples of tuff, and to search for pyrite in carbonates.

8/2/96
DAP

NFA96 Samples for Chemical Analysis

Splits of WR powders will be taken for chemical analysis to be provided by Melanie Barnes of Texas Tech Univ.
Conduct in same manner as XRD powders (pp. 3-4), using same vials.
Want ~ 5 g this time.
Different naming scheme for replicates. See table.

Sample	wt.	wt. of parent vial + powder after	
NFA96-01-WR1-CH	5.45 g	27.57 g	
NFA96-01-WR2-CH	4.82	26.00	
NFA96-02-WR1-CH	5.00	27.55	
NFA96-07-WR1-CH	4.88	30.08	
NFA96-09-WR1-CH	5.33	34.83	
NFA96-10-WR1-CH	5.23	29.22	
NFA96-11-WR1-CH	4.95	27.87	
NFA96-12-WR1-CH	5.02	25.80	
NFA96-13-WR1-CH	4.83	27.56	
NFA96-14-WR1-CH	4.69	28.73	
NFA96-15-WR1-CH	4.90	27.68	
NFA96-16-WR1-CH	5.07	28.00	
NFA96-17-WR1-CH	4.01		
NFA95-01-WR1-CH	4.20	21.55	Blind replicate of NFA96-17-WR1-CH
NFA96-18-WR1-CH	4.61	27.66	
NFA96-19-WR1-CH	4.99	18.99	
NFA96-20-WR1-CH	4.95	27.03	
NFA96-21-WR1-CH	5.20	31.72	
NFA96-22-WR1-CH	4.85	24.90	
NFA96-23-WR1-CH	4.91	31.46	
NFA96-24-WR1-CH	4.84	32.19	
NFA96-26-WR1-CH	4.87	26.17	DAP 8/2/96
~~NFA95~~ DAP 8/2/96			
NFA95-02-WR1-CH	4.69		Blind replicate of NFA96-26-WR1-CH
NFA96-27-WR1-CH	4.43	18.98	

continued

table continued 8/2/96

Sample	wt.	wt of parent after
NFA96-28-WRI-CH	4.89 g	27.59 g
NFA96-29-WRI-CH	4.90	26.22
NFA95-03-WRI-CH	2.98	USGS Standard G-2
NFA95-04-WRI-CH	3.81	USGS Standard SCO-1

As on p. 4, these weights are not quality-affecting.

8/5/96 "CH" samples mailed to Melanie Barnes, Texas Tech University, for analysis of major and trace elements by ICP.
28 samples in all.
Parafilm wrapped around cap to keep vials closed.

8/14/96

8/14/96
DAP

First Look at XRD data on NFA96 Samples

Have XRD data files (*.MDI format) from Jim Spencer, Div. 6 — see p. 3-4.
Take a quick look at spectra to see what important minerals are.

Using ~~"Jde DAP 8/14/96~~ "Jade" software package.
General steps taken:

Read .MDI file
Analyze, Fit Background
Type = spline, spacing = 1, auto-noise = Yes, sigma = 1.0, strip Ka2.
These were all default settings.
Bkgr Purge button.
WRITE. — as both .DIF and .BIN types
Read — .BIN file
Analyze, Find peaks
Search filter = 25. Defaults for all.
For now, don't edit selections.
Write, Peaks → Files
Write Peaks → Printer
Identify, Search/Match
MINERALS PDF subfile
Preferred orientation — Yes
Single Phase — No
Chemistry filter — No
Min. # matching lines — User, 3
Analyze button — Only done with first sample. Too time consuming.
Print Hits button
Save button — saves hit list.

First Sample was 01WRI → NFA96-01-WRI-XRD.
"Analyze" option increased confidence in Clinop. vs. heulandite, made sanidine and tridymite more likely. Use this for all later.

.MDI and other files are named so:
NFA96-01-WR1-XRD = 01WR1.*
NFA96-01-WR2-XRD = 01WR2.* etc.

Analysis done today (w/o more detailed "Analyze") on:

01WR1
01WR2 - qtz best, but terrible F.O.M. (?)
02WR1
07WR1
09WR1
10WR1
11WR1
12WR1
13WR1
14WR1 - very messy spectrum. Probably need to edit peaks. True for many of these.
15WR1
16WR1
17WR1
17WR2
18WR1
19WR1
19WR2
20WR1
21WR1
22WR1
23WR1
24WR1
26WR1
27WR1 - very broad peak 15-35 2θ. Many probably spurious peaks found.
28WR1 - Similar to 27WR1
29WR1 - " " "

8/15/96 DAP

Preliminary Interpretation of NFA96 XRD

Based on quick, rough processing of XRD data (see p. 7-8), these appear to be important phases:

01WR1: qz, heu/clp (= heulandite/clinoptilolite)
01WR2: qz, ab (albite), microcline; no zeolites.
02WR1: alk. feldspars, cristobalite, opal
07WR1: " "
09WR1: qz, alunite (?)
10WR1: qz
11WR1: qz
12WR1: qz
13WR1: clp/heu/mordenite, alk. feldspar
14WR1: heu, others?
15WR1: heu/clp/mord
16WR1: clp/heu/mord, alk. feldspar
17WR1: heu/clp/mord
17WR2: clp/mord/heu, albite, anorthite
18WR1: heu/clp
19WR1: calcite (cc)
19WR2: "
20WR1: qz
21WR1: qz, alk. feldspar
22WR1: " "
23WR1: cc
24WR1: cc
26WR1: cc
27WR1: alk feldspar, anorthite
28WR1: ? Many minerals with similar figures of merit
29WR1: Same as 28WR1.

I have reviewed this notebook and find it in general compliance with QAP-001. There is adequate information for another qualified person to repeat the activity.

E.C. Perry
1/9/97

8/6/99
DAP

Nopal Water Sample

Because I am in a hurry to filter this water, I will record details of its collection, etc., later. I do not yet have location info.

IR-06-99 Nopal I adit (Level 00)

seep water collected by I. Reyes.
Mailed in 1 liter polypropylene bottle.

First make a cursory examination of its chemistry using Hach Water Quality Test Strips 5-in-1 (Cat. # 27552-50, lot 001068X, expire 09/00).

Pour 20-30 ml of sample into a small beaker and dip test strip in it. Estimate chemical features from colors of strips following directions and color guide on bottle.

		2nd reading (new water)
total hardness	25 ppm as $CaCO_3$	25
total alkalinity	0-40 ppm as $CaCO_3$	closer to 0
pH	7.2	7.2
chlorine - total	0 ppm	0
chlorine - free	0 ppm	0

IR-06-99-F Filter the sample using "Clyde" disposable filter system, 0.45 μ, LT#95[redacted].
Filter into a 500 ml bottle labeled IR-06-99-F.
~420 ml

IR-06-99-R
Remainder of original sample - decant into 500 ml bottle labeled IR-06-99-R (R = remainder).
Leave a small amt in original bottle w/ solids.
(Not very much solids)

8/9/99 DAP

Acidify IR-06-99-F.

Acid: Conc. HNO_3 diluted 1:1 by P. Bertetti, 5/13/99. Made from Trace Metal Grade HNO_3, Fisher Lot # 118110. ~6 M HNO_3.

Problem: did not empty weigh the IR-06-99-F bottle. Take five identical bottles (Nalgene 500 ml PP) and weigh.

66.59 g
65.74
65.85
66.30
65.99

IR-06-99-F

weight with orig filtrate	485.15	g
after adding 1.5 ml acid	487.00	
after removing ~25 ml	455.64	(well mixed)

↓

Sample for analysis

CNWRA-02 + IR-06-99-F 42.84
empty 60 ml PP bottle 11.48 g

DAP 9/16/00

CNWRA-01 for anion analysis. Use IR-06-99-R
+ ~25 ml IR-06-99-R 41.50
wt. empty bottle 11.42 g

IR-06-99-R wt before 492.31
wt after 462.20

Note: Notebook # 126 renamed to #127 on 8/25/2000. DAP 12/11/00

8/16/00 DAP

Continuation of Nopal I geochronology work recorded in notebook ~~#126~~ 127, pp. 79-161.

See pp. 79-81 in notebook ~~#126~~ 127 for initial entry.

Calculate maximum U concentrations in prepared leachates. Assume that all U in sample powder is in the carbonate and thus, the leachate. This is undoubtedly an overestimate of the U content of the carbonate. Take the powder mass (notebook 127 ~~126~~, pp. 145, 151-152, 155) and multiply by the U concentration (measured at UT-Austin, corrected for mass loss during firing, and recorded in notebook ~~126~~, 127 pp. 144 and 155), then divide by solution mass (notebook # ~~126~~, 127 pp 159-160) to get U concentration in solution.

Calculation done and recorded in Excel file "Find summary of U-Th concs.xls" on David Pickett's computer ("SYREEN"). This information may be useful to analyst.

Another calculation done in the same Excel file is the amount of residue not removed by the HNO_3 leaching (notebook ~~126~~ 127, pp. 149-161). The dry weight of residue after leaching was calculated by subtracting from the final weight of the centrifuge tube after drying (notebook ~~126~~ 127 p. 161) the empty weight of the centrifuge tube (notebook ~~126~~ 127 pp. 145, 151-152, 155). This weight was compared to the original powder weight (notebook ~~126~~, 127 pp 145, 151-152, 155) to calculate a percent non-carbonate. This value can be compared with the percent non-carbonate determined from 900°C firing (notebook ~~126~~, 127 pp. 106-121), also recorded in the same Excel file.

Red changes this page: DAP 12/11/00

The comparison of the two calculated non-carbonate fractions is good.

sample #	CNWRA NOPI-#-F	type	est. % non-carb from firing	est. % non-carb from leaching	leach calc minus firing calc
N99-9	164-SEP1	cc, gray?	56.8	57.0	0.2
N99-10	164-SEP4	cc, gray?	31.2	35.5	4.3
N99-13	179-SEP1-P	cc, gray	15.0	13.3	-1.7
N99-28	305-L1-SEP4	cal	22.2	25.2	3.0
N99-29	305-L2-SEP1	cal	26.4	27.6	1.1
N99-30	305-L2-SEP4	cal	18.7	18.1	-0.6
N99-32	306-SEP4	cal, sil	35.9	39.3	3.5
N99-33	434-SEP2	cal, sil	4.2	7.1	2.9
N99-34	434-SEP4	cal, sil	7.8	11.0	3.2
N99-17	436-L1-SEP1	cal	16.1	18.2	2.1
N99-18	436-L1-SEP4	cal	9.6	12.1	2.4
N99-19	436-L2-SEP2	cal	17.8	22.7	4.9
N99-20	436-L2-SEP4	cal	14.6	18.6	4.0
N99-35	458-SEP1	cal, sil	92.6	99.5	6.9
N99-36	458-SEP4	cal, sil	91.4	98.9	7.6
N99-23	499-L2-SEP1	cal	27.8	32.1	4.3
N99-24	499-L2-SEP3	cal	24.4	29.5	5.1
N99-26	499-L3-SEP4	cal, sil	30.8	35.0	4.2
N99-16	501-G-SEP3	cc, gray	6.0	2.3	-3.7
SPC00543702-U		cc/breccia YM		20.9	

The leaching result tends to be higher than the firing result. This makes sense, because the excess mass lost during firing is probably H_2O. Hydrous minerals would tend to be unaffected by leaching. At any rate, agreement is very good.

DAP 12/11/00

Opal Solutions See notebook # ~~126~~ 127, pp. 147-148 and 155.
Calculate weight of solutions, HF molarity, HNO_3 molarity.

	g solution	molal HF	molal HNO_3
IR-99-1 Opal 1 [U]	4.0014 g	7.8	6.9
IR-99-1 Opal 2 [U]	4.1356	7.6	6.7
IR-99-10 Opal Sep 1 [U]	4.4310	7.1	6.2
Blank [U]	3.9076	8.0	7.1

Need to prepare a leachate blank and two blind replicates

SPC00603876-U Leachate
This is a dummy name for a blind replicate of SPC00543702-U Leachate

Remove from "SPC00543702-U leachate"
wt before 26.2070
wt after 16.4901
g

Add to "SPC00603876-U Leachate"
bottle + soln 17.7043
empty bottle 7.9871

NOPI-501-D-SEP1-L Leachate
This is a dummy name for a blind replicate of NOPI-501-G-SEP3-L Leachate.

Remove from "NOPI-510-G-SEP3-L Leachate"
wt before 26.3507
wt after 16.6732

Add to "NOPI-501-D-SEP1-L Leachate"
bottle + soln 17.6594
empty bottle 7.9829

Leachate Blank
Combine acid and water to similar extent as done in leaching exercise in a centrifuge tube.
empty bottle = 7.9612 g
Add 3 ml 1.0 M HNO_3 to centrifuge tube, then pipet into bottle. Repeat with 2 ml 0.1 M HNO_3, then with 5 ml H_2O. Then add 0.5 ml 1.0M HNO_3 directly to bottle.
final bottle = 18.7432 g

Spike 39A - Removed 384.4 g of U-233 spike solution 39A (preparation described in notebook 031, p 278-280). Transferred to Div 1 - Mike Dammann. Concentration is 9.595 nCi/g, so transferred activity is 3688 nCi.
Sub1 ID # 470-68-2.

8/17/00 DAP

Binoc Microscope Photos Taken Earlier

Two rolls of slides were taken earlier (notebook ~~126~~ 127, pp. 128-133 and 137-139) DAP 12/11/00

The boxes containing the slides are labelled "Nopal Binoc 1" (pp 128-133 of ~~126~~ 127) and "Nopal Binoc 2" (pp 137-139 of ~~126~~ 127).

Electronic versions were supplied in Kodak Photo CD format (file extension ".pcd") and saved in the following locations on David Pickett's PC:

D:\Documents\ENFE KTI\carb-sil U-Th geochronology\photos\binoc scope photos 1
and
...\binoc scope photos 2

12/11/00 DAP

binoc scope photos 1 (slide box Nopal Binoc 1)

Opened in Adobe Illustrator and saved as an A.I. file (*.ai) and exported to JPEG (*.jpg).

File names altered to read:

Nopal binoc 1 Img0001.*
to
Nopal binoc 1 Img0024.*

The final two digits refer to the photo numbers recorded in notebook ~~126~~ 127, pp 128-133.

binoc scope photos 2 (slide box Nopal Binoc 2)

Same as ...1, with file names:

Nopal binoc 2 Img0001.* (* = ai or jpg or pcd)
to
Nopal binoc 2 Img0024.*

Which exposures yielded the best results?

Among photos 1, 2, and 3: photo 3 has best contrast. Exposure was set to $-\frac{2}{3}$. Photo 2 → $-\frac{1}{3}$, Photo 1 → default. (see notebook ~~126~~ 127, p. 137)

Photos 4 + 5: Photo 5 (exposure = $-\frac{1}{3}$) is much better. Photo 4 → default exposure.

Red changes this page: DAP 12/11/00

Photos 6+7: Again, exposure set to $-\frac{1}{3}$ (7) is better than default (6).

Photos 8 + 9: Same. $-\frac{1}{3}$ exposure (9) better.

Photos 10, 11, and 12: These didn't work well. I was trying to capture a picture of grains of clear opal. Photo 11 (exposure $-\frac{1}{3}$) is perhaps best (10 → default, 12 → $-\frac{2}{3}$), but 12 is OK. None are useful.

Photos 13 + 14: Likewise, these shots of bright yellow opal did not come out well. 14 (exposure $-\frac{1}{3}$) is best.

8/18/00 DAP

Compare Roll 2 re-dos of Roll 1 photos (notebook ~~126~~ 127, pp 138-139). DAP 12/11/00 new = 2, old = 1

new 15 - old 6: Both suffer from focus difficulties. Otherwise, not much difference in quality of exposure. "old 6" is better because more of image is in focus. The color is a little better, as well.

new 16 - old 1: "new 16" exposure is better, more contrast, not washed out.

new 17 - old 2: new 17 a little better. Shows embedded needles better.

new 18 - old 3: new 18 is a better exposure, but prefer old 3 because better focused.

new 19 - old 4: new 19 better in every way, including the absence of dust.

new 20 - old 5: exposure is OK in each, but focus much better in old 5.

new 21 - old 10: color + focus better in new 21. Good shot of yellow opal on top of clear.

new 22 - old 11 : new 22 better. Good shot of needles over yellow opal over whitish opal.

new 23, old 12: Compositions are quite different. New 23 best in every way.

new 24, old 13: old 13 poorly focused. Better contrast in new 24.

9/15/00 DAP On the following pages are materials relevant to the new U-Th isotopic analyses conducted by Larry Mack at the University of Texas - Austin.

p. 19-20 - Notes to accompany the invoices. This lays out the argument for QA acceptance.

p. 21 - Spreadsheet supplied by Larry Mack. I have added the 2nd and 3rd columns. Note written on p. 21 ~~regarded~~ DAP 9/15/00 explains that data are provisional - however, they are unlikely to change substantially.

pp. 22-26 - Methodology document supplied by Prof. Jay Banner, UT-Austin.

p. 27 - Table of replicate analyses of U and Th concentrations from earlier UT-Austin work.

Notes to accompany two University of Texas invoices titled "Invoice for Isotope Clean Laboratory Analytical Services Acct. 18-0008-62," dated August 30, 2000, and September 13, 2000.

David Pickett
September 14, 2000

Supplied Data

page 21 DAP 9/15/00

The attached hard copy of Microsoft Excel file "Sep 11 2000 Age_data1.xls" shows the data obtained by the invoiced analyses. The Excel file resides on the personal computer in David Pickett's office, Room A217 of Building 189. Sample preparation performed at CNWRA is documented in notebook # 127.

Data Quality

pp 22-26 DAP 9/15/00

Also attached is a statement provided by the University of Texas describing analytical procedures and data quality assurance measures. As noted on the first page, the discussion is excerpted from an unpublished article and so should not be circulated publicly. A final published version will be supplied later. Notable features of the methodology are:

- The procedure is based on established methods accepted in the geochemistry community, using equipment commonly employed, such as the Finnigan-MAT thermal ionization mass spectrometer.
- U and Th concentrations are obtained using solutions traceable to standard reference materials.
- Procedural blank U and Th levels are negligible.
- The discussion in the first paragraph of page 3 concerns age corrections and refers to specific samples from another University of Texas project. The discussion of corrections for initial $^{230}Th/^{232}Th$ is not directly applicable to data quality, because CNWRA will perform its own correction calculations.
- Accuracy of U and Th isotope ratios are established with reference to standard reference materials, interlaboratory standards, and age determinations. Some of the cited references contain further data relevant to accuracy (for example, as discussed in the section on "^{235}U-^{231}Pa Analysis"). The complete reference list will be supplied later with the published article.

Blind Replicates

Blind replicates were not supplied to the vendor because of the time and expense involved in each sample analysis. Three blind replicates were supplied in an earlier set of 34 related analyses

provided by the same vendor. These analyses involved U and Th concentration measurements, which form a major part of the analyses performed in the new work. These analyses involve the same tracer solutions, chemical separation procedures, and equipment used in the new work. As the attached table shows, U and Th concentrations and U/Th ratios were repeated to within five percent. This is an acceptable level of reproducibility considering that no special effort was made to homogenize the powders prior to taking the replicate splits. These results demonstrate the reliability of the laboratory's U and Th measurements.

Sep 11 2000 Age_data1.xls

Sample	NOPI-		Delta 234 U today	238 U ppm	232 Th ppb	232/238 atomic	230/238 atomic	230/234 atomic	232/238 activity	230/238 activity
n99-1	12-SEP1	cc	4.0	48.2	1860	0.0395	0.0000172	0.312	0.0126	1.016
n99-4	19-SEP2	cc, gray	227.0	17.2	193	0.0116	0.0000214	0.318	0.00369	1.263
n99-5	24-SEP1	cc	-0.6	30.2	964	0.0327	0.0000173	0.315	0.0104	1.021
n99-11	166-SEP1-P	cc, gray	551	25.7	1173	0.0468	0.0000245	0.288	0.0149	1.449
n99-16	501-G-SEP3	cc, gray	222	19.4	497	0.0263	0.0000216	0.321	0.00839	1.273
n99-18	436-L1-SEP4	cal	670	47.4	3430	0.0743	0.0000138	0.150	0.0237	0.813
n99-26	499-L3-SEP4	cal,sil	1066	86.1	334	0.00398	0.0000097	0.0853	0.00127	0.571
n99-28	305-L1-SEP4	cal	233	186	289	0.00160	0.0000076	0.112	0.000509	0.446
n99-29	305-L2-SEP1	cal	207	278	256	0.000946	0.0000070	0.105	0.000302	0.412
n99-30	305-L2-SEP4	cal	209	265	458	0.00178	0.0000072	0.108	0.000566	0.423
n99-32	306-SEP4	cal, sil	237	436	527	0.00124	0.0000154	0.227	0.000396	0.910
n99-33	434-SEP2	cal, sil	109	144	4300	0.0305	0.0000030	0.0499	0.00973	0.179
n99-35	458-SEP1	cal, sil	-8.0	109	7865	0.0740	0.0000176	0.323	0.0236	1.037

Sample	NOPI-	230/234 activity	234/238 activity	230/232 activity	Age (Ky)
n99-1	12-SEP1	1.012	1.004	80.6	too old
n99-4	19-SEP2	1.030	1.226	342.3	370 ± 13 ??
n99-5	24-SEP1	1.022	0.999	98.2	too old
n99-11	166-SEP1-P	0.934	1.551	97.2	213 ± 3
n99-16	501-G-SEP3	1.041	1.223	151.7	406 ± 18 ??
n99-18	436-L1-SEP4	0.487	1.669	34.3	68.1 ± 1.3
n99-26	499-L3-SEP4	0.276	2.069	449.6	34.3 ± 0.2
n99-28	305-L1-SEP4	0.362	1.232	876.2	48.2 ± 0.3
n99-29	305-L2-SEP1	0.341	1.208	1364.2	45.0 ± 0.3
n99-30	305-L2-SEP4	0.350	1.209	747.3	46.3 ± 0.3
n99-32	306-SEP4	0.736	1.236	2298.0	136.1 ± 1.6
n99-33	434-SEP2	0.162	1.105	18.4	18.4 ± 0.8
n99-35	458-SEP1	1.045	0.992	43.9	too old

Note - data are subject to revision, and ages are model ages that may be altered by subsequent calculations.

DAP 9/15/00

Methodology of uranium-thorium isotope measurements at the University of Texas at Austin

Note: The description of methods and data for blanks and isotopic standards presented below are excerpted from a manuscript by Musgrove et al., currently under peer review at the Geological Society of America Bulletin. This is being provided at the request of SWRI, and is not to be circulated or copied. A final copy of the complete manuscript will be provided to SWRI when accepted for publication, at which time this document is to be returned to the University of Texas at Austin.

Chemical Separation

Chemical separation procedures followed those detailed in Edwards (1988), Edwards et al. (1987, 1993), and Cheng et al. (2000). Samples were dissolved in concentrated HNO_3, then spiked with ^{229}Th and mixed ^{233}U - ^{236}U ($^{233}U \cong {}^{236}U$) tracers. U and Th tracer solutions were calibrated using gravimetric solutions of New Brunswick Laboratories (NBL) Standard Reference Material 112-A (formerly NBS U960) and purified Th metal prepared by the Standard Materials Preparation Center at Ames Laboratory, Iowa, respectively. U and Th were co-precipitated from the mixed sample-tracer solutions with $FeOH_3$ and purified by ion-exchange chemistry. A two-column separation (750 μL and 160 μL) was performed using Bio-Rad anion exchange resin AG1 X8, 100-200 mesh. Yields are approximately 90% for both U and Th. Total procedural blanks (chemistry plus filament loading) are ≤ 4.0 pg for U and ≤ 2.0 pg for Th.

Mass Spectrometry

Uranium and Th isotopic analyses were conducted at UT using a Finnigan-MAT 261 thermal ionization mass spectrometer (TIMS) upgraded with an ion-counting detection system using a MasCom secondary electron multiplier (SEM). Uranium and Th separates were loaded onto zone-refined Re filaments (pre-screened for Th content) with colloidal graphite and run in single filament configuration. Ionization efficiencies for Th average 0.4 ‰. Instrumental fractionation of U isotopes is corrected using the $^{233}U/^{236}U$ ratio of the tracer. The range of fractionation values observed for U measurements is α = -3.2‰ to +1.5‰ per AMU (mean = -0.8‰; n = 73). Applying this range of fractionation values to the Th isotope measurements has a

negligible effect relative to the analytical uncertainty. In addition, the change in Th isotope ratios during the course of an analysis is less than the analytical uncertainty. Thus, thorium isotope ratio measurements are not normalized for instrumental fractionation.

Abundance sensitivity (tail at mass 237/peak at mass 238) varied within the range 0.6 to 1.1 ppm during the course of this study. To constrain the effects of tailing from the large ^{238}U and ^{232}Th peaks, baselines in the U and Th mass range were profiled in detail under varying run conditions. For the U mass spectrum from 232.5 to 237, the shape of the background between adjacent background positions follows a linear model, and allows precise interpolation and extrapolation of backgrounds from measurements at 233.5, 234.4, and 235.5. Based on similar analysis of the Th mass spectrum, backgrounds are measured at 229.5.

Mass bias in the SEM was determined (following Cheng et al., 2000) to be 0.1 ± 0.6‰ and 0.1 ± 0.2‰ per AMU (lower mass is over-counted), respectively, for the two SEMs used during the course of this study. Normalization for U fractionation also accounts for mass bias and consequently a mass bias correction is applied only to Th measurements (Cheng et al., 2000). The effects of dead time and intensity bias were calibrated by measurements on isotopic standards over a range of ion beam intensities, and a correction for these effects was made to all measurements. The uncertainties associated with the corrections for instrumental fractionation, analytical blanks, backgrounds, mass bias, intensity bias and dead time are small compared with the overall analytical uncertainty on U and Th isotope ratio measurements.

Ages are calculated using the $^{230}Th/^{238}U$ decay equation for closed U-Th systems (Broecker, 1963):

$$\left[\frac{^{230}Th}{^{238}U}\right]_{Act} = 1 - e^{-\lambda_{230}\times T} + \left(\left[\frac{^{234}U}{^{238}U}\right]_{Act} - 1\right) \times \left(\frac{\lambda_{230}}{\lambda_{230} - \lambda_{234}}\right) \times \left(1 - e^{-(\lambda_{230}-\lambda_{234})\times T}\right)$$

$[^{230}Th/^{238}U]_{Act}$ indicates the activity ratio and "T" is the ^{230}Th age. Values for λ_{230}, λ_{234}, and λ_{238} used are 9.1577×10^{-6} y^{-1} (Cheng et al., 2000), 2.8263×10^{-6} y^{-1} (Cheng et al., 2000), and 1.55125×10^{-10} y^{-1} (Jaffey et al., 1971) respectively. The ^{230}Th ages and uncertainties include analytical errors (which are between ± 0.4 and 1% for all except five samples) as discussed above, and corrections for initial ^{230}Th abundance at the time of calcite growth. Age corrections for initial ^{230}Th were calculated using a sample's measured ^{232}Th concentration and an assumed initial $^{230}Th/^{232}Th$ value of 1.5 (±1.5) x 10^{-5}. This value is larger and is a more conservative estimate of initial $^{230}Th/^{232}Th$ than the commonly used ratio of 4.4 (± 4.4) x 10^{-6} (the value for a material at secular equilibrium with an average crustal $^{232}Th/^{238}U$ value of 3.8; e.g., Banner et al., 1991; Dorale et al., 1998). The 1.5 (± 1.5) x 10^{-5} value is constrained by the ages and stratigraphic order of neighboring samples. The corrections to a sample's ^{230}Th age and its associated uncertainty for initial $^{230}Th/^{232}Th$ are smaller than the analytical errors for most samples. Sample ISS2-H-n is the most notable exception, with an error of 5%, because of the very high ^{232}Th content of this sample. The uncertainty in ^{230}Th age that is introduced by the uncertainty in the initial $^{230}Th/^{232}Th$ value is greater for samples with high ^{232}Th contents and for younger samples (e.g., CWN 4-11), for which the fractional error in age introduced by the correction may be large compared to the amount of radiogenic ^{230}Th. Analysis of modern speleothem calcite, the insoluble residues of speleothem calcite, and modern cave drip waters will place more rigorous constraints on initial $^{230}Th/^{232}Th$ values.

NBL Standard Reference Material 112-A was used as a U standard. Uranium isotope compositions are reported as $\delta^{234}U$ in per mil notation:

$$\delta^{234}U = \{[(^{234}U/^{238}U)/(^{234}U/^{238}U)_{eq}] - 1\} \times 10^3$$

$(^{234}U/^{238}U)_{eq}$ is the atomic ratio at secular equilibrium and is equal to $\lambda_{238}/\lambda_{234}$. Note that our $\delta^{234}U$ values are calculated with a newly determined λ_{234} value (Cheng et al., 2000), which gives

a $\delta^{234}U$ value about 3 per mil lower (for materials close to secular equilibrium) than values calculated using earlier decay constant values (e.g., those used in Edwards et al., 1987). Thirty-three measurements over the three-year course of this study yield a mean $\delta^{234}U$ value of -37.0 ± 3.2 ‰ (error = external 2σ). This compares with values reported from the University of Minnesota of -37.1 ± 1.2 ‰ (n=8, error = external 2σ, Edwards et al., 1993, recalculated with the Cheng et al. (2000) λ_{234} value) and -36.9 ± 2.1 ‰ (n=21, error = external 2σ, Cheng et al., 2000). In terms of accuracy, the UT value is in agreement with the true isotopic value of NBL-112a (-36.9 ± 1.7, $2\sigma_{mean}$ of 21 measurements plus systematic errors; Cheng et al., 2000) and is also in agreement within error with values reported by other laboratories (e.g., Chen et al., 1986; Goldstein et al., 1991; Stirling et al., 1995).

^{235}U - ^{231}Pa Analysis

In order to test the accuracy of the ^{230}Th ages, six additional samples were analyzed for both ^{230}Th ages and ^{231}Pa ages at UM. The combined ^{231}Pa and ^{230}Th systems provides two independent chronometers, analogous to those of the U-Pb system, which can potentially be used to constrain diagenetic alteration (Edwards et al, 1997; Cheng et al., 1998). ^{231}Pa ages are based on the radioactive decay of ^{235}U to ^{231}Pa (half-life = 32,760; Robert et al., 1969). The ^{231}Pa age equation is (Ku, 1968):

$$\left[\frac{^{231}Pa}{^{235}U}\right]_{Act} = 1 - e^{-\lambda_{231} \times T}$$

Samples analyzed for U-Pa were also analyzed for U-Th at UM so that comparisons between the dating systems could be made on the same solution. Pa procedures are those of Pickett et al. (1994) modified as described by Edwards et al. (1997). U-Th analyses are modifications of

those of Edwards et al. (1987) and are described in Edwards et al. (1993) and Cheng et al. (2000). Calcite samples of approximately three grams were dissolved and aliquoted into two fractions, one for Pa analysis and one for U-Th analysis. The Pa aliquot was spiked with a ^{233}Pa tracer milked from a solution of ^{237}Np. The Pa, U, and Th fractions were isolated by $Fe(OH)_3$ co-precipitation and ion exchange chemistry and run on a Finnigan MAT 262-RPQ TIMS. Pa and Th were run on single zone-refined rhenium filaments with colloidal graphite. Uranium was run using double rhenium filaments without graphite.

sample #	CNWRA NOPI-#-F	U ppb	% diff	Th ppb	% diff	Th/U	% diff
N99-5	24-SEP1	30800		927		0.030097	
N99-22	24-SEP1 rep	29300	-4.9	924	-0.3	0.031536	4.8
N99-9	164-SEP1	34600		20700		0.598266	
N99-21	164-SEP1 rep	34800	0.6	21900	5.8	0.62931	5.2
N99-31	306-SEP1	461000		643		0.001395	
N99-37	306-SEP1 rep	479000	3.9	666	3.6	0.00139	-0.4

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7/5/01
DAP

Weigh out opal and uranophane samples to send to UT Austin.

Weighing IR-99-1 OPAL 1, IR-99-1 OPAL 2, IR-99-10 OPAL SEP 1, and IR-99-1 Uph 4 into 7 ml teflon vials (Savillex) provided by Larry Mack at UT-Austin. Vials were cleaned and filled with clean H_2O in their lab.

IR-99-1 OPAL 1 — For sample, name NØ1-OPAL-1 to be sent to Austin.

+ chips	15.11209	
empty vial	15.10797	g
	0.00412	g

Add ~1 ml nanopure H_2O to sample vial.
It appears that this used less than half of the sample that was in IR-99-1 OPAL 1.
Note: chips, not powder.
For sample info, see notebook #127, p. 134. Opal was leached in 1M HNO_3, then 1M HCl.

IR-99-1 OPAL 2 — For sample to Austin: NØ1-OPAL-2
Notebook #127, p. 136.

+ chips	15.28499	
empty vial	15.28001	g
	0.00498	

Add ~1 ml nanopure H_2O to sample.
Used much less than ½ of IR-99-1 OPAL 2 sample.
Note: chips, not powder.

IR-99-10 OPAL SEP 1 — for Austin sample: NØ1-OPAL-3
Notebook #127, p. 139. Was leached in 1M HCl.

+ chips	15.05690	
empty vial	15.05059	
	0.00631	g

Add ~1 ml nanopure H_2O to sample.
Chips, not powder.
This was only a small fraction of available IR-99-10 OPAL SEP1.

IR-99-1 Uph 4 — for Austin sample NØ1-UPH-1
Notebook #127, p. 149. Hand-picked uranophane. Very small sample.

+ powder	15.26965	
empty vial	15.26791	
	0.00174	g

Add ~1 ml nanopure H_2O.
Used approximately ½ of sample; perhaps less.
Probably biased toward large grains because smaller grains tended to stick to walls of parent vial (IR-99.1 Uph 4).
Not really "powder"; chips.

Calculate amounts of U in UT-Austin samples:
(U concentrations are from Division 1 data on solns described on p. 14) except Uph, which is stoichiometric guess

NØ1-OPAL-1 : 0.00412 g × 10,200 ppm = 42 μg
NØ1-OPAL-2 : 0.00498 g × 150,000 ppm = 750 μg
NØ1-OPAL-3 : 0.00631 g × 9300 ppm = 59 μg
NØ1-UPH-1 : 0.00174 g × 520,000 ppm = 905 μg

8/27/01 DAP — New U-Th isotopic data are being analyzed in Excel file "Sep 11 2000 Age_data1.xls"

9/3/01 DAP — Received a new file from Larry Mack (UT-Austin) Excel file "Sep 2001 Age-data.xls"
Continue calculations on caliche dates already in hand on file "Sep 11 2000 Age_data1.xls"

9/4/01 DAP — Received another file from Larry Mack with uncertainties added: "Sep 4 2001 Age_data.xls"

All these Excel files are located on D. Pickett's PC "Syreen" and are backed up on a Zip disk labelled "Pickett start 4/23/01."

9/17/01 DAP — The following files were copied to the floppy disk attached to this notebook:
Sep 4 2001 Age_data.xls
Sep 11 2000 Age_data.xls
Final summary of U-Th concs.xls

Calculations of Alpha Decay + Ingrowth in CSNF

2/10/03 DAP — These notes document calculations done for a paper by Pickett and Murphy under 20.01402.871, published in the proceedings of the 2001 MRS. CNWRA QA record # Q200201020004.
Calculations originally were not recorded in a scientific notebook. These support the data in Table I of the paper.
The motivation of this work is the observation of high degrees of alpha daughter product enrichment in groundwaters. Could alpha daughters in commercial spent nuclear fuel (CSNF) be released preferentially, affecting dose, perhaps?

This analysis is based on inspection of Fig. 3-9 and Table 19-1 of the TPA 4.0 user's guide: CNWRA, Total-System Performance Assessment (TPA) Version 4.0 Code: Module Descriptions and User's Guide, 2002.
These are attached on pp 32-34 of this notebook.
Remember: these are for CSNF.
The radionuclides in the figure and table were inspected for those that are products of alpha decay of another inventory radionuclide.

Figure 3-9 (p. 30 of these notes) reveals several radionuclides whose inventories increase by orders of magnitude over 100,000 years. These are:
^{231}Pa – granddaughter of ^{235}U
^{230}Th – daughter of ^{234}U
^{226}Ra – daughter of ^{230}Th
^{210}Pb – product of several alpha + beta decays in chain.
^{233}U – granddaughter of ^{237}Np.
^{227}Ac – daughter of ~~^{231}Ac~~ DAP 2/10/03 ^{231}Pa
^{229}Th – daughter of ^{233}U.

Go to page 35.

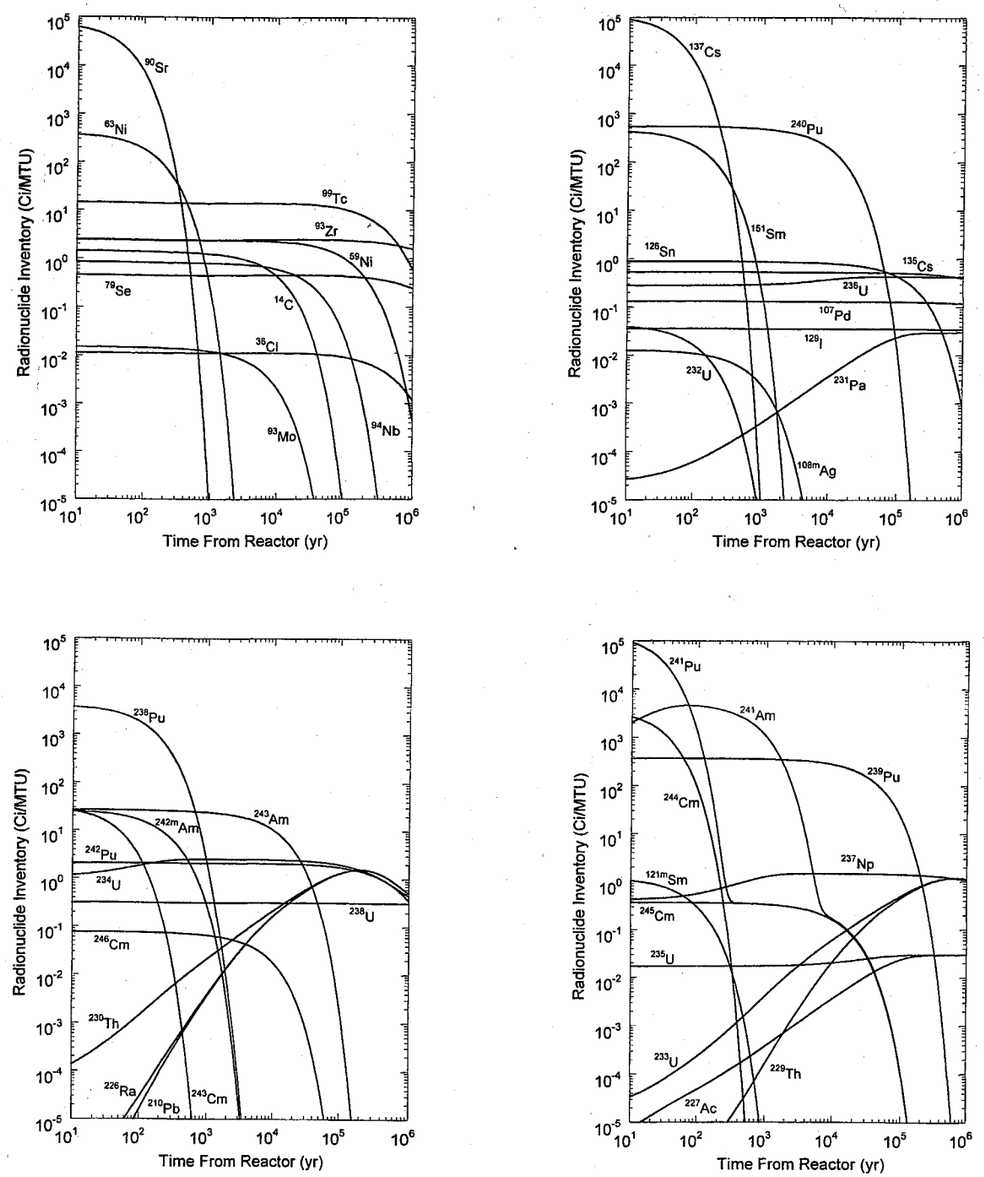


Figure 3-9. Radionuclide inventories as a function of time (calculated by the INVENT module)

From CNWRA's TPA 4.0 user's guide, 2002.

Table 19-1. List of 43 radionuclides in the TPA Version 4.0 code with associated half-lives, isotopic weights, and initial waste package inventories

Radionuclide	Half-life (yr)	Mol. Wt. (Isotopic Wt.)	Initial WP Inventory (Ci/MTU at 10 yr)
^{14}C	5.729×10^{3}	14	1.44×10^{0}
^{36}Cl	3.010×10^{5}	36	1.15×10^{-2}
^{59}Ni	8.000×10^{4}	59	2.44×10^{0}
^{63}Ni	9.200×10^{1}	63	3.72×10^{2}
^{79}Se	6.496×10^{4}	79	4.58×10^{-1}
^{90}Sr	2.912×10^{1}	90	6.25×10^{4}
^{93}Zr	1.530×10^{6}	93	2.47×10^{0}
^{93}Mo	3.498×10^{3}	93	1.51×10^{-2}
^{94}Nb	2.030×10^{4}	94	8.48×10^{-1}
^{99}Tc	2.130×10^{5}	99	1.45×10^{1}
^{107}Pd	6.496×10^{6}	107	1.31×10^{-1}
^{108m}Ag	1.270×10^{2}	108	1.26×10^{-2}
^{121m}Sn	4.997×10^{1}	121	1.04×10^{0}
^{126}Sn	1.000×10^{5}	126	8.85×10^{-1}
^{129}I	1.570×10^{7}	129	3.57×10^{-2}
^{135}Cs	2.300×10^{6}	135	5.36×10^{-1}
^{137}Cs	3.000×10^{1}	137	9.15×10^{4}
^{151}Sm	8.999×10^{1}	151	4.28×10^{2}
^{210}Pb	2.230×10^{1}	210	5.67×10^{-8}
^{226}Ra	1.600×10^{3}	226	4.11×10^{-7}
^{227}Ac	2.177×10^{1}	227	7.51×10^{-6}
^{229}Th	7.339×10^{3}	229	2.75×10^{-7}
^{230}Th	7.700×10^{4}	230	1.37×10^{-4}
^{231}Pa	3.277×10^{4}	231	2.69×10^{-5}
^{232}U	7.200×10^{1}	232	3.93×10^{-2}

From CNWRA's TPA 4.0 user's guide, 2002.

Continued on next page.

Table 19-1. List of 43 radionuclides in the TPA Version 4.0 code with associated half-lives, isotopic weights, and initial waste package inventories (cont'd)

Radionuclide	Half-life (yr)	Mol. Wt. (Isotopic Wt.)	Initial WP Inventory (Ci/MTU at 10 yr)
^{233}U	1.585×10^{5}	233	3.44×10^{-5}
^{234}U	2.445×10^{5}	234	1.18×10^{0}
^{235}U	7.038×10^{8}	235	1.71×10^{-2}
^{236}U	2.341×10^{7}	236	2.81×10^{-1}
^{237}Np	2.140×10^{6}	237	4.34×10^{-1}
^{238}Pu	8.774×10^{1}	238	3.77×10^{3}
^{238}U	4.468×10^{9}	238	3.15×10^{-1}
^{239}Pu	2.406×10^{4}	239	3.69×10^{2}
^{240}Pu	6.537×10^{3}	240	5.44×10^{2}
^{241}Pu	1.440×10^{1}	241	9.22×10^{4}
^{241}Am	4.322×10^{2}	241	2.08×10^{3}
^{242}Pu	3.869×10^{5}	242	2.10×10^{0}
^{242m}Am	1.520×10^{2}	242	2.48×10^{1}
^{243}Cm	2.850×10^{1}	243	2.55×10^{1}
^{243}Am	7.380×10^{3}	243	2.64×10^{1}
^{244}Cm	1.811×10^{1}	244	2.68×10^{3}
^{245}Cm	8.499×10^{3}	245	3.66×10^{-1}
^{246}Cm	4.731×10^{3}	246	7.62×10^{-2}

```
**
constant
ElevationOfRepositoryHorizon[m]
1072.0
**
constant
WastePackagePayload[MTU]
9.76
**
```

The first value is used in the NFENV module and shows the elevation of the upper block of the repository is 1,072 m above sea level. The second constant, in the EBSREL consequence module, indicates the average WP has a waste payload of 9.76 MTU.

(continued from page 31)

Because each of these increases in inventory by at least a factor of 1000, it can be concluded that essentially all the inventory is alpha product by 100,000 (in fact, this can also be said for 10,000 years).

Other alpha daughter radionuclides were studied:

^{239}Pu

Fig 3-9 suggests a negligible inventory increase.
The mass ratio of the parent to ^{239}Pu gives an idea of the relative amount of ^{239}Pu that can grow in over several half-lives of the parent (note that this calculation neglects the differences in atomic weight, which are less than 2%).
Use the 10-year "initial inventory" values from Table 19-1 (pp. 33-34 of this notebook).
Wait - the Table 19-1 data are in Curies per metric ton of uranium. Therefore, I can calculate atom ratios - thus, atomic weights do not come into the calculation.
Because $A = \lambda N$ A = activity, N = number atoms, λ = decay constant (where A & λ have reciprocal units)

~~you can calculate~~ DAP 2/10/03
and $t_{1/2} = \frac{\ln 2}{\lambda}$ where $t_{1/2}$ = half-life (shown in Table 19-1)

you can calculate the atom ratio with

$$\frac{N_1}{N_2} = \frac{A_1 \lambda_2}{A_2 \lambda_1} = \frac{A_1 t_{1/2,1}}{A_2 t_{1/2,2}}$$

So, for $\frac{^{243}Am}{^{239}Pu} = \frac{(26.4\ Ci/MTU)(7380\ y)}{(369\ Ci/MTU)(2.406 \times 10^4\ y)} = 0.022$ atomic

^{239}Pu is the granddaughter of ^{243}Am via short-lived ^{239}Np.

^{243}Cm decays directly to ^{239}Pu.

$$\frac{^{243}Cm}{^{239}Pu} = \frac{(25.5\ Ci/MTU)(28.5\ y)}{(369\ Ci/MTU)(2.406\times10^4\ y)} = 8.2\times10^{-5}$$

These two atomic ratios are very small. Only a small portion of ^{239}Pu will be alpha product. Can neglect in this analysis.

^{235}U

Alpha daughter of ^{239}Pu, which has a half-life of 24,000 years. Figure 3-9 shows ^{235}U has risen and leveled off by ~ 10^5 years. This is ~ five half-lives of ^{239}Pu, so almost all ^{239}Pu has decayed to ^{235}U.

(To calculate precisely: $^{239}Pu\ (10^5 y) = {}^{239}Pu_{init}\, e^{-(100000)(2.88\times10^{-5})}$
$= {}^{239}Pu_{init}\,(0.06)$]

Initial atom ratio (Table 19-1)

$$\frac{^{239}Pu}{^{235}U} = \frac{(369)(2.406\times10^4)}{(0.0171)(7.038\times10^8)} = 0.74$$

Round to 0.7 (considering actually 0.94×0.74 at 10^5 y)

Thus, at 10^5 y, ^{235}U inventory has gone up by a factor of 1.7. The proportion of ^{235}U that has grown in by alpha decay is

$$\frac{0.7}{1.7} = 0.41$$

And ^{235}U decay is slow.

2/12/03
DAP

^{240}Pu

Alpha daughter of ^{244}Cm

Initial $\frac{\text{mass}}{\text{atom}}$ ratio $= \frac{^{244}Cm}{^{240}Pu} = \frac{(2680)(18.11)}{(544)(6537)} = 0.014$

DAP 2/10/03

So, ingrowth negligible (though it all happens in first ~100 years).

^{236}U

Alpha daughter of ^{240}Pu ($t_{1/2} = 6537$ y). At 10^4 y, ^{240}Pu starts decaying relatively rapidly on Fig 3-9.

Initial atom ratio:

$$\frac{^{240}Pu}{^{236}U} = \frac{(544)(6537)}{(0.281)(2.341\times10^7)} = 0.54$$

So, by 10^5 y, ^{236}U goes up by factor of 1.54.

The proportion of ^{236}U in alpha decay sites =

$$\frac{0.54}{1.54} = 0.35$$

and ^{236}U decay is slow ($t_{1/2} = 2\times10^7$ y).

^{241}Pu

Alpha daughter of ^{245}Cm (8499 y $t_{1/2}$), but ^{241}Pu has a short $t_{1/2}$ of 14.4 y. Its inventory goes down rapidly. By ~ 300 y, it is fully supported by ^{245}Cm. (Fig 3-9).

^{241}Am

Alpha ~~daughter of~~ DAP 2/10/03 granddaughter of ^{245}Cm, beta daughter of ^{241}Pu. Initially, decays until reach equil with ^{245}Cm and ^{245}Cm-supported ^{241}Pu. By that time, all are minor inventory components. (Fig 3-9)

^{237}Np

Alpha daughter of ^{241}Am. Fig 3-9 shows a rise in inventory by ~ 5000 y. This is due to decay of some of the ^{245}Cm ($t_{1/2}$ 8500 y), and essentially all of the ^{241}Pu and ^{241}Am because their $t_{1/2}$ are ≤ 430 y and the mass that ends up being supported by ^{245}Cm is negligible compared to initial inventories (Fig 3-9).

Note: ^{237}Np decay is negligible up to 10^5 y ($t_{1/2} = 2\times10^6$ y)

Initial ~~mass~~ atom ratios:

DAP 2/12/03

$$\frac{^{245}Cm}{^{237}Np} = \frac{(0.366)(8499)}{(0.434)(2.14\times10^6)} = 0.0033$$

Can neglect this contribution to ^{237}Np.

$$\frac{^{241}Pu}{^{237}Np} = \frac{(9.22\times10^4)(14.4)}{(0.434)(2.14\times10^6)} = 1.43$$

$$\frac{^{241}Am}{^{237}Np} = \frac{(2080)(432.2)}{(0.434)(2.14\times10^6)} = 0.97$$

$$\overline{2.40}$$

So, by $\sim10^3$ y, ^{237}Np will increase by a factor of 3.4. Thus, the proportion of ^{237}Np that is in alpha decay sites is

$$\frac{2.4}{3.4} = 0.71$$

^{242}Pu

Alpha daughter of ^{246}Cm ($t_{1/2} = 4700$ y). DAP 2/12/03 ^{242}Pu Fig 3-9 doesn't suggest there's much increase.

DAP 2/12/03 initial ~~mass~~ atom ratio:

$$\frac{^{246}Cm}{^{242}Pu} = \frac{(7.62\times10^{-2})(4731)}{(2.1)(3.869\times10^5)} = 0.0004$$

Can neglect. (Note: Assumed a typo in inventory for ^{246}Cm in Table 19-1. By looking at figure 3-9, can see that a minus sign is missing.)

^{238}U

Alpha daughter of ^{242}Pu, which is long-lived ($t_{1/2} = 390000$ y)

DAP 2/12/03 Initial ~~mass~~ atom ratio

$$\frac{^{242}Pu}{^{238}U} = \frac{(2.1)(3.869\times10^5)}{(0.315)(4.468\times10^9)} = 0.0006$$

Can neglect.

^{238}Pu

Alpha daughter of ^{242}Cm and descendant of ^{242m}Am.

Initial mass ratio:

$$\frac{^{242m}Am}{^{238}Pu} = \frac{(24.8)(152)}{(3770)(87.74)} = 0.011$$

Can neglect.

^{234}U

Alpha daughter of ^{238}Pu and descendant of ^{238}U.

Initial activity ratio of ~~^{238}U to~~ DAP 2/12/03 ^{234}U ~~to~~ ^{238}U is ~~(0.315)~~

$$\frac{1.18}{0.315} = 3.7$$

So the increase in inventory seen in fig 3-9 must be due to ^{238}Pu decay.

Initial mass ratio:

$$\frac{^{238}Pu}{^{234}U} = \frac{(3770)(87.74)}{(1.18)(2.445\times10^5)} = 1.15$$

^{238}Pu $t_{1/2} = 88$ y, so all goes to ^{234}U by a few hundred years. ^{234}U goes up by a factor of 2.15, so the proportion of alpha ingrowth sites is

$$\frac{1.15}{2.15} = 0.53$$

DAP 3/1/04

TPA Simulations of Alpha-Related Preferential Release

3/1/04 DAP

This work is a follow-up to that described on pages 31-39. The account number has changed to 20.06002.01.071, but it is still ENFE. The objective is to take what we have learned about potentially enhanced radionuclide release and test its potential dose effect using TPA.

The challenge in using TPA is that we wish to enhance release of only that portion of inventory that has grown in by decay since the waste was emplaced. For Np-237, the inventory consists of two components:

$$X_t = X_i + X_d\left[f(X_p, t)\right]$$

X_t = total inventory $[f(X_i, X_p, t)]$ of Np-237

X_i = initial inventory of Np-237

X_d = ingrown inventory

X_p = parent initial inventory

We want X_d to be released at a higher rate than X_i. It is not practical to create new species in TPA so we must apply the enhancement to the Np-237 total inventory. Because most radionuclides are released congruently with waste form dissolution, with a solubility, the only practical way within TPA to enhance release is to enhance inventory. And because we only want to enhance the inventory of that portion of the radionuclide that has grown in, we can simulate the enhancement by artificially increasing the parent initial inventory. See equation above: increase X_t by

increasing X_d by increasing X_p. X_i is unaffected.

See discussion of Np-237 on pages 37 and 38. Ingrown Np-237 is a function mainly of Pu-241 and Am-241 (contribution from Cm-245 is negligible. It would not be enough to increase the Am-241 initial inventory, even though it is an alpha-emitter and Pu-241 is not. This would fail to account for the portion of Np-237 that grows from Am-241 that has grown from Pu-241. Therefore, you need to increase the initial inventories of both Pu-241 and Am-241 by the same factor.

Note that this approach ensures that radionuclide release will still be subject to solubility limits.

Which radionuclides to study?

Our previous paper, supported by the calculations on pages 31-39, was: W.M. Murphy + D.A. Pickett, "Radioisotope Fractionation and secular disequilibrium in performance assessment for geologic disposal of nuclear waste," Sci. Basis Nucl. Waste Mgt. XXV, MRS Proceedings vol 713, p. ~~558.7.1~~ DAP 3/1/04 867-874, 2002. In Table I, we identified the following radionuclides as having a potentially "high" dose effect based on ingrown proportion of inventory: Pb-210, Ra-226, Th-230, U-233, U-234, Np-237. All of these except U-233 are in the TPA nominal groundwater release scenario model. Therefore, I will test the effect on the five that are included. It is OK to neglect U-233 because it does not become a significant inventory component until well after 10^4 years.

By what factor to enhance release?

In natural systems, U-234 enrichment over U-238 of up to a factor of five is not unusual. In fact, factors of up to ten are observed.

Enhancement is related to some degree by the alpha decay energy. How do the parents of our selected five radionuclides compare to U-238?

Np-237 Am-241 data
Use data from http://ie.lbl.gov/toi/nuclide.asp?iZA=950241

Branching ratio %	alpha energy
84.5	5485.6 keV
13.1	5442.8
1.6	5388.2

* U-234 U-238 data (decays to Th-234 → U-238)
Data from http://ie.lbl.gov/toi/nuclide.asp?iZA=920238

Note: the web data are accessed from http://ie.lbl.gov/education/isotopes.htm

Branching ratio %	alpha energy
79.0	4198 keV
20.9	4151

Th-230 U-234 data (same web source shown above)

71.4 %	4774.6 keV
28.4	4722.4

* Note added 3/5/04 DAP: U-234 is more affected by Pu-238 alpha decay:

Branching ratio %	alpha energy
29.0	5456 keV
70.9	5499 keV

Ra-226 Th-230 data

76.3 %	4687.0
23.4	4620.5

Pb-210 Multiple alpha parents, with energies ranging from 4780 to ~~7830~~ 7687 keV DAP 3/1/04
↑ Po-214, immediate parent.

In all cases, alpha energies exceed those for U-238 decay. ~~Therefore, it is likely to be conservative to use enhancements based on~~ DAP 3/1/04 Therefore, we would not be overestimating an enhancement by basing it on observations of U-238/U-234.

Keep in mind that four of these five are from the same decay series. Need to consider effect of increasing initial inventories of one or all. Probably need to increase all above the radionuclide being tested.

3/1/04 DAP

Preparing for TPA runs

On 2/27/04, copied TPA version 4.1jp files from CD-ROM onto hard drive on my Windows NT desktop named "SYREEN." The directory tpa41jp1kcd was copied from the CD into a directory on the PC named D:\tpa. I also created a directory under D:\tpa called "tpa run." I will use this directory for running the specified input file. All necessary code files are in tpa41jp1kcd.

Go to Control Panels → System → Environment tab and set, under "User variables for dpickett:"

variable	value
TPA-DATA	D:\tpa\tpa 41jp 1kcd
TPA_TEST	D:\tpa\tpa41jp 1kcd

The procedure for running the code is to ① set up "tpa.inp" as desired within D:\tpa\tpa run (make sure keep an unaltered read-only version in D:\tpa\tpa41jp1kcd)

② go to Command Prompt in Start → Programs menu

③ type cd d:\tpa\tpa run

④ type %tpa_test%\tpa

I found that, to ensure a successful run, keep as few other applications open as possible.

Under D:\tpa I created a directory called "my TPA files." After a TPA run, I move all files from D:\tpa\tpa run to a newly created folder under "my TPA files." I delete the *.exe files in the new folder.

I performed three runs with the default tpa.inp values before starting my tests. The names I show were used for the "storage" folders for output files created in "my TPA files"

2-27-04 Basecase 350 realizations

Mohanty et al, 2002, "System-Level Performance Assessment of the Proposed Repository at Yucca Mountain Using the TPA Version 4.1 Code," CNWRA 2002-05, Rev. 1, suggests that 350 realizations are optimal. I edited "tpa.inp" to set 350 realizations (i.e., "NumberofRealizations" = 350) and ran. Took nearly 48 hours to complete.

2-29-04 Basecase 100 realizations

For comparison and to possibly allow faster runs, I set NumberOfRealizations to 100 and ran. Took 13:40 hours to complete

3-1-04 Basecase Mean Value

"tpa.inp" was a copy of the tpameans.out file from the 2-27-04 run. This file is created automatically by TPA and sets all parameters to constants. Those that were stochastic in the original input file are set to their mean values. If distribution was log-based, mean of log is used to calculate mean value. Run took 10 minutes.

Note: in all cases, scenarios in the default tpa.inp were not changed, i.e. Volcanism and Faulting disruptive scenarios were not enabled, but Seismic was.

I noticed that I did not get output files showing intermediate results. (*.ech, *.rlt, *.cum). Take the mean value input file and re-run with "Output Mode (0=None, 1=All, 2=User Defined)" set to 1.

3-1-04 Basecase Mean Value – Re-do

Overwrite previous results. Now will have intermediate results. See above.

Note: want to make sure cumulative release of daughter during simulation period does not exceed inventory that should be present without parent enhancement.

I noticed that the Np solubility limit is different from what R. Pabalan and D. Turner suggested in a Feb 6, 1998, memo to J. Weldy (provided to me by Pabalan). Specifically, the suggested max value of 2.4 kg/m³ is ten times higher than what is in the default tpa.inp. I found discrepancies also for Cm, U, Th, Ra, Pb, ~~Cs~~, Ni, and Nb. In all cases except Np (for which an incorrect max was used), the tpa.inp file assigns a constant value where Pabalan and Turner suggested a distribution.

DAP 3/1/04

I will change my default tpa.inp to accurately reflect their recommendations and place an explanatory note in the file.

Cm old: constant 2.4e-4 kg/m³

new: uniform 2.4e-8 to 2.4e-4 kg/m³
(note: makes lower mean solub limit)

U old: constant 7.6e-3 kg/m³

new: logtriangular
min log ~~(2.4e-7)~~ (2.4e-6) DAP 3/1/04
max log (2.4e+0)
peak log ~~(2. DAP 3/1/04 7.6)~~ (7.6e-3)

Np old: logtriangular
min log (1.2e-3) DAP 3/1/04
max log ~~(3.4e-2)~~ (2.4e-1)
peak log (3.4e-2)

new: logtriangular
min log (1.2e-3)
max log (2.4e0)
peak log (3.4e-2)

Note: for U & Np, one actually enters the values – not logs in tpa.inp.

Th old: ~~loguniform 2.3~~ DAP 3/1/04
constant 2.3e-4 kg/m³

new: loguniform 2.3e-~~7~~ 2.3e-1
DAP 9/30/04

Ra old: constant 2.3e-5

new: logtriangular
min 2.3e-7
max 2.3e-3
peak 2.3e-5

Pb old: constant 6.6e-5

new: logtriangular
min 2.1e-6
max 2.1e-3
peak 6.6e-5

~~Cs~~ ~~old:~~ DAP 3/1/04

Ni old: constant 1.1e-1 kg/m³

new: logtriangular
min 5.9e-5
max 5.9
peak 1.1e-1

Nb old: constant 9.3e-7

new: loguniform 9.3e-8, 9.3e-6

Now, redo 2-22-04 Basecase 100 realizations.
Also change "OutputMode..." to 1.

(Still will need to redo Mean Value)

But place in new directory so can keep old results.
3-1-04 Basecase 100 realizations.

3/2/04
DAP

How did new solubility distributions affect the mean values? Compare tpameans.out from earlier ~~runs~~ DAP 3/2/04 run on Feb 27 (renamed "tpameans.out.basecase" and moved to "my tpa files") with that generated by last night's "3_1_04 Basecase 100 realizations" run (renamed "tpameans.out.basecase.new" and copied to "my tpa files"). Unless noted here mean solubility values were identical in the two data sets.

	old tpameans		new tpameans	
Np	0.0214	kg/m³	0.0461	kg/m³
U	7.6e-3	(const)	3.52e-3	
Cm	2.4e-4	(const)	1.20e-4	
Ni	1.1e-1	(const)	0.0337	

Summarizing by tabulating old values for max, peak, and mean for changed elements. In some cases for old values, max = const. All in kg/m³.

	max		peak		mean	
	old	new	old	new	old	new
Cm	2.4e-4	2.4e-4	—	—	2.4e-4	1.2e-4
U	7.6e-3	2.4	—	7.6e-3	7.6e-3	3.5e-3
Np	2.4e-1	2.4	3.4e-2	3.4e-2	2.1e-2	4.6e-2
Th	2.3e-4	2.3e-1	—	—	2.3e-4	2.3e-4
Ra	2.3e-5	2.3e-3	—	2.3e-5	2.3e-5	2.3e-5
Pb	6.6e-5	2.1e-3	—	6.6e-5	6.6e-5	6.6e-5
Ni	1.1e-1	5.9	—	1.1e-1	1.1e-1	3.4e-2
Nb	9.3e-7	9.3e-6	—	—	9.3e-7	9.3e-7

Note: for both tpameans.out files, set # realizations to one and OutputMode to one.

renamed ebsrel.rlt.3_2_04mean.xls DAP 3/3/04

Run a single-realization run using tpameans.out.basecase.new as tpa.inp.
Call the folder "3-2-04 Basecase New Mean Value."
The "new" mean values are those in the final column in the table on page 48.

$\boxed{\text{Np-237}}$ Now analyze the potential effect of enhanced Np-237 release due to alpha ingrowth.

Look at mean value results: 3_2_04 Basecase New Mean Value."
Want to see EBS release for Np-237, so look at ebsrel.rlt.
Copy Np-237 into Excel spreadsheet; i.e., Ci/yr released Np-237 as a function of time (300 time steps up to 10⁵ years) for each of ten subareas.
Actually, it is easier to open ebsrel.rlt in Excel, then save as Excel file, named "ebsrel.rlt.xls", within 3.2-04 Basecase New Mean Value folder. Total up Np-237 release values for all ten subareas.
Peak release rate is ~~3.82e-2 Ci/yr at~~ DAP 3/2/04 4.01×10^{-2} Ci/yr at ~~72,1000~~ DAP 3/2/04 72,100 yr.
For the compliance period, the peak is 2.15×10^{-3} Ci/yr at 10,000 yr. No releases until 8290 y.
Parent Am-241 peak release is 3.85×10^{-5} Ci/yr at 72,100 yr.
Pre-10,000 peak is 2.15×10^{-5} Ci/yr at 9110 yrs.
Now look at dose using rgwna.tpa in Excel file as rgwna.tpa.xls.
Np-237 dose peak: 3.71×10^{-3} rem/yr at 10^5 yr.
There is no dose before 10,000 yr. This is likely due to the mean values for Ra and Rn through the system.
Compare with peak total dose of 3.82×10^{-3} rem/yr at 10^5 yr; 3.46×10^{-5} rem/yr at 10^4 yr.
So, at 10^5 yr, Np-237 is the major dose contributor.
At 10^4 yr, it is I-129 and Tc-99.

Now look at 3-1-04 Basecase 100 Realizations, which also had the new solubility numbers.
It is going to be very cumbersome to try to extract the mean EBS release history for Np-237.
This type of information is not automatically output in an easy-to-use format. Furthermore, the file containing the relevant data (ebsrel.rlt) is 92 MB.
Therefore, I will only look at dose for multivector runs.
Well, maybe useful to look at cumulative EBS release.
3/3/04 DAP Paste Np-237 rows from ~~ebs~~ DAP cumrel.res into Excel spreadsheet an calculate average of the 100 realizations of "ebscumrl" or cumulative release from the EBS, in Ci. Average is 2.95×10^3 Ci.
Minimum is Ø, Maximum is 3.11×10^4 Ci.
Name Excel file "cumrel compilation," and this worksheet ~~"3204 100 realiz."~~ DAP 3/3/04 "3104 100 realiz."

Average for UZ cumul release is 1.52×10^3 Ci, for SZ " " 6.60×10^2

Note: These are 100,000 year values.
10,000 years calculated same way from file cumrel.c.res:

DAP 3/3/04 ~~EBS~~	max	min	avg	
UZ	1.23×10^2	0	3.21	Ci
SZ	7.08×10^{-2}	0	1.15×10^{-3}	Ci
EBS	2.23×10^2	0	6.70	Ci

Look at same values from "3-2-04 Basecase New Mean Value"
No need to use spreadsheet; just one realization cumrel.res, 100,000 y cumul release for Np-237

EBS	1.15×10^3 Ci
UZ	5.67×10^2
SZ	5.36×10^1

cumrel.c.res ~~cumrel.res~~, 10,000 y:

EBS	2.77 Ci
UZ	1.21
SZ	Ø

DAP 3/3/04

Want to check case with higher solubility limits.

Create "tpameans.out.basecase.new.maxsolubs" modified from "tpameans.out.basecase.new" with the following changes

Solubility Np [kg/m³]	from	4.6e-2	to	2.4
Solubility U [kg/m³]	from	3.5e-3	to	2.4
Solubility Th [kg/m³]	from	2.3e-4	to	2.3e-1
Solubility Ra [kg/m³]	from	2.3e-5	to	2.3e-3
Solubility Pb [kg/m³]	from	6.6e-5	to	2.1e-3

Note that, when look at other radionuclides, may want to avoid increasing parent solubility, which may negate the ingrowth effect if more soluble.
So, make separate solubility-enhanced input file for each radionuclide
"tpameans.out.basecase.new.maxnp"
Change tpameans.out.basecase.new by changing Solubility Np [kg/m³] from 4.6e-2 to 2.4

Run TPA 4.1; using this Np max input.
"3-3-04 Basecase Mean Value Max Np"
Open ebsrel.rlt as Excel file and name it ebsrel.rlt 3_3_04meanmaxNp.xls.
~~Calculate~~ DAP 3/3/04 Total up releases for Np-237 (Ci/yr rate) for all subareas and find peaks.
100,000 y: peak is 4.01e-2 Ci/yr at 72,100 y
10,000 y: peak is 1.32e-2 Ci/yr at 8900 y.
Compared to using mean Np solubility, the 100,000 value is the same, the 10,000 yr value is six times higher; suggests that pre-10,000, Np-237 is ~~not~~ DAP 3/3/04 solubility-limited for the mean-value case.
(compare to page 49)

Compare cumulative release.

		10^4 y	10^5 y
Max Np solub	EBS	1.52e1 Ci	1.15e3 Ci
	UZ	7.41eØ	5.69e2
	SZ	Ø	5.51e1

Compared to mean value run (bottom p. 50), cumulative Np-237 release is 5.5 times higher for EBS for 10^4 yrs, and the same for 10^5 yrs.

For max Np, look at dose with ngwma.tpa:
No Np-237 dose for 10^4 yr
peak dose of 3.75×10^{-3} rem/yr at 10^5 yr. A little higher than mean value case (3.71×10^{-3}).

Now, test parent enhancement approach.

tpameansout.basecase.new.NpParent5X

Make this file by altering tpameans.out.basecase.new by – wait – Pu241 is not in the basecase set of radionuclides. Need to add its contribution to Am241 up front. Following the approach on page 35-38 calculate initial atom ratio of Pu241 to Am241

$$\frac{^{241}Pu}{^{241}Am} = \frac{(9.22 \times 10^4)(14.4)}{(2080)(432.2)} = 1.48$$

Therefore, initial Am241 inventory should be increased by this factor.

However – I just discovered that inventory is not tracked in tpa.inp. Initial inventories are in nuclides.dat in the ..\tpa41jp\kcd\data folder. Preserve a copy of the original installed version (date 4/30/01) in the TPA folder.

Modify the copy still in "data" thus:

Pu241,	Ci/MTU from	9.22d+04	to 4.61d+05
Am241,	" "	2.08d+03	to 1.04d+04

These are each a factor of five higher.

Not used DAP 3/3/04

This file needs to still be named nuclides.dat, so the old version gets deleted. (Thus, I'd saved a copy.)

Run using tpameans.out.basecase.new:
"3-3-04 Basecase Mean Value Np Parents 5X" folder
This has mean Np solubility value.
Open ebsrel.rlt in Excel and save as
"ebsrel.rlt.3-3-04meanNpParents5X.xls"
Total Np-237 release from all subareas; Ci/yr:
100,000 y peak is 1.40e-1 at 72,100 yr
10,000 y peak is 2.20e-3 at 10,000 yr
Compare to mean value results on page 49.
100,000 y peak is 3.49 x higher
10,000 y peak is only a factor of 1.02 higher.
Why? → Solubility-limited release.
So run same case with Np solubility at its maximum value of 2.4 kg/m³.
"3-3-04 Basecase Mean MaxNp Parents 5X"
i.e., mean value, Np at max solubility, Am-241 + Pu-241 inventories 5x higher.
As before, create Excel file "ebsrel.rlt.3-3-04meanMaxNpParents5X.xls"
Total Np-237 release from all subareas, Ci/yr
100,000 y peak is 1.42e-1 at 72,100 y
10,000 y peak is 4.65e-2 at 8900 y.
Again, 10^5 y peak release is unaffected: not solubility limited.
~~10^4 y peak is~~ DAP 3/3/04 It is still, however 3.54 times higher than case without parent enhancement and mean Np solubility.

☆ Note: good thing about pre-10,000 y case is you don't have spring effect of parent release possibly skewing results.
10,000 y case: peak is 21.1 times higher than mean solub case with enhancement, or 3.52 times higher than case with max Np solub but no enhancement (p. 51).

Two questions

1. Why a factor of ~3.5 higher peak release rate when solubility limit is not a factor?
Our 2002 MRS paper (reference on page 41) showed that by a few thousand years, 71% percent of Np-237 inventory is produced by alpha decay. We are enhancing that portion of inventory by a factor of five. 5 x 0.71 = 3.55 — this is the artificial inventory enhancement. So TPA is essentially getting the same result as we got early — when we remove solubility as a factor.

2. Why is Np-237 solubility-limited for pre-10,000 years but not for 10,000 – 100,000 years?
Talking to S. Mohanty and looking at "TPA Version 4.0 Code: Module Description and User's Guide," CNWRA, January 2002, see that infiltration is higher after 10,000 years than before – a result of the climate model. Looking infilper.res output file from any of my mean-value runs, can see change in water availability:

	7900 years	55,000 years
average UZ infiltration	13.2 mm/yr	36.7 mm/yr
average flow after reflux	6.0	36.7
average flow after diversion	0.27	1.6

Reflux and diversion show an even greater contrast than infiltration – due to cooling and, thus, diminishment of thermal effects.
So, with much more water flowing through the waste package in later years – if waste form degradation rate is relatively unchanged – there is more water available for diluting radionuclides, so concentrations are smaller. Thus, solubility limit is less likely to be a factor.

Because release values for Np-237 are not scaling directly with solubility limit, at some point between the mean and maximum solubility values for Np, release becomes non-solubility-limited.

Look at cumulative release for Np-237.

see revised page DAP 3/3/04

		10^4 y		10^5 y	
Max Np solub, Parents 5X	EBS	5.39e1	Ci	4.06e3	Ci
from cumrel.res and	UZ	2.62e1	Ci	2.01e3	Ci
cumrel.c.res	SZ	Ø	Ci	1.95e2	Ci

These are all ~3.5 times higher than the non-parent-enhanced results, top of page 52.

Dose: Max Np Parents 5X using rgwna.tpa
100,000 yr : peak dose 1.33e-2 rem/yr Np-237
10,000 yr peak dose: none Np-237

Mean Solub Parents 5X
100,000 yr peak dose : 1.30 e-2 rem/yr "
10,000 yr peak dose: none "

Compare to non-parent-enhanced
~~New~~ Mean Value (such Np) "
100,000 yr peak dose : 3.71 e-3 rem/yr "
10,000 yr : none "

New Mean Value Np Max: ~~3.~~ DAP 3/3/04
100,000 yr peak dose: 3.75 e-3 rem/yr "
10,000 yr : none "

Corresponding parent-enhanced results are 3.50 – 3.55 times higher.

Cumulative release for Parent 5X, Mean Np Solub case
(3_3_04 Basecase Mean Value Np Parents 5X)
files cumrel.res and cumrel_c.res

		10^4 y	10^5 y
Np-237	EBS	2.77e0	4.05e3 Ci
	UZ	1.21e0	2.00e3
	SZ	0	1.86e2

10^5 yr results just slightly lower than max Np results.
10^4 yr results are ~ $\frac{1}{20}$ of max Np solub results.

Compared to Mean Solub case with no parent enhancement, (p. 50), 10^5 yr results are ~3.5 times higher. 10^4 yr results are the same. Solubility limited in earlier period, as usual.

Do a 100-realization run with Parent 5X enhancement. Use revised tpa.inp with new solubility data, and use altered nuclides.dat with enhanced Pu241 and Am241.

3/4/04 DAP

Run halted because taking too long. Only 74 realizations over ~10 hours. Nevertheless, retain results in folder "3_3_04 Basecase Np Parent 5X 100 realizations."
Some results are available, reflecting 73 realizations.
gwpkdos.res and gwpkdos_c.res show peak dose and individual radionuclides at time of peak dose for 10^5 yr and 10^4 yr, respectively.
10^4 yr - open in Excel, save as
~~gwpkdos_c.res.3_3_04mean~~ DAP 3/4/04
DAP 3/4/04 gwpkdos_c.res.3_3_04Np Parents5X100.xls
Of 73 realizations, in only 9 does Np-237 yield a dose. And in only one of those is the Np-237 portion of peak dose significant: 4.62×10^{-5} of 1.61×10^{-4} rem/yr at 10^4 years (vector 23).
Can't conclude much here.

Now look at gwpkdos.res for 10^5 yr results. Don't really need to open in Excel.
On second thought, yes, open in Excel and save as gwpkdos.res.3_3_04NpParents5X100.xls"
For 73 realizations, the average peak Np-237 dose is 4.19×10^{-2} rem/yr at ~ 78,000 yrs.
Total peak dose average is 4.27×10^{-2} rem/yr.
Even though peak Np-237 doses are not tabulated, this gives you a good idea that it is the dominant dose contributor.
Compare to earlier basecase 100 realization run (p 50).
It has a peak Np-237 dose of 1.39×10^{-2} rem/yr at 98,000 yr. Factor of 3.1 times lower.
Need to make an apples vs apples comparison.

TPA is running too slowly on my PC. Install on "BEMORE" Windows XP and use.
Check installation by running single vector mean value case with Np parents enhanced 5X in nuclides.dat.
Get same peak Np-237 dose of 1.30×10^{-2} rem/yr at 10^5 yr - see old run on page 55.
Also compare cumrel.res and cumrel_c.res to results on top of page 56. Identical.
Installation OK.
"TPA" folder has same structure as on SYREEN and is located at D:\dpickett\
BEMORE is located in Room A251.

Run a baseline 350 realization run with
- new solubility distributions (pages 46-47)
- Default nuclides.dat (i.e., not 5X enhanced)

In "data" directory, change name of altered nuclides.dat to nuclides.dat.npenhanced and place old nuclides.dat back in "data."
(copy, so old version copy remains in "TPA" folder)

My default "tpa.inp" file, located in "tpa4ljplked," has new solubility limits of pages 46-47. Copy over to "TPA run" and change NumberofRealizations to 350 and OutputMode to 1.
Start run at 10:08 AM
Finished at 2:10 PM. Four hours.

Move most ~~oft~~ DAP 3/4/04 of the files across the network to a folder on my hard drive named "3_4_04 Basecase New 350 Realizations"
(I left behind the very large *.rlt and *.ech files.)

Remove "nuclides.dat" from "data" folder and change "nuclides.dat.npenhanced" to "nuclides.dat."
Start new 350 realization run. Am-241 and Pu-241 are enhanced 5X. (bottom p. 52).

3/5/04 DAP Move most of the output files across the network to to a folder on my hard drive:
"D:\tpa\my TPA files\ 3_4_04 Basecase New Np Parent 5X 350 Realizations"

Look at p. 54 argument concerning factor ~3.5 increase in Np-237 with 5X parent enhancement. Correct?
Go back to page 38. Based on those calculations, by number of atoms:
initial Np = x (say)
initial Pu-241 = 1.43 x
initial Am-241 = 0.97 x
By a few thousand years, all Pu-241 and Am-241 have decayed, so:
total Np-237 = x + 1.43x + 0.97x = 3.4x
If initial Pu-241 and Am-241 are five times higher, by a few thousand years:
total Np-237 = x + 5(1.43x) + 5(0.97x)
= 13.0 x

5X DAP 3/5/04

So, the parent enhancement effect on Np-237 inventory should be $\frac{13.0}{3.40} = 3.82$

This is ~10% higher than observed values around 3.5. Why? Don't yet know, but the difference is not significant, for my purposes.

$\boxed{\text{U-234}}$ Parent enhancement effect.
Calculations on page 39 showed that Pu-238 alpha decay is most responsible for U-234 increased inventory.
Let's check whether or not U-238 could have a significant effect, and what Pu-238 and U-238 contribute to ingrowth also of Th-230, Ra-226, and Pb-210.
Use the code RADDECAY 2.02, by way of executable RAD2000.EXE. Code is from Oak Ridge National Laboratory, and calculates simple decay and ingrowth.
Calculate how much activity of radionuclides is produced by the starting inventories of parents up the chain. Initial inventories are taken from the table reproduced on pp. 33 + 34. Half-lives in RADDECAY are consistent with the same table

3770 Ci Pu-238

	1000 y	10,000 y	100,000 y
U-234	1.35 Ci	1.32 Ci	1.019 Ci
Th-230	0.0106	0.113	0.6843
Ra-226	0.0018	0.0882	0.6770

0.315 Ci U-238

	1000 y	10,000 y	100,000 y
U-234	0.0069	0.0088	0.0778
Th-230	4×10^{-6}	0.00039	0.0275

U-234 ingrowth from U-238 versus Pu-238 is small at 1000 y and 10,000 y. At 100,000 y, U-238 contribution is 7% of total ingrowth. I believe this can be neglected in enhancement because enhancing U-238 inventory five times is especially artificial. 7% difference is not significant.

Now for other three decay daughters

1.18 Ci ~~U-238~~ U-234 DAP 3/5/04

	1000 y	10,000 y	100,000 y
U-234	1.18	1.15	0.889
Th-230	0.0106	0.100	0.597
Ra-226	0.0020	0.0781	0.591

(Pb-210 will track Ra-226)

1.37×10^{-4} Ci Th-230

	1000 y	10,000 y	100,000 y
Th-230	1.36×10^{-4}	1.25×10^{-4}	5.57×10^{-5}
Ra-226	4.79×10^{-5}	1.26×10^{-4}	5.69×10^{-5}

(Pb-210 will track Ra-226)

Th-230: Total ingrown is

1000 y	10,000 y	100,000 y
0.0212	0.213	1.31

Contributions from Pu-238 and U-234 dominate (100%, 100%, and 98%, respectively)

Ra-226 and Pb-210: Total ingrown:

1000 y	10,000 y	100,000 y
0.0038	<0.167	<1.30

Contributions from Pu-238 and U-234 dominate (100%, 100%, and >97%, respectively)

Conclusion: we can simulate the alpha daughter effect by enhancing the following parents:

U-234 : Pu-238
Th-230 : Pu-238 and U-234
Ra-226 : Pu-238 and U-234
Pb-210 : Pu-238 and U-234

Apply Pu-238 to Mean Value TPA case.

3_5_04 Basecase Mean Value Pu238 5X (folder name)

For tpa.inp use "tpameans.out.basecase.new," which was generated on page 48. Mean Value, with new solubility distributions. One realization.

In "nuclides.dat" in "data" folder, change Pu238 inventory from 3.77d+03 to 1.89d+04, an increase of a factor of five.

(Checked that Pu-241 and Am-241 were original values - not the enhanced values used for Np runs.)

Look at cumulative U-234 releases:

cumrel-c.res (10^4 y):	EBS	6.20e-4 Ci
	UZ	2.71e-4
	SZ	∅
cumrel.res (10^5 y):	EBS	4.20
	UZ	2.63
	SZ	1.91e-2

Compare to "3_2_04 Basecase New Mean Value" (no enhancement)

cumrel-c.res (10^4 y)	EBS	4.19e-4 Ci
	UZ	1.83e-4 Ci
	SZ	∅
cumrel.res (10^5 y)	EBS	2.84
	UZ	1.78
	SZ	1.29e-2

DAP 3/5/04

Enhanced case, cumulative EBS releases are a factor of 1.48 higher for both time periods relative to basecase unenhanced.

Solubility should not be an issue, because U-234 is a minor isotope of U by mass.
Again, neglecting U-238, look at number of atoms based on calculation on page 39:

initial U-234 = x (say)
initial Pu-238 = $1.15x$

Pu-238 half-life is 87.74 y, so after 1000 years:

DAP 9/30/04 U-234 = $x + 1.15x = 2.15x$

If initial Pu-238 is set five times higher, this 1000-year value would be:

U-234 = $x + 5(1.15x) = 6.75x$

So inventory is raised, by the enhancement, a factor of $6.75/2.15 = 3.14$

I do not yet know why the apparent inventory increase from TPA runs is only 1.48. Need to investigate.

3_5_04 Basecase Mean Value Max U Pu238 5X

In tpa.inp (mean value), raise Solubility_U[kg/m³] from 3.5e-3 to 2.4 (see pages 46-48).
Still use enhanced Pu238 in nuclides.dat.

U-234 cumrel-c. res	(10^4) y	EBS	0.422 Ci
		UZ	0.185
		SZ	Ø
U-234 cumrel.res	(10^5 y)	EBS	1528
		UZ	898
		SZ	13.0

Compared to mean U solubility case (p. 61), the two 10^4 y results are a factor of ~680 higher — consistent with the factor by which solubility was increased. It makes sense for U solubility to affect cumulative release because, though the isotopic proportion of U-234 is higher, the total mass of U released is also higher when the solubility limit is higher.

For 10^5 y results, EBS cumulative release is a factor of $1528/4.20 = 364$ times higher than mean U solubility case (p. 61). UZ is $898/2.63 = 341$ times higher and SZ is $13.0/0.0191$ 680 times higher. This makes sense in terms of cumulative relative depletion of U-234 from the waste form due to preferential release. Thus, as time passes, the source has a continually lower 234/238 ratio — and this goes down faster at higher solubility because total U is removed faster. The SZ value is ~~the same as the~~ DAP 3/5/04 increased by the same factor as the 10^4 y EBS and UZ values because, by 10^5 y, it is releasing the U that came through the EBS and UZ during the first 10^4 y.

But see p. 65 DAP 3/7/04

3_5_04 Basecase New Pu238 5X 350 Realizations

On "BEMORE", start another 350-realization run.
Ensure that tpa.inp has (1) new solubility distributions
(2) 350 realizations
(3) OutputMode = 1

Use old default nuclides.dat, but change Pu238 inventory from 3.77d+03 to 1.89d+04, an increase of a factor of five.

3/6/04 DAP Over the network, move all but the largest output files from this run to my PC at:
D:\tpa\my TPA files\3_5_04 Basecase New Pu238 5X 350 realizations

This run is for U-234 alpha daughter enhancement.

3_6_04 Basecase New Pu238 U234 5X 350 Realizations

On "BEMORE", use the same tpa.inp file, but change nuclides.dat so that U234 inventory is changed from 1.18d+00 to 5.90d+00, a factor of five.
Pu238 is still enhanced at 1.89d+04. Start run.
This run is for enhancement of Th-230, Ra-226, and Pb-210.

3/7/04 DAP

3_7_04 Basecase New Np Parent 10X 350 Realizations

On "BEMORE." Same tpa.inp and nuclides.dat as analogous 5X run described on page 58, except that, in nuclides.dat:

DAP 9/30/04

Pu241 = 9.22d+05 Ci/MTU
Am241 = 2.08d+04 Ci/MTU

These are ten times higher than default values.

Back to U234. Want to compare 5X results with max U solubility to non-enhanced U solubility max. I have not yet done a max-U-solubility, non-enhanced TPA run. Set up on my PC:

"3_7_04 Basecase Mean Value Max U"

Single-realization with mean-value tpa.inp, except Solubility_U[kg/m³] is set to 2.4. Use the same tpa.inp as for "3.5.04 Basecase Mean Value Max U Pu238 5X" (p. 62), but use default nuclides.dat (no parent enhancement).

U-234 Cumulative release:

cumrel-c.res (10^4 y)	EBS =	0.285	Ci
	UZ =	0.125	
	SZ =	∅	
cumrel.res (10^5 y)	EBS =	1032	Ci
	UZ =	607	
	SZ =	8.80	

The Pu238-enhanced results (p. 62), compared to these, are all a factor of 1.48 higher.

~~General conclusions:~~

~~1. As expected, solubility does not limit the magnitude of the effect of the enhancement~~

DAP 3/7/04

~~1. As expected, the magnitude of the enhancement is not affected by the solubility limit until U234 depletion starts showing up (Max case). The ratio of releases with max~~

Compare max U solubility case (p. 64) to mean solub case (p. 49, 61).

Neither is enhanced.

		max U / mean		
10^4 y	EBS	0.285/9.19e-4	=	680
	UZ	0.125/1.83e-4	=	683
10^5 y	EBS	1032/2.84	=	363
	UZ	607/1.78	=	341
	SZ	8.8/0.0129	=	682

This shows that U release is solubility-limited for the mean-value case up to 10^4 y, and raising the solubility limit by a factor 680 yields the same factor increase in release: even at the high limit, it is solubility-limited for pre-10^4 y. At later times, EBS release increases but not by as much (363). Therefore, for the mean value case, U release was solubility-limited, but is not for the max solubility case after 10^4 y. This is consistent with the Np-237 results – see page 54. Higher flow rates later → lower aqueous concentrations. On average, U ~~solubility limits~~ concentrations after 10^4 years, are between the mean and maximum values for solubility limit. DAP 3/7/04

This is a correction to the discussion on p. 63.

The enhancement effect is the same, independent of solubility limits. This makes sense, because U234 is a minor isotope → its release does not affect U solubility limit versus concentration, unlike Np case.

Still don't know why factor increase is only 1.48.

3_7_04 Basecase Mean Value Pu238 10X

Same as analogous 5X case (p. 61), but Pu238 in nuclides.dat is set to 3.77d+04 Ci/MTU – ten times higher than default. U solubility is mean.

U-234 cumulative release

cumrel_c.res	(10^4 y)	EBS =	8.70e-4 Ci
		UZ =	3.81e-4
		SZ =	Ø
cumrel.res	(10^5 y)	EBS =	5.89
		UZ =	3.69
		SZ =	2.69e-2

Compare to 5X and non-enhanced, mean value runs on page 61.

Compared to 5X, these results are all 1.40 to 1.41 factor higher. Would expect ~twice as high. Actually, using calculation analogous to that on p. 62, would expect this case to be 1.85 times higher than 5X, 5.81 times higher than non-enhanced. It is 2.07 times higher than non-enhanced.

3_7_04 Basecase Mean Value All U234 Parents 5X

Use same tpa.inp as for previous run, with mean solubilities and one realization. This time in nuclides.dat, set initial inventories of all U-234 parents five times higher than default

Change

Cm246	from	7.62d-02	to	3.81d-01 Ci/MTU
Pu242	from	2.10d+00	to	1.05d+01
U238	from	3.15d-01	to	1.58d+00
Am242m	from	2.48d+01	to	1.24d+02
Pu238	from	3.77d+03	to	1.89d+04

Look at cumulative U-234 release

cumrel_c.res	(10^4 y)	EBS =	1.24e-4 Ci
		UZ =	5.41e-5
		SZ =	Ø
cumrel.res	(10^5 y)	EBS =	0.838
		UZ =	0.525
		SZ =	3.82e-3

Unexpectedly, these are lower than the case when only Pu238 was raised 5X. ?? (p. 61)

~~Compare tpa.inp for the two cases.~~ DAP 3/7/04

The new results divided by the Pu238-enhanced-only results equals 0.2. Hmmm..

Compare tpa.inp for the two cases: no differences

Compare nuclides.dat files: Pu238 is the same, and U238, Cm246, Pu242, and Am242m are, in fact, five times higher in the 3_7_04 case.

Wait – I think this is because we are raising the U concentration in the waste by a factor of five – thus, U-234 is "diluted" in the waste U, and thus dissolved U, by a factor of five. OK. Can explain. ✓

So, another good reason to not raise a parent inventory artificially if it is the same element as the daughter.

3_7_04 Basecase Mean Value All U234 BUT U238 5X

Same as previous run, except U238 inventory in nuclider.dat set back to 3.15d-01.

Cumulative U-234 release

cumrel_c.res	(10^4 y)	EBS =	6.20e-4
		UZ =	2.72e-4
		SZ =	Ø
cumrel.res	(10^5 y)	EBS =	4.20
		UZ =	2.63
		SZ =	1.91e-2

These are the same as the Pu238-only results (p. 61). So, using Pu238 is good enough. Problem is elsewhere.

Return to Np-237

Have already compiled and totalled Np-237 EBS release rates with time in four Excel files – see pp. 49, 51, 53 – for Base case Mean Value, with max Np, with + without parent enhancement. Combine the total EBS results in a single Excel file "Compiled Np Mean Value runs.xls"

DAP 3/7/04

Compile 350-realization release and dose results

"Compiled Np Mean Value runs.xls"
This Excel file brings together the total Np-237 release rate from the EBS for all subareas for each of four mean value TPA runs. The data are from the corresponding ebsrel.rlt output file for each. Shows EBS's release rate versus time. The included mean value runs are:
3_2_04 Basecase New Mean Value
3_3_04 Basecase Mean Value Max Np
3_3_04 Basecase Mean Value Np Parents 5X
3_3_04 Basecase Mean Max Np Parents 5X.
Plots were saved within the new Excel file, which is located on my PC at "D:\TPA\my TPA files"

3/8/04 DAP

"rgwsa.tpa.compil.350.xls"
This Excel file, also at "D:\TPA\my TPA files," compiles dose results versus time averaged over all realizations, for the 350-realization runs. Included are the basecase and parent-enhanced runs, with total dose and dose by radionuclide for Np-237, U-234, Th-230, Ra-226, and Pb-210.
Source files are rgwsa.tpa (total dose) and rgwna.tpa (dose by radionuclide), which show groundwater dose histories, from these runs:
3_4_04 Basecase New 350 Realizations
3_4_04 Basecase New Np Parent 5X 350 Realizations
3_5_04 Basecase New Pu238 5X 350 realizations
3_6_04 Basecase New Pu238 U234 5X 350 Realizations
Plots of dose versus time were saved in the Excel file.

3/9/04 DAP

How much Np-237 is available for release from initial failures? In mean value case, the fraction of failed packages – initially defective – is 5.05×10^{-3}.
Total repository waste is 70,040 MTU.
Thus, available waste is 354 MTU.

Initial Np-237 inventory is 0.434 Ci/MTU (p. 34).
Within a few thousand years, this grows to ~~1.548~~ 1.476 Ci/MTU (p. 38). DAP 3/4/04

Thus, available Np-237 is 354 MTU × 1.476 Ci/MTU
= 522 Ci
(mean value case, initial failures)
DAP 3/9/04

In "Compiled Np Mean Value runs.xls," I calculated an estimated cumulative release of Np-237 from the EBS using the release rate at each time step times the length of the time step. These values do not reach above 136 Ci for all Np mean value cases until after the corrosion failures at ~70,000 years. Thus, the drop off in release rates at ~10,000 years is not due to large inventory depletion. see page 70. DAP 3/11/04

3/10/04 DAP

Take original tpa.inp file installed on 2/27/04 (pp. 43-44) and copy to D:\TPA. Set Realizations to 350 and OutputMode to 1. Check that has old solubility values. Name it:
tpa.inp.oldsolub.350.outputmode1
Copy to S:\DDiduett

Corrected on p. 70 DAP 3/11/04

At BEMORE (Dell PC), copy this file to my TPA directory, then copy to TPA\TPA run and rename tpa.inp. Run TPA.
Create folder for results:
3_10_04 Basecase 350 old solub.

Note: used command %tpa_test%\tpa_ >tpa.out
to create an output file that captures screen output. (Downside to this is that you don't see most of the screen output.)

3/11/04 DAP

Copy all but largest output files to S:\DPickett.

Use same ("old") tpa.inp and set nuclides.dat so that Pu-241 and Am-241 are five times larger (see p. 52).

WAIT! Found error. nuclides.dat had 10X increases in Pu-241 and Am-241 — left over from 3/7/04 run. Change name of 3/10/04 results to

3_10_04 Basecase 350 old solub Np parents 10X

Now, run non-enhanced case again. Use same tpa.inp (see above), with 350 realizations and old solubility values. Copy original nuclides.dat (modification date 4/30/2001) into "data," overwriting "10X" file.

New TPA run:

~~3_10~~ DAP 3/11/04

3_11_04 Basecase 350 old solub

Go back to Np-237 inventory questions addressed on pp. 68-69. Not all the spent fuel in a waste package is seen by the water, so not all the inventory is being depleted. The relevant parameters are "SF Wetted Fraction ..." In the mean value case these values are all 0.5. Thus, only ½ the inventory is available for release. So, adjusting calculations on page 68-69 available Np-237 is 261 Ci.

Wait — another factor is the Sub Area Wet Fraction. It is also 0.5 in the mean value case. So, available Np-237 is actually 131 Ci.

Look at "Compiled Np Mean Value runs.xls" and see what my calculated cumulative release is at the time the release rate begins to drop.

for ~10^4 y (not later WP failures)

	Mean	Max Np	Mean Np 5X	Max Np 5X
time max release rate	12,700 y	8900.	20,800	8900
max rate	5.24e-3 Ci/y	1.32e-2	8.33e-3	4.65e-2
cumul at max	15.3 Ci	6.32	72.6	22.3
cumul at break in slope	23.6 Ci	~~12,700~~ DAP 3/11/04 21.7	98.4	76.6
time break in slope	16,300 y	12,700	28,000	12,700

See plots on page 72.

3/12/04 DAP

On BEMORE, move output files in "TPA run" (except *.exe) to folder

3_11_04 Basecase 350 old solub

Copy back tpa.inp into "TPA run" (with old solubilities).

~~In nuclides.dat~~ DAP 3/12/04

In "data" folder, delete nuclides.dat and make a copy of "nuclides.dat.nonenhanced.txt," renaming it "nuclides.dat." This file has Am-241 and Pu-241 inventories increased by a factor of five. (see bottom p. 52)

Create a folder:

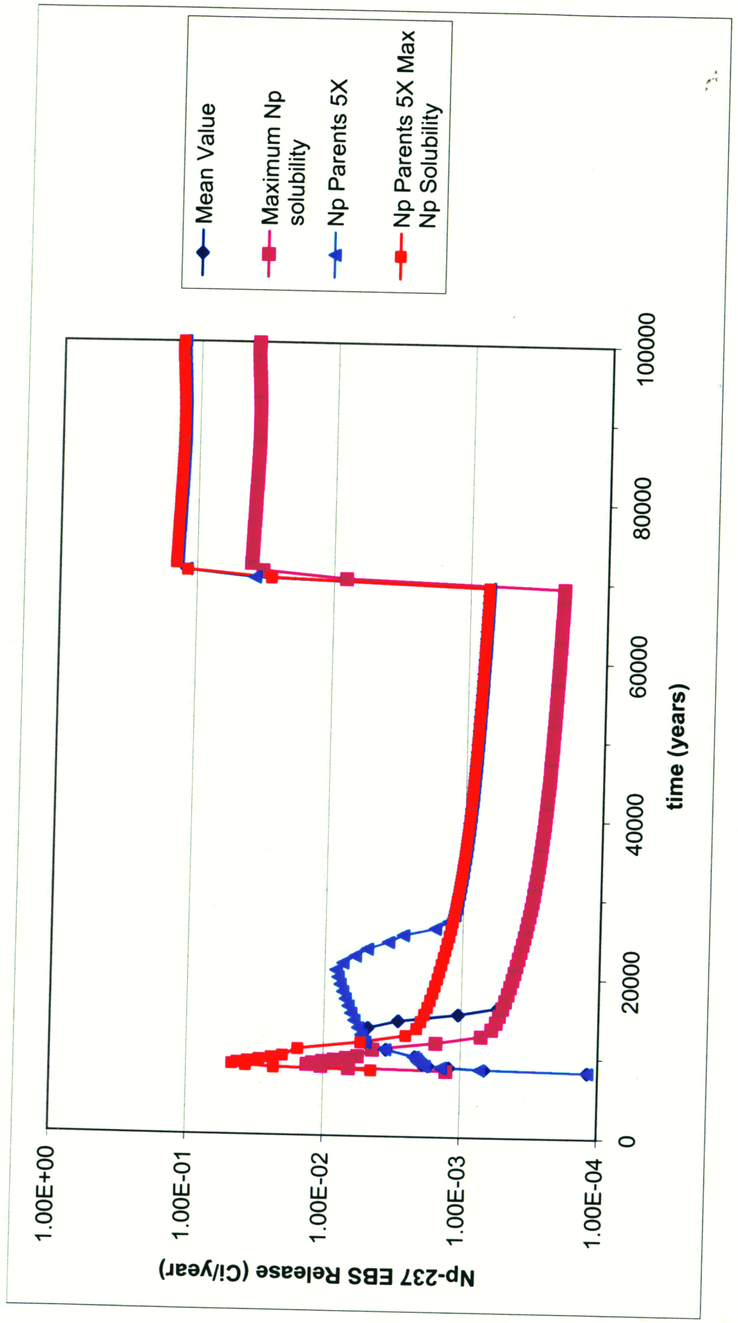
"3_12_04 Basecase 350 old solub Np parents 5X"

Run tpa as on page 69.

For 3_11_04... run, copy all but 14 largest output files to my S: directory.

Back at my PC move these into a folder with the same "3_11_04..." name.

From Excel file "Compiled Np Mean Value runs.xls"



Review TPA Neptunium Solubility Limit

2/16/2005 DAP

On longer time scales, ^{237}Np is an important radionuclide for dose from a potential Yucca Mountain repository. It is therefore important to appropriately model its release from degraded waste form, which may under certain circumstances be controlled by its solubility limit. The Np solubility limit in TPA is currently sampled from a log-triangular distribution:

min : 1.2e-3 kg/m^3 = 1.2 mg/L
peak : 3.4e-2 kg/m^3 = 34 mg/L
max : 2.4e-1 kg/m^3 = 240 mg/L

The mean of this distribution is =

$$10^{\left[\frac{\log(1.2e\text{-}3) + \log(3.4e\text{-}2) + \log(2.4e\text{-}1)}{3}\right]}$$

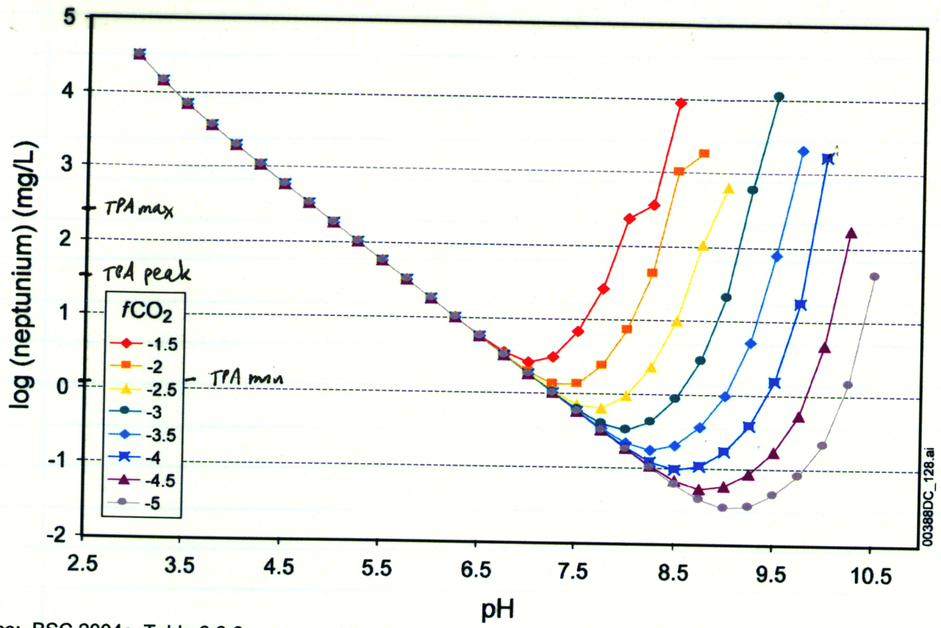
= 2.1e-2 kg/m^3 = 21 mg/L

DOE in the latest relevant documents states that for Np, the solubility limit is calculated for TSPA using a look-up table that selects a value based on model pH and $f(CO_2)$.

On the following page, I have taped the figure from "Technical Basis Document No. 7: In-Package Environment and Waste Form Degradation and Solubility," Revision 1, Bechtel SAIC Company, LLC, July 2004, showing look-up table values for Np solubility limit as a function of pH and $f(CO_2)$.

I have marked on the figure on the Y axis the minimum, peak, and maximum values from the current TPA distribution. (The mean is just a little bit below the peak.)

Note that the document cited on the figure as the source of the data – BSC 2004c – is not publicly available (ANL-WIS-MD-000010 Rev 03B).



Source: BSC 2004c, Table 6.6-3.

Figure 6-3. Solubility of Neptunium Modeled as a Function of fCO_2 and pH

Figure printed from document cited on page 73.

I want to get a sense of what values are likely to be sampled in DOE's TSPA.
Pages 3-17 to 3-19 of TBDoc No. 7 (reference on page 73) discusses the abstraction of in-package pH, which is used for the Np solubility limit abstraction. Here are the relevent details:

Spent Nuclear Fuel

Time 0 – 600 years, pH range 4.5 to 7.0 or 8.1, depending on $f(CO_2)$.
Time 600 – 20,000 year, pH range 4.5 to 7.0.
In both cases, pH is sampled uniformly.

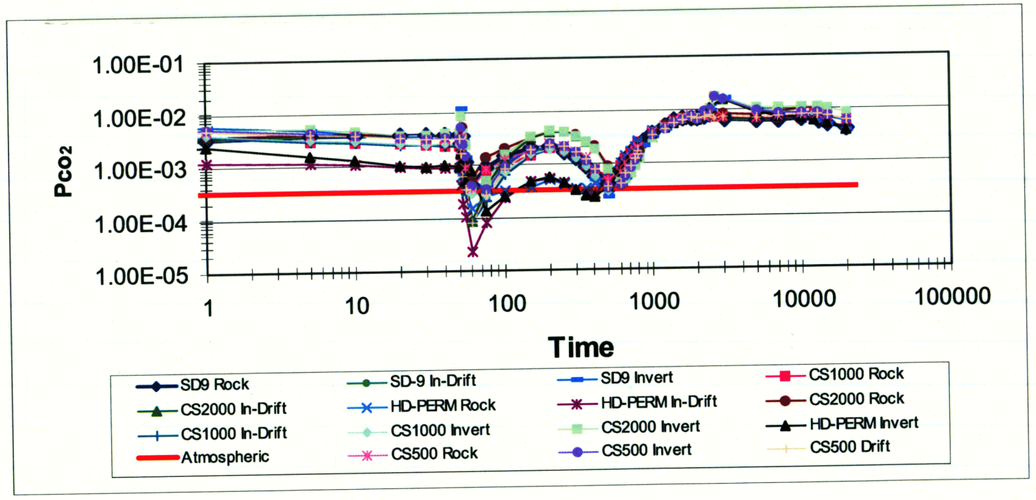
Codisposal

All times: 4.5 to 7.0 if waste package flux < 150 L/yr
4.5 to 9.0 if " " " > 150 L/yr.
Uniform.

We can see that, under almost all circumstances, DOE model pH in-package will be uniformly sampled from the range 4.5 to 7.0.

2/17/05 DAP

What about $f(CO_2)$? According to page 6-2 of TBDoc No. 7, $f(CO_2)$ is taken from the report Engineered Barrier System: Physical and Chemical Environment Model, ANL-EBS-MD-000033 Rev 02, 2004. Figures 6.7-5 and 6.7-6 of that report show the TSPA abstractions of $p(CO_2)$ ($\approx f(CO_2)$) for various water chemistry types. Values start at between 10^{-3} and 10^{-2} atm, fluctuate to as low as 10^{-4} atm between 50 and 500 years, then steadily rise to close to 10^{-2} atm. See figure taped below.



DTN: MO0308SPACO2GL.001

NOTE: See Table 4.1.3.1-1 for description of labels in the legend

Figure 6.7-5. Pco_2 Concentration in the Drift and Near-drift Environment Through Time (Log Scale)

From ~~TBDoc 7.~~ ANL-EBS-MD-000033 Rev 02.

DAP 5/19/05

From the figure, we can conclude that $f(O_2)$ will tend to lie between 10^{-3} and 10^{-2} atm at most times.

In Figure 6-3 taped onto page 74, we see that this range is captured by the orange, yellow, and green symbols. We also see that up to pH 7.0, these three curves more or less coincide.

Therefore, one proposed TPA Np solubility limit abstraction would be as follows:

1. Assume a uniform sampling of pH between 4.5 and 7.0. This is not done explicitly. It is an underlying assumption.
2. Assume $f(CO_2)$ gets no higher than ~ 10^{-2} atm.
3. Use the DOE abstraction in Fig 6-3 (page 74) to sample uniformly from the curve over that pH range.
4. Assume the curve is linear. Use the $f(CO_2) = 10^{-3}$ values.

We need values. While TBDoc 7 cites Revision 03 of the "Dissolved Concentration Limits of Radioactive Elements" report, this document has not been released. Table 6.6-2 of Revision 02 (ANL-WIS-MD-000010) is the most recent tabulation of the Np solubility limit look-up values. Here are selected values from that table for log[Np], mg/L: (kg/m³)

	log f(CO2) = -2.0		-3.0	
pH = 4.5	2.77	(-0.23)	2.77	(-0.23)
pH = 7.0	0.289	(-2.74)	0.263	(-2.74)

Again, we see that the curves are close.

Translate these log values to use ~~mg~~ DH 2/12/05 kg/m³

Write in parentheses in table.

Therefore, the proposed distribution is:

log-uniform, min = -2.74, max = -0.23

for Np solubility limit in kg/m³.

Mean is $\frac{-2.74 - 0.23}{2} = -1.49$, or 3.27×10^{-2} kg/m³.

See page 73. This mean is not very different from the existing TPA distribution. The maximum value is 5.89e-1 kg/m³, and the minimum is 1.82e-3 kg/m³. These are also comparable.

Let's look in a table, using kg/m³:

	Old log [Np]	New log (Np)	Old [Np]	New [Np]
min	-2.92	-2.74	1.2e-3	1.8e-3
mean	-1.68	-1.49	2.1e-2	3.3e-2
max	-0.62	-0.23	2.4e-1	5.9e-1

New distribution is about 0.2 - 0.4 log units higher, and is uniform rather than triangular. Thus, sampled values will be more spread out, meaning that it is more likely that high sampled values will influence the mean Np release.

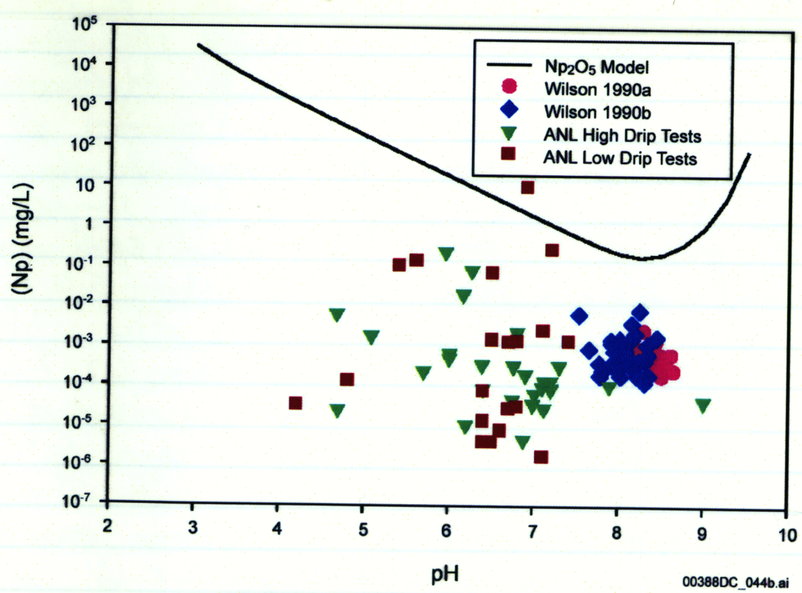
I have not yet checked the thermodynamic calculations that resulted in Figure 6-3 on page 74.

Is it reasonable to uniformly sample pH down to 4.5? Is 4.5 as likely as, say, 7.0? As discussed on page 3-18 of TBDoC 7, the minimum pH of 4.5 is intended to account for temperatures up to 90°C. At temperatures below 50°C, their simulations of in-package pH for both commercial spent nuclear fuel and codisposal give values above 5.0 (see, e.g., Figure 3-5 in TBDoc 7) at times after a few hundred years. According to Figure 6.7-7 of ANL-EBS-MD-000033 Rev 02, modeled temperature at the waste package surface will be above 90°C through about 2000 years, and above 50°C through about 13,000 years. Thus, it seems reasonable to account for elevated temperature by considering pH values down to 4.5.

Note: I have neglected DOE's stochastic uncertainty terms.

Higher water flux through waste package in models leads to higher pH. See, for example, Figure 3-6 of TBDoc 7. Note also (bottom page 74) that flux > 150 L/yr moves the codisposal pH range up to 8.0. However, from discussions with S. Mohanty, it appears such high fluxes are relatively unlikely. Therefore, at this point, 7.0 seems like a reasonable upper bound to in-package pH based on DOE's models.

The DOE model is based on solubility control of Np by the solid phase Np_2O_5. It has been pointed out that this model yields solubility limits well in excess of laboratory-determined Np concentrations during spent nuclear fuel leach tests. DOE uses this observation to support the conservatism of their approach. See the figure below, from TBDoC 7. The model curve was calculated for T = 25°C and log (f_{CO_2}) = -3.5 bar (atmospheric).



Source: BSC 2004c, Figure 7-2.

Figure 6-12. Comparison of Np_2O_5 Neptunium Solubility Model with Pacific Northwest National Laboratory and Argonne National Laboratory Measurements

Such a result is not necessarily unexpected. The solubility curve, after all, is a concentration limit. The experiments were designed not to measure a Np concentration limit, but to measure Np concentration during fuel leaching. There is no reason to expect, a priori, that Np would be released at its solubility limit during leaching. DAP 2/17/05

Nevertheless, it is useful to considering whether Np is being controlled in some other way, say, by another Np pure solid phase that is kinetically favored over Np_2O_5 (or thermodynamically more stable) or by solid solution with secondary phases formed during fuel degradation.

DOE considered these alternative models in TBDoc 7, albeit briefly. The most current discussion appears to be in an unreleased document, ANL-WIS-MD-000010 Rev 03.

NpO_2 The alternative model with Np control by $Np(IV)O_2$ is discussed in ANL-WIS-MD-000010, Rev 02, pages 67 and 75-81. The shapes of the curves are similar to those for Np_2O_5 taped on page 74 of this notebook. Using the lookup table (Table 6.6-6 in ANL-WIS-MD-000010 Rev 02) and the same approach as I used for Np_2O_5 — see page 76), I get the following values for a proposed uniform distribution for Np concentration limit:

(loguniform, min = ~~-1.45~~ -3.95, max = ~~0.954~~ -1.45 DAP 2/17/05

mean = ~2.70

Corresponding values in kg/m³: ~~min = 35.5 kg/m³,~~ ~~max =~~ DAP 2/17/05

min = 1.11e-4 kg/m³ max = 3.55e-2 kg/m³

mean = 2.00e-3 kg/m³

These values are about 1.2 log units lower than the Np_2O_5 values (bottom page 76). In other words, the NpO_2 model yields solubility limits about 1/15 the values of the Np_2O_5 model.
The cited DOE report discusses how NpO_2 should be thermodynamically favored over Np_2O_5, but that the latter is what has been observed in low-temperature experiments. NpO_2 has been reported from solubility experiments at 150° and 200°C, and has been seen to coexist with Np_2O_5 at 90°C. (Note that one of the references for these results – Adkins, 2003, ~~MOL #~~ ACC # MOL.20030619.0100 – was not available from the DOE YMP website nor the LSN. The other reference is a published paper.) These results suggest that the lack of observed NpO_2 in low-T experiments could be a kinetic effect, and that NpO_2 may be relevant for long-term solubility control in a repository.

4/7/05 DAP

DAP 2/17/05

One way to account for this possibility would be to use, for performance assessment, the maximum value from the Np_2O_5 model and the minimum value from the NpO_2 model. This would account for uncertainty regarding which solid phase is appropriate. Such a "hybrid" abstraction would look like:

			kg/m³
loguniform, $[Np]$ in kg/m³	min =	−3.95	1.12e−4
	max =	−0.23	5.89e−1
	mean =	−2.09	8.13e−3

Secondary Phase Retention of Np

Discussed extensively in TBDoc 7 (page 6-17) and ANL-WIS-MD-000010 Rev 2 Sections 6.6.1.2 and 6.6.4.5. The bottom line is that the experimental basis is not strong enough to use as a basecase model. DOE came to this conclusion, but they continue to study the issue. Note: Bill Murphy agreed in September 2003 report to the CNWRA.

TPA Parameter "Negative Log10 Carbonate Concentration [mol/L]"

I was asked to revise this TPA parameter, if necessary. It is the negative of the $\log_{10}$ of total carbonate in water inside the waste package. It is used in an alternate spent fuel degradation model to set the dissolution rate.
The current value is a constant equal to 3.71. This has been the value for at least six years, and has apparently not been critically reviewed for some time.

We do not have independent in-package chemistry calculations, so I will rely on DOE models and parameters. According to the AMR "In-Package Chemistry Abstraction" (ANL-EBS-MD-000037 Rev 02), pp. 124-126, DOE has an analogous ~~gap~~ parameter for total carbonate concentration. However, because I know the AMR has been superceded, and the new revision is not publicly available, I refer to Technical Basis Document No. 7 – In-Package Chemistry (see full reference on page 73 of this notebook). The equation for total carbonate concentration is on page 3-23 of TBDoc 7:

DAP 4/3/05

$$\text{Total } C = fCO_2\left(10^{K_1} + 10^{(pH+K_1+K_2)} + 10^{(2pH+K_1+K_2+K_3)}\right)$$

According to page 3-18 of TBDoc 7, fCO_2 (i.e., carbon dioxide gas fugacity) values are taken from "Engineered Barrier System: Physical and Chemical Environment," ANL-EBS-MD-000033 Rev 02. pH is from the in-package chemistry abstraction, and the values for K_1, K_2, and K_3 are defined constants.
Osvaldo Pensado tells me that for the purposes of TPA, a reasonable upper bound for total carbonate, defined as a constant, is a reasonable approach because this is not a base case model.

Therefore, I should use reasonable upper bounds for fCO_2 and pH to calculate a value for this parameter.

fCO_2

That fCO_2 is supplied by calculations in ANL-EBS-MD-000033 Rev 02 is confirmed on page 6-2 of TBDoc 7.
Tables 6.7-1 through 6.7-5 of ANL-EBS-MD-000033 Rev 02 ~~show~~ ~~the~~ ~~values~~ are look-up tables for partial pressure of CO_2 (g) in bars ($\approx fCO_2$) for the drift and invert, in TSPA-LA, for five different water compositions. The highest drift value is 1.0×10^{-2} bar. This is not an outlier, because values at up to 8×10^{-3} bar are common. See also the figure taped to page 75 of this notebook.
Therefore, 1.0×10^{-2} bar is an upper bound for fCO_2.

pH

As discussed on pages 74 and 75 of this notebook, 7.0 is a reasonable upper bound for pH under typical repository conditions after 600 years.

Back to the equation on page 81. According to page 3-23 of TBDoc 7, values for the "constants" are dependent on temperature. The same equations and values were used in ANL-EBS-MD-000037 Rev 02 (In-Package Chemistry Abstraction), and figure 39 of that AMR shows that total carbonate is higher for lower temperature. Therefore, use 25°C to calculate K_1, K_2, and K_3 according to Table 3-10 in TBDoc 7. This gives:

$$K_1 = 0.0438 - 0.3975 - 1.1023 = -1.4560$$
$$K_2 = 0.0078 - 0.1250 + 0.3300 - 6.5804 = -6.3676$$
$$K_3 = -0.0500 + 0.3200 - 10.618 = -10.3480$$

Plugging these into the equation on page 81, along with $fCO_2 = 10^{-2}$ bar and pH = 7.0, gives:

Total carbonate = 1.85×10^{-3}

Using this to calculate the TPA parameter gives:

$$\boxed{\text{Negative Log10 Carbonate Concentration [mol/L]} = 2.73}$$

(Note that the use of bar and mol/L units is consistent with the thermodynamic calculation.)

6-9-05 BALW

9 JUNE 05 BAW

Removal of Aliquots from Nopal Rock Powder Samples for Stable Isotope Analyses

Task initially assigned to: Bradley Werling by David Pickett

Objectives: To characterize Nopal rock powder samples by the following stable isotope analyses: oxygen isotope of silicates and oxygen and carbon isotope of carbonates.

Samples: Nopal I rock powder samples provided by David Pickett (172/13-30)

Equipment: Mettler Electronic Balance Model AE240, Serial Number 101237

Supplies: Weighing Paper
2.5 mL polyethylene sample vials
Parafilm

Procedure:

BW 6-9-05

Fifty-five aliquots were taken. Eight of these were replicates. New sample IDs were assigned to these aliquots. The legend that relates the CNWRA sample ID with the SMU aliquot sample ID is found in 172/85-87. The target and actual aliquot masses are also found in 172/85-87. The aliquot mass varied because the mass of the parent sample varied. ~~Ideally the minimum aliquot mass should be 0.2 grams.~~ In some cases the entire parent sample was used for the aliquot. These cases were indicated by the word "all" in the third column (Target mass (g) of aliquot sent to SMU) found on 172/85-87.

A piece of weighing paper was folded in half, opened back up, and placed on the pan of the balance. The balance was tared. The appropriate mass of sample was carefully poured from the original sample container onto the weighing paper. The mass was recorded on 172/85-87. The aliquot was carefully poured into a prelabled sample vial. This vial was capped and sealed with parafilm.

Target Mass for Balance Challenge = 20.0001g
At start = 20.0002g
At end = 20.0003g

Target masses provided by David Pickett.

9 JUNE 05 CONT BAW

CNWRA Sample ID	SMU Sample ID	Target mass (g) of aliquot sent to SMU	Actual mass (g) of aliquot sent to SMU
	BW 6-9-05		
NOPI-12-SEP1	N05-1	0.25	0.2518
NOPI-19-SEP1-P	N05-2	0.4	0.3998
NOPI-19-SEP2	N05-3	0.3	0.3075
NOPI-24-SEP1	N05-4	0.26	0.2636
NOPI-24-SEP1 replicate	N05-13	0.26	0.2650
NOPI-24-SEP2	N05-5	0.15	0.1510
NOPI-29-SEP1	N05-6	all *	0.5034
		* some left over	
NOPI-29-SEP2	N05-7	0.2-(all)	0.1310
NOPI-164-SEP1	N05-8	0.5	0.5044
NOPI-164-SEP1 replicate	N05-36	0.5	0.5009
NOPI-164-SEP2	N05-9	0.5	0.5031
NOPI-164-SEP3	N05-10	0.5	0.5485
NOPI-164-SEP4	N05-11	0.2-(all)	0.1287
NOPI-166-SEP1-P	N05-12	all	0.2553
NOPI-166-SEP2	N05-14	0.3-(all)	0.2799
NOPI-179-SEP1-PB	N05-15	all	0.1074
NOPI-179-SEP2	N05-16	0.3-(all)	0.0946
NOPI-436-L1-SEP2	N05-18	0.5	0.5194
NOPI-436-L1-SEP3	N05-19	0.3	0.2991

9 JUNE 05 CONT BAW

Contiunation of Table

CNWRA Sample ID BW 6-9-05	SMU Sample ID	Target mass (g) of aliquot sent to SMU	Mass (g) of aliquot sent to SMU
NOPI-436-L1-SEP4	N05-20	all	0.1780
NOPI-436-L2-SEP2	N05-22	all	0.1518
NOPI-436-L2-SEP3	N05-23	0.4	0.4192
NOPI-436-L2-SEP3 replicate	N05-40	0.4	0.3987
NOPI-436-L2-SEP4	N05-24	all	0.1060
NOPI-499-L2-SEP2	N05-26	0.2	0.2119
NOPI-499-L2-SEP3	N05-27	all	0.0820
NOPI-499-L2-SEP4	N05-28	all	0.1688
NOPI-499-L3-SEP2	N05-30	0.5	0.4931
NOPI-499-L3-SEP2 replicate	N05-62	0.5-(all)	0.4942
NOPI-499-L3-SEP3	N05-31	0.3	0.3021
NOPI-499-L3-SEP4	N05-32	all	0.1681
NOPI-305-L1-SEP2	N05-34	0.2	0.1990
NOPI-305-L1-SEP3	N05-35	0.2	0.1987
NOPI-305-L1-SEP4	N05-37	all	0.1362
NOPI-305-L2-SEP2	N05-39	0.4	0.4017
NOPI-305-L2-SEP2 replicate	N05-60	0.4	0.4008
NOPI-305-L2-SEP3	N05-41	0.3	0.3006
NOPI-305-L2-SEP4	N05-42	all	0.1202

9 JUNE 05 CONT BAW

Contiunation of Table

CNWRA Sample ID BW 6-9-05	SMU Sample ID	Target mass (g) of aliquot sent to SMU	Mass (g) of aliquot sent to SMU
NOPI-306-SEP2	N05-44	0.4	0.4041
NOPI-306-SEP2 replicate	N05-63	0.4	0.4010
NOPI-306-SEP3	N05-45	0.3	0.3015
NOPI-306-SEP4	N05-46	all	0.1356
NOPI-434-SEP2	N05-48	0.2	0.2018
NOPI-434-SEP3	N05-50	0.5	0.5004
NOPI-434-SEP4	N05-51	all	0.1664
NOPI-501-W	N05-52	0.2	0.2007
NOPI-501-G-SEP1	N05-53	0.2	0.2120
NOPI-501-G-SEP2	N05-54	0.5	0.5008
NOPI-501-G-SEP2 replicate	N05-64	0.5	0.5009
NOPI-501-G-SEP3	N05-55	0.2-(all)	0.1874
NOPI-501-G-SEP4	N05-56	0.2	0.2039
NOPI-458-SEP2	N05-58	0.4	0.3994
NOPI-458-SEP2 replicate	N05-49	0.4	0.4011
NOPI-458-SEP3	N05-59	0.4	0.4047
NOPI-458-SEP4	N05-61	all	0.1258

6-9-05 BW

9 JUNE 05 CONT BAW

Column 3 (172/85-87) has some handwritten comments relating the target mass to the actual mass.

For 6 samples the entire mass (all) of the parent material was used and the actual mass was less than the target mass See N05-7, N05-11, N05-14, N05-16, N05-62 and N05-55

For 1 sample (N05-6), the target mass called for all of the parent sample. The aliquot was taken to about ~0.5g and stopped with material left over.

~~10 JUNE 05 BAW~~ 6-10-05 BW

6-10-05 BW

10 JUNE 05 BAW

Shipping of Nopal Rock Powder Samples for Stable Isotope Analyses

Task initially assigned to: Bradley Werling by David Pickett

Objectives: To characterize Nopal rock powder samples by the following stable isotope analyses: oxygen isotope of silicates and oxygen and carbon isotope of carbonates.

Samples: 55 Nopal I rock powder samples from 172/84-88
47 samples were aliquots from unique Nopal I samples
8 samples were replicates selected from the 47 uniques samples.

Purchase Requisitions: PR # 05025169 for the carbon and oxygen isotope analyses of carbonates and
PR # 05025190 for the oxygen isotope analyses of silicates

Synopsis:

These analyses were divided between two purchase requisitions (PRs). This should help streamline the payment process for us since the two analyses are expected to be completed within different timeframes. Using two PRs allows us to treat the carbonate and silicate analyses independently. We can send payment for each PR after we receive the results. If both analyses were on a single PR, we could not make payment until sample results for both analyses were received.

At the request of The Stable Isotope Laboratory at SMU, a sample submittal form was included in the package with the samples. A copy of this form is included as part of this entry. Information on this form included SMU sample ID, sample type, estimated % silicate, and mass. The legend that relates SMU sample ID to CNWRA sample ID is found on 172/85-87. The Stable Isotope Laboratory is not on the ASL so a procurement plan was included as an attachment to each PR.

6-10-05 BAW

10 JUNE 05 CONT BAW

Sample Submittal Form for Stable Isotope Laboratory

Analyses requested: carbon and oxygen isotope analyses of carbonates (PR # 05025169) and oxygen isotope analyses of silicates (PR # 05025190)

Name: David Pickett
Address: CNWRA, Southwest Ressearch Institute
6220 Culebra Road
San Antonio, TX 78238-5166
Phone: (210) 522-5582
Fax: (210) 522-5155

SMU Sample ID	Sample type	Estimated % silicate	Mass (g) provided
N05-01	calcite	5	0.2518
N05-02	calcite	6	0.3998
N05-03	calcite	8	0.3075
N05-04	calcite	4	0.2636
N05-05	calcite	6	0.1510
N05-06	calcite	4	0.5034
N05-07	calcite	6	0.1310
N05-08	calcite	57	0.5044
N05-09	calcite	57	0.5031
N05-10	calcite	57	0.5485
N05-11	calcite	36	0.1287
N05-12	calcite	7	0.2553
N05-14	calcite	8	0.2799
N05-15	calcite	13	0.1074
N05-16	calcite	13	0.0946
N05-18	caliche	18	0.5194
N05-19	caliche	15	0.2991
N05-20	caliche	12	0.1780
N05-22	caliche	23	0.1518
N05-23	caliche	20	0.4192
N05-24	caliche	19	0.1060
N05-26	caliche	30	0.2119
N05-27	caliche	29	0.0820
N05-28	caliche	30	0.1688
N05-30	caliche	34	0.4931
N05-31	caliche	34	0.3021
N05-32	caliche	35	0.1681
N05-34	caliche	25	0.1990
N05-35	caliche	25	0.1987
N05-36	calcite	55	0.5009
N05-37	caliche	25	0.1362
N05-39	caliche	25	0.4017
N05-40	caliche	19	0.3987
N05-41	caliche	21	0.3006
N05-42	caliche	18	0.1202
N05-44	caliche	38	0.4041

10 JUNE 05 CONT BAW

SMU Sample ID	Sample type	Estimated % silicate	Mass (g) provided
N05-45	caliche	38	0.3015
N05-46	caliche	39	0.1356
N05-48	caliche	7	0.2018
N05-49	caliche	98	0.4011
N05-50	caliche	9	0.5004
N05-51	caliche	11	0.1664
N05-52	calcite	<4	0.2007
N05-53	calcite	2	0.2120
N05-54	calcite	2	0.5008
N05-55	calcite	2	0.1874
N05-56	calcite	2	0.2039
N05-58	caliche	99	0.3994
N05-59	caliche	99	0.4047
N05-60	caliche	24	0.4008
N05-61	caliche	99	0.1258
N05-62	caliche	34	0.4942
N05-63	caliche	38	0.4010
N05-64	calcite	2	0.5009

20 JUL 2005 BAW

Challange of Balance - Target = 20.0001g

At start of day, = 20.0002g

At end of day, = 20.00002g

20-05 BW

20 JUL 2005 BAW CONT

Removal of Aliquots from Nopal Rock Powder Samples for Stable Isotope Analyses

Task initially assigned to: Bradley Werling by David Pickett

Objectives: To characterize Nopal rock powder samples by the following stable isotope analyses: oxygen isotope of silicates and oxygen and carbon isotope of carbonates.

Background: Previously (172/84-91), 55 Nopal rock powder samples were sent to SMU for silicate and carbonate analyses. A sufficient amount of material was not initially sent for several samples. David opted to send additional material for two of these samples. The analyses of these two samples (NOPI-12-Sep1 and NOPI-24-Sep1) will be conducted under the previous purchase requisitions. The aliquot collection will be documented in this entry. Some missing Nopal rock powder samples were also located after the initial samples were sent (172/84-91). David opted to have 10 of these new samples analyzed, so new aliquots and purchase requisitions were prepared for these 10 samples. This work will also be documented in this entry.

Samples: Nopal I rock powder samples provided by David Pickett (172/13-30)

Equipment: Mettler Electronic Balance Model AE240, Serial Number 101237

Supplies: Weighing Paper
2.5 mL polyethylene sample vials
Parafilm

Procedure:

A total of twelve aliquots were taken. Two were to augment material previously sent under purchase requisitions 05025169 and 05025190 (172/89-91). Ten were new aliquots that required new purchase requisitions. The aliquots were labeled with SMU sample IDs. The legend that relates the CNWRA sample ID with the SMU aliquot sample ID is found in 172/93. The target and actual aliquot masses are also found in 172/93. The aliquot target masses were determined by David. If enough parent sample was not available, David was contacted and any changes were recorded.

A piece of weighing paper was folded in half, opened back up, and placed on the pan of the balance. The balance was tared. The appropriate mass of sample was carefully poured from the original sample container onto the weighing paper. The mass was recorded on 172/93. The aliquot was carefully poured into a prelabled sample vial. This vial was capped and sealed with parafilm.

20 JUL 2005 BAW CONT

Note: sample NOPI-166-Sep1 needs to be powdered before analyses. SMU will be informed and SMU will perform the powdering task.

Augmenting aliquots for purchace requisitions 05025169 and 05025190.

CNWRA Sample ID	SMU Sample ID	Target Mass (g) of aliquot sent to SMU	Actual Mass (g) of aliquot sent to SMU
NOPI-12-Sep1	NO5-1B	all	0.4130
NOPI-24 Sep1	NO5-4B	all	0.4092

New aliquots for new purchase requisitions (PR #s not available at this time)

CNWRA Sample ID	SMU Sample ID	Target Mass (g) of aliquot sent to SMU	Actual Mass (g) of aliquot sent to SMU
NOPI-166-Sep1	NO5-65	1.5	1.5278
NOPI-436-L1-Sep1	NO5-17	all	0.2031
NOPI-436-L2-Sep1	NO5-21	all	0.3328
NOPI-499-L2-Sep1	NO5-25	all	0.0741
NOPI-499-L3-Sep1	NO5-29	0.3	0.3124
NOPI-305-L1-Sep1	NO5-33	0.2	0.2026
NOPI-305-L2-Sep1	NO5-38	0.2	0.2033
NOPI-306-Sep1	NO5-43	0.3	0.3019
NOPI-434-Sep1	NO5-47	0.3	0.3367
NOPI-458-Sep1	NO5-57	all	0.0895

7-22-05 BW

22 JUL 05 BAW

Shipping of Nopal Rock Powder Samples for Stable Isotope Analyses

Task initially assigned to: Bradley Werling by David Pickett

Objectives: To characterize Nopal rock powder samples by the following stable isotope analyses: oxygen isotope of silicates and oxygen and carbon isotope of carbonates.

Samples: 12 Nopal I rock powder samples
2 samples (172/92-93) augmented material previously sent (172/84-91)
10 samples (172/92-93) were aliquots from new Nopal I samples

Purchase Requisitions:
The two "augment" samples fall under PR # 05025169 for the carbon and oxygen isotope analyses of carbonates and PR # 05025190 for the oxygen isotope analyses of silicates

The 10 new samples are under PR # 05029563 for the carbon and oxygen isotope analyses of carbonates and PR # 05029545 for the oxygen isotope analyses of silicates

Synopsis:

The new analyses were divided between two purchase requisitions (PRs). This should help streamline the payment process for us since the two analyses are expected to be completed within different timeframes. Using two PRs allows us to treat the carbonate, and silicate analyses independently. We can send payment for each PR after we receive the results. If both analyses were on a single PR, we could not make payment until sample results for both analyses were received.

At the request of The Stable Isotope Laboratory at SMU, a sample submittal form was included in the package with the samples. A copy of this form is included as part of this entry. Information on this form included SMU sample ID, sample type, estimated % silicate, and mass. The legend that relates SMU sample ID to CNWRA sample ID is found on 172/93. The Stable Isotope Laboratory is not on the ASL so a procurement plan was included as an attachment to each PR.

7-21-05 BAW

22 JUL 05 CONT BAW

Sample Submittal Form for Stable Isotope Laboratory

Analyses requested: carbon and oxygen isotope analyses of carbonates (pr # 05029563) and oxygen isotope analyses of silicates (pr # 05029545)

Name: David Pickett
Address: CNWRA, Southwest Ressearch Institute
6220 Culebra Road
San Antonio, TX 78238-5166
Phone: (210) 522-5582
Fax: (210) 522-5155

SMU Sample ID	Sample type	Estimated % silicate	Mass (g) provided
NO5-1B*	calcite	5	0.4130
NO5-4B*	calcite	4	0.4092
NO5-17	caliche	18	0.2031
NO5-21	caliche	28	0.3328
NO5-25	caliche	32	0.0741
NO5-29	caliche	33	0.3124
NO5-33	caliche	25	0.2026
NO5-38	caliche	28	0.2033
NO5-43	caliche	38	0.3019
NO5-47	caliche	7	0.3367
NO5-57	caliche	99	0.0895
NO5-65	calcite	7	1.5278

*Augmenting aliquots for samples from pr #s 05025190 and 05025169

8/31/05 DH

8/31/05 DAP

By email on 8/26/05, Ian Richards of SMU provided a final compilation of oxygen and carbon isotope analyses of the samples discussed on pages 84-95. The data are in a Microsoft Excel spreadsheet titled "SWRI from SMU.xls," located on Pickett's hard drive in the folder D:\Documents\Nopal\carb-sil U-Th geochronology." I made a working copy of this Excel file for analysis and plotting, titled "Final SMU stable isotope data.xls."

The spreadsheet as delivered by SMU is taped to pages 97 and 98. The columns labeled "Repeat" show the results of replicate analyses that SMU performed as part of their standard procedure. All of the isotope ratio results are reported as delta values, i.e., the deviation from a standard isotope ratio in parts per thousand, or "permil." For instance:

$$\cancel{\delta^{18}O = \left(\frac{\delta^{18}O_{measured}}{\delta^{18}O_{SMOW}} - 1\right) \times 1000}$$ DAP 8/31/05

~~where~~ DAP 8/31/05

$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{measured}}{(^{18}O/^{16}O)_{SMOW}} - 1\right] \times 1000$$

where SMOW = standard mean ocean water.

The SMU replicate values are all within 0.5 permil of the original value with one exception: N05-40 $\delta^{18}O$ for calcite, for which the original measurement was 23.0 and the repeat was 23.6.

We sent blind replicates, and I have compared the results as part of our procurement plan, which calls for an acceptance criterion of ±0.5 permil on duplicate analyses.

Sample	Type	calcite d13C (PDB)	repeat	calcite d18O (SMOW)	repeat	silicate d18O (SMOW)	repeat	weight % calcite	repeat
N05-01	calcite	-0.8		17.3		20.1		78.2	
N05-02	calcite	0.0		20.9		5.6		69.0	
N05-03	calcite	-0.1		20.9		5.7		80.7	
N05-04	calcite	-1.3		18.8		21.6		76.6	
N05-05	calcite	-1.3		18.8				78.3	
N05-06	calcite	-1.6		19.8				91.5	
N05-07	calcite	-1.6		20.0				78.8	
N05-08	calcite	-3.1		22.1		14.1	14.0	36.4	
N05-09	calcite	-3.4		21.7		14.0		49.8	
N05-10	calcite	-3.6		21.7		12.5		51.1	
N05-11	calcite	-3.6		21.7		14.1		60.3	
N05-12	calcite	-0.8		21.3				79.2	
N05-13		-1.4		19.1				80.5	
N05-14	calcite	-0.6		21.4		16.2		88.9	
N05-15	calcite	-4.9		21.7				63.6	
N05-16	calcite	-5.0	-5.2	21.7		28.4		76.6	66.2
N05-17	caliche	-5.7		23.3		29.3		76.3	
N05-18	caliche	-5.7		23.7		29.6		79.8	
N05-19	caliche	-5.5		24.1		28.2		33.7	
N05-20	caliche	-5.6		23.6		25.4		81.7	
N05-21	caliche	-6.4	-6.5	23.2		22.6		66.1	58.0
N05-22	caliche	-6.3		23.0		22.2		80.0	
N05-23	caliche	-6.5	-6.4	23.1		24.1	23.9	71.0	74.7
N05-24	caliche	-6.5		23.3				75.8	
N05-25	caliche	-7.7		23.3		21.9		59.9	
N05-26	caliche	-7.6		23.5		22.2	22.0	61.8	
N05-27	caliche	-7.6		23.4		19.5		66.6	
N05-28	caliche	-7.4		23.5		20.4		61.7	
N05-29	caliche	-10.4	-10.3	22.6		31.8	31.8	57.4	55.2
N05-30	caliche	-10.3		22.6		30.5	30.3	59.5	
N05-31	caliche	-10.1	-10.1	22.6		29.6		59.2	58.7
N05-32	caliche	-10.3		22.1		30.5		56.9	
N05-33	caliche	-6.2		23.6		31.9		60.9	
N05-34	caliche	-6.1	-6.1	23.9		31.9	32.1	68.3	
N05-35	caliche	-6.1		23.7		32.2		70.6	68.5

DAP 8/31/05

Sample	Type	calcite d13C (PDB)	repeat	calcite d18O (SMOW)	repeat	weight % calcite	repeat	silicate d18O (SMOW)	repeat
N05-36	calcite	-3.1		21.8		37.2		15.0	
N05-37	caliche	-6.0		23.8		70.2		30.5	
N05-38	caliche	-5.7		23.2		64.5		32.0	31.7
N05-39	caliche	-5.7		23.2		70.2		~~31.1~~ 32.1	
N05-40	caliche	-6.5	-6.4	23.0	23.6	72.3	71.7	23.8	24.1
N05-41	caliche	-5.7		23.5		72.3		31.2	
N05-42	caliche	-5.7		23.3		75.1		31.3	31.6
N05-43	caliche	-7.8		22.2		52.4		30.7	
N05-44	caliche	-7.8		22.3		56.3		30.7	
N05-45	caliche	-7.8		22.5		57.0		31.0	
N05-46	caliche	-7.8		22.5		55.1			
N05-47	caliche	1.1	1.1	23.5	23.5	84.3	86.5	18.7	19.0
N05-48	caliche	1.1		23.4		81.5			
N05-49	caliche	-1.4		23.6		0.1		20.1	
N05-50	caliche	1.1	1.1	23.5	23.6	83.1	76.4	16.5	16.8
N05-51	caliche	1.1		23.5		81.3			
N05-52	calcite	1.2		17.3		93.9			
N05-53	calcite	-1.1		21.1		88.6			
N05-54	calcite	-1.1		21.3		92.8		17.6	
N05-55	calcite	-1.3	-1.3	21.5	21.4	83.1	79.7		
N05-56	calcite	-1.3		21.2		82.2			
N05-57	caliche	-0.6		20.5		0.5		21.4	
N05-58	caliche							20.8	
N05-59	caliche							21.4	21.1
N05-60	caliche	-5.7	-5.7	23.6	23.4	66.9		32.0	
N05-61	caliche							20.5	
N05-62	caliche	-10.4		22.8		63.4		30.2	
N05-63	caliche	-7.8		23.1		56.5		30.1	30.5
N05-64	calcite	-1.2		21.6		86.2		15.2	
N05-65	calcite	-0.6		21.3		84.0		13.0	

The blind replicate pairs are (all have "N05-" prefix)

04 + 13
08 + 36
23 + 40
30 + 62
39 + 60
44 + 63
54 + 64
58 + 49.

$\delta^{13}C$ calcite

The permil difference between original + replicate is:

04 + 13 = -1.4 - (-1.3) = -0.1
08 + 36 = 0.0
23 + 40 = 0.0
30 + 62 = -0.1
39 + 60 = 0.0
44 + 63 = 0.0
54 + 64 = -0.1
58 + 49 = Insufficient carbonate for analysis of N05-58.

All $\delta^{13}C$ blind replicates successfully met the acceptance criterion of ±0.5 permil.

$\delta^{18}O$ calcite Permil difference is:

04 + 13 = 0.3
08 + 36 = -0.3
23 + 40 = -0.1
30 + 62 = 0.2
39 + 60 = 0.4
44 + 63 = 0.8
54 + 64 = 0.3

One result is outside the acceptance criterion: 44 + 63.

Note that because SMU performed repeat analyses on both N05-23 and N05-40, there are a total of four results for sample NOP1-436-L2-SEP3 (see page 86). The four values for calcite $\delta^{18}O$ are 23.1, 23.3, 23.0, and 23.6. These span a total range of 0.6 permil - there is only one pair of results - 23.0 and 23.6 - that yield a difference outside the acceptance criterion of ±0.5 permil. In fact, the values all fall within ~~and~~ DAP 9/3/05 a ±0.5 permil range as a whole. I therefore judge that the SMU repeat analysis does not violate the acceptance criterion.

Today, Ian Richards sent another Excel that includes data on sample sizes & oxygen yield. I saved it as "SWRI from SMU Aug 31.xls" in the same directory. He corrected one number - I have changed it on the print-out on page 98 (N05-39).

9/1/05 DAP

$\delta^{18}O$ Silicate — Replicate permil difference is:

- 04 + 13 = insufficient residue for measurement in N05-13
- 08 + 36 = 0.9
- 23 + 40 = -0.3
- 30 + 62 = -0.3
- 39 + 60 = -0.1
- 44 + 63 = -0.6
- 54 + 64 = -2.4
- 58 + 49 = -0.7

Of the seven measured, four are outside the acceptance criterion of ± 0.5 permil. Discussions with Ian Richards at SMU suggest the following:

- These samples were, in general, on the small side of the range they typically measure.
- The SMU internal standards, which are run with every ten samples, give a +/- 0.3 permil reproducibility for $\delta^{18}O$ of silicates and ±0.2 permil for $\delta^{18}O$ of carbonates.

- Our samples are particularly fine-grained, a feature that can compromise analyses. For example, the high sample surface area makes it more difficult to achieve a vacuum in the sample chamber because of adsorbed water.
- SMU's repeat analyses of our samples were all better than ±0.4 permil for $\delta^{18}O$ of silicate.
- Some of our samples have appreciable iron contents, based on color and observations of dark crystalline inclusions in calcite. Iron can complicate the oxygen extraction process and add additional uncertainty to results.

For $\delta^{18}O$ of "silicates" in our sample set, these considerations suggest that ± 0.5 permil was too ambitious an acceptance criterion. Our samples were not systematically split to ensure powder heterogeneity. Given the small masses of residue after acid treatment to remove carbonate, heterogeneity could play a significant role in affecting replicate results. I conclude that, for $\delta^{18}O$ of silicates, ±1 permil would have been a more appropriate acceptance criterion.

That still leaves the 2.4 permil difference for the N05-54 / N05-64 blind replicate pair. Richards does not see an obvious reason for the disparity, but he will try to re-analyze one or both of them. NOP1-501-G is a gray crystalline calcite riddled with dark metal oxide inclusions. This sample could have behaved quite differently from the others during analysis. I will consider these results unreliable in light of a repeat by SMU. Note that the other grain size separates for NOP1-501-G (N05-53, 55, 56) had insufficient ~~feld~~ DAP 9/3/05 residue for "silicate" analysis.

For $\delta^{18}O$ silicate, SMU's internal standards and repeats – and all blind replicates but one – suggest ± 1 permil is fine for an uncertainty – if N05-54 + N05-64 results are not included.

For $\delta^{18}O$ carbonate, I already discussed the 0.6 permil difference for the SMU repeat of N05-40 on page 100 – these results are satisfactory. This leaves the 0.8 permil difference for the N05-63 / N05-44 blind replicate pair. Based on the considerations on page 100-101, I am inclined to attribute this to sample heterogeneity. Richards is going to attempt to repeat the analyses. It should be mentioned that, with a ± 0.5 permil uncertainty, it is possible to have a 0.8 permil difference between two analyses.

To Summarize

$\delta^{13}C$ carbonate

Meets acceptance criterion. Lab repeats and blind replicates show a reproducibility of ± 0.2 permil.

$\delta^{18}O$ carbonate

One of seven blind replicates did not meet acceptance criterion. Given the nature of the samples and analyses, results are acceptable. A difference of 0.8 permil lies writhin a ± 0.5 permil uncertainty band. Will await repeats of N05-44 + N05-63 with interest.

$\delta^{18}O$ silicate

Acceptance criterion was too ambitious. Accept the data, reporting a ± 1 permil uncertainty. Will not report results on N05-54 and N05-64 until repeat analysis is available. Suspect sample heterogeneity.

9/2/05 DAP

Plotting and analysis of stable isotope data are recorded in the Microsoft Excel file "Final SMU stable isotope data.xls". File is located on D. Pickett's computer (SYREEN) in:
D:\Documents\Nopal\carb-sil U-Th geochronology.

9/6/05 DAP

New plotting and analysis of U-Th isotopic data on calcites, caliches, opals, and uranophane (see pages 13-30 of this notebook) are recorded in the Microsoft Excel files:
Apr 2002 plotting.xls and
April 2002 Age_data.xls
located in SYREEN at
D:\Documents\Nopal\carb-sil U-Th geochronology.

9/13/05

The following email from Ian Richards, Southern Methodist University, cites papers describing the analytical procedures employed for stable isotope analyses of the samples described on pp 84-102.

From: Ian Richards [irichard@mail.smu.edu]
Sent: Wednesday, September 07, 2005 9:20 AM
To: dpickett@cnwra.swri.edu
Subject: Re: Update SWRI spreadsheet

Hi David,

The stable isotopic composition of calcite was determined by reaction with orthophosphoric acid using the method of McCrea (1950). The oxygen isotopic composition of silicate minerals was determined by reaction with ClF3 using the method of Borthwick and Harmon (1982).

McCrea JM (1950) On the oxygen isotope geochemistry of carbonates and a paleotemperature scale. J Chem Phys 18: 849-857

Borthwick J, Harmon RS (1982) A note regarding ClF3 as an alternative to BrF5 for oxygen isotope analysis. Geochim Cosmochim Acta 46: 1665-1668

I will let you know when we receive payment.

Thanks,

Ian

5/26/06
DAP

Proposed Revision of TPA Plutonium Solubility Limit

I am recording here analyses and calculations aimed at revising the plutonium solubility limit parameter used in the TPA to place an upper bound on the plutonium concentration in water at the waste form. The existing value ~~is:~~ DAP 5/26/06 for SolubilityPu[kg/m3] is a uniform distribution between 2.4e-6 and 2.4e-4.
The basis for this distribution is listed in Appendix A of the 2002 CNWRA report "Total-System Performance Assessment (TPA) Version 4.0 Code: Module Description and User's Guide." It is attributed to an expert elicitation conducted for TSPA-1995, and the table entry notes, "Continue evaluating."
Compare this with the most recent available evaluation by DOE, which is reported in ANL-WIS-MD-000010 Rev. 03, "Dissolved Concentration Limits of Radioactive Elements." Table 6.5-1 shows the adopted look-up table for DOE's TSPA abstraction of Pu solubility. A detailed review of the abstraction will not be discussed here, but the abstraction appears to do a reasonable job compromising between a purely thermodynamic approach and a direct use of empirical data. In lieu of further review, we will use the DOE abstraction as the basis of reviewing and revising the TPA parameter distribution.
Table 6.5-1 of ANL-WIS-MD-000010 Rev. 03, gives values of the Log_{10} of plutonium concentration expressed as mg/L, as a function of pH and log fCO_2. What ranges of these two values are appropriate?

pH: Review of the information presented in "In-Package Chemistry Abstraction," ANL-EBS-MD-000037 Rev 03, suggests that a range of 5.5 to 8.0 is

likely to bound in-package conditions. The DOE lower bound of 4.5 is based only on high-temperature conditions and several phases and reactions are likely to keep pH from getting that low. Likewise, pH is unlikely to exceed 8.0 due to reactions with schoepite and stainless steel.

Log fCO_2: See page 75 or 76 of this notebook. Log fCO_2 is likely to be confined to the range -2 to -3.

Attached below is a table extracted from the DOE look-up table.

Log [Pu], mg/L
ANL-WIS-MD-000010 REV 03, Table 6.5-1

pH	Log f(CO2) -2	-2.5	-3
5.5	-0.762	-0.87	-0.911
5.75	-0.917	-1.08	-1.15
6	-1.03	-1.27	-1.37
6.25	-1.12	-1.42	-1.58
6.5	-1.17	-1.54	-1.77
6.75	-1.21	-1.62	-1.92
7	-1.23	-1.67	-2.04
7.25	-1.24	-1.7	-2.12
7.5	-1.24	-1.72	-2.17
7.75	-1.23	-1.72	-2.2
8	-1.17	-1.71	-2.2

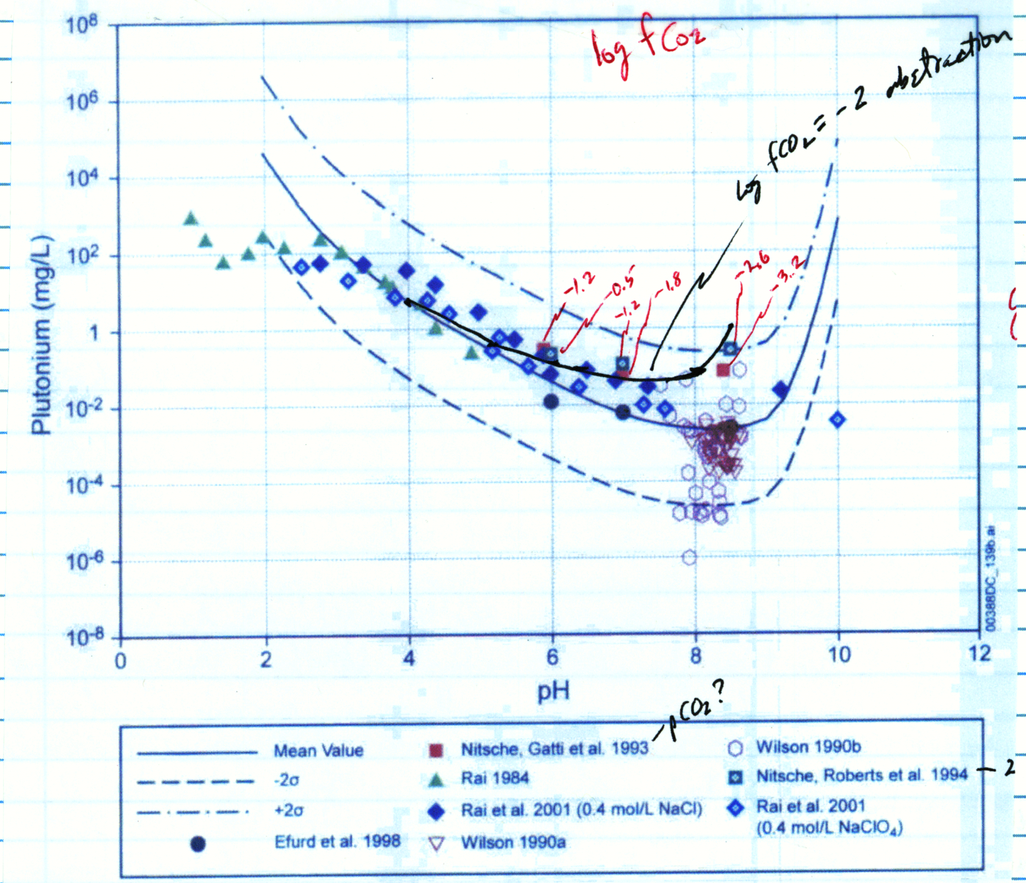
We are assuming, in the absence of conflicting information, that these values are all equally likely, i.e. that pH and Log fCO_2 are uniformly distributed. We now want to construct a distribution of Log [Pu] values that reflects this.
Note that we are moving from uniform to loguniform for the [Pu] distribution. This makes sense for thermodynamic quantities that are functions of logarithmic environmental variables.

Uncertainty

In the DOE Pu abstraction (ANL-WIS-MD-000010 Rev 03), an uncertainty term is sampled and added to or subtracted from the looking table value. The most important uncertainty term is due to thermodynamic data uncertainty (a fluoride term is much smaller). This data uncertainty takes the form of a sampled number – from a normal distribution with mean Ø and $\sigma = 1.0$, truncated at 2.0 (log units). The basis for $2\sigma = 2.0$ is discussed on pp 6-52 and 6-53 of the above DOE report, and is due chiefly to an attempt to bound the uncertainties in all aqueous species that contribute significantly to Pu over the entire chemical range.

Looking at only our chemical range, the important aqueous species are: PuO_2^+, $PuO_2CO_3(aq)$, and $PuO_2(CO_3)_3^{4-}$ – based on inspection of Figs 6.5-2 and 6.5-3 of ANL-WIS-MD-000010 Rev 03, and considering that higher fCO_2 will stabilize the third species and make it significant at pH ~8. Thermodynamic uncertainties considered by DOE include other species and do not use the most recent NEA compilation ("Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium," Chemical Thermodynamics Series Vol. 5, Nuclear Energy Agency, 2003). Table 5-2 of the NEA volume shows that 2σ uncertainties in Log K for reactions involving these three species plus the solubility-limiting solid PuO_2 (am, hyd) are all ≤ 0.5 Log units. Under most conditions, only two of these reactions are relevant. Therefore, an uncertainty of $2\sigma = 1.0$ would reasonably bound the resulting Pu aqueous concentrations.

This is substantiated by looking at the solubility experimental data shown in Fig 6.5-6 of ANL-WIS-MD-000010 Rev 03, attached below.



Source: *pu solb 110.jnb* in Appendix I.

NOTE: Modeled results are for log fCO_2 = -3.5

Figure 6.5-6. Comparison of Experimental Data with the Predictions of Plutonium-Solubility Model

While the printed solubility limit abstraction curve is for Log $fCO_2 = -3.5$, the curve for -3.0 will be only slightly higher. I have drawn an approximate curve for Log $fCO_2 = -2.0$, based on data in Table 6.5-1 of the same report. (black, labelled)

by more than one log unit DAP 5/24/06

It can be seen that none of the experimental data exceed the highest curve, especially for the pH 4.5 to 8 range. In fact, some of the results that do exceed the curve can be attributed to the higher fCO_2 in the experiments (red labels on figure, hand drawn). Therefore, a 2σ uncertainty of 1.0 is not likely to yield a value that underestimates a reasonable value for solubility.

5/30/06 DAP Note: the Wilson 1990a and 1990b data points are not from solubility experiments.

We wish to translate this lookup table and the associated uncertainty into a probability distribution function that can be used in TPA.
Scott Painter performed the following calculations that resulted in a distribution. His work is recorded in Scientific Notebook 318E.
Scott took the table taped on page 105, assumed all values were equally probable, and produced functions by interpolating. He then sampled pH and Log fCO_2 to produce a probability distribution of plutonium solubility. As part of this calculation, he added an uncertainty term with a mean of zero, 0.5 1-sigma of ~~1.0~~ log units, and truncated at 2σ. DAP 5/30/06
(His notebook includes a comparison ~~with the~~ between distributions with and without the uncertainty.)
Scott was able to fit a normal distribution to the result that fit very well. That result, shown below, is the proposed TPA distribution:

Solubility Pu [kg/m3]: lognormal
mean = -4.5
σ = 0.55

However, this is not the way the parameter is shown in the input file.

For TPA, we need to express the distribution (i) using non-log values and (ii) using the 0.1 and 99.9 percent quantiles. These values are at +/- 3.29 sigma from the mean, i.e.

0.10 quantile = $-4.5 - 3.29(\cancel{0.55}\ 0.55)$ = -6.31 DAP 5/30/06

99.9 quantile = $-4.5 + 3.29(0.55)$ = -2.69

~~Therefore~~ DAP 5/30/06
Therefore, in the TPA input file this parameter would be expressed as:

lognormal
Solubility Pu [kg/m³]
4.9e-7, 2.0e-3

Problem with this is that it extends the range of the value perhaps more than we would like. I discussed with Painter, and we decided he would instead produce a user-defined distribution so we can directly define the upper and lower bounds of the parameter.

6/5/06 DAP Painter provided the piecewise, user-defined distribution for the plutonium solubility limit, as discussed above on this page. This allows ~~up~~ us to bound the range at the desired values. DAP 6/5/06
The distribution is taped to the next page.

The first column is the plutonium solubility limit in kg/m³ and the second column is the cumulative probability.

Painter's calculations were performed in Scientific Notebook 318E.

2/26/07
DAP

```
TableForm[ SetPrecision[result, 4] ]
```

7.112×10^{-7}	0
3.792×10^{-6}	0.05000
6.274×10^{-6}	0.1000
8.414×10^{-6}	0.1500
0.00001070	0.2000
0.00001370	0.2500
0.00001683	0.3000
0.00002019	0.3500
0.00002424	0.4000
0.00002855	0.4500
0.00003355	0.5000
0.00004011	0.5500
0.00004608	0.6000
0.00005533	0.6500
0.00006729	0.7000
0.00008216	0.7500
0.0001001	0.8000
0.0001251	0.8500
0.0001679	0.9000
0.0002549	0.9500
0.0003228	0.9700
0.0005152	0.9900
0.001324	1.000

2/26/07
DAP

Revise TPA Neptunium Solubility Limit

These notes follow up on those recorded two years ago on pages 73–80.
As noted on page 104, a more recent evaluation concluded that a reasonable range of pH expected inside the waste package is 5.5 to 8.0. My previous Np solubility evaluation assumed 4.5 to 7.0.
Also, I am not so confident that the NpO_2 model is valid and so will not rely on it to define the lower end of the range (p. 80).

I will again use DOE's Np_2O_5 solubility limit model as found in "Dissolved Concentration Limits of Radioactive Elements," ANL-WIS-MD-000010 Rev 05, 2005. Note that the Rev 05 look-up table (Table 6.6-7) differs somewhat from Rev 02 (Table 6.6-1), but only significantly for pH 8 values. I will use the more recent Rev05 values. Use only pH 5.5 to 8.0.

Maximum – the highest Np concentration is at pH 5.5 for all fCO_2. 57.7 mg/L.

Minimum – I chose the lowest value at pH 8.0 from among the three values for $Log\,fCO_2$ = -2, -2.5, and -3. This is 0.296 mg/L.

Uncertainty – For the Np_2O_5 model, DOE applies an uncertainty term that is sampled from a normal distribution about a mean of zero, with $1\sigma = 0.8$ log units. It would not be reasonable to apply this amount to the top and bottom of a loguniform distribution, because the sampled value is applied to all waste packages at all times in a realization. In a loguniform distribution, the maximum value should be a reasonable upper bound that does not need to account for highly unlikely extreme values

when all waste packages are given the value.
However, to account for some degree of uncertainty, I will add 0.4 log units to the maximum value and subtract it from the minimum value.

Note that it was not necessary to compute the distribution explicitly, as was done for Pu (see p. 109), because the different log fCO2 curves do not diverge for Np until pH is above 8.
(ANL-WIS-MD-000010 Rev 05, Figure 6.6-2).

The range of values in mg/L is 0.296 to 57.7 mg/L.

In kg/m³, this is 2.96×10^{-4} to 0.0577.
Log values are −3.53 to −1.24.
Adding + subtracting 0.4 log units at either end:
−3.93 to −0.84

This leads to a loguniform distribution of
max = 0.14 kg/m³
min = 1.2×10^{-4}

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