SOFTWARE RELEASE NOTICE

01. SRN Number: GS-SRN-022

02. Project Title:
FITEQL2.0 - A Program for the Determination of Chemical Equilibrium Constants from Experimental Data.

Project No.
20-5702-424

03. SRN Title: FITEQL2.0

04. Originator/Requester:
Thomas J. Ratchford

Date:
03/22/94

05. Summary of Actions

- ■ Release of new code admitted to CM System (D. Turner)
- ☐ Release of modified code:
  - ☐ Enhancements made
  - ☐ Corrections made
- ■ Change of access code (L. McKague)

06. Persons Authorized Access

Name	RO/RW	A/C/D

07. Element Manager Approval: Date:

08. Remarks:

A copy of the software package FITEQL2.0, Ver. 1.1 was retained by the Principle Investigator for use in the CNWRA work center; therefore, a new release may not be necessary.

SOFTWARE SUMMARY FORM

01.Summary Date: 03/22/94	02. Summary prepared by(Name and Phone) T.J. Ratchford 522-3083	03. Summary Action: New
04. Software Date: 8/15/93	05. Short Title: FITEQL2.0	
06. Software Title: FITEQL2.0 - A Program for the Determination of Chemical Equilibrium Constants from Experimental Data.		07. Internal Software ID: NONE

08. Software Type:	09.Processing Mode:	10. APPLICATION AREA
☐ Automated Data System	☐ Interactive	A. General:
■ Computer Program	☐ Batch	■ Scientific/Engineering ☐ Auxiliary Analyses
☐ Subroutine/Module	■ Combination	☐ Total System PA
		☐ Subsystem PA ☐ Other
		b. Specific:

11. Submitting Organization and Address:	12. Technical Contact(s) and Phone:
CNWRA, SwRI, San Antonio, Texas	D. Turner, (210) 522-2139

13. Narrative:

FITEQL2.0 is a Program for the Determination of Chemical Equilibrium Constants from Experimental Data..

14. Computer Platform	15. Computer Operating System:	16. Programming Language(s):	17. Number of Source Program Statements:
CRAY/XMP	UNIX	FORTRAN	3,116 lines of code
18. Computer Memory Requirements: UNKNOWN	19. Tape Drives: NONE	20. Disk/Drum Units: N/A	21. Graphics: UNKNOWN

22. Other Operational Requirements

NONE

23. Software Availability:	24. Documentation Availability:
■ Available ☐ Limited ☐ In-House ONLY	■ Available ☐ Inadequate ☐ In-House ONLY

25. Submission Package Status:

Acceptance Criteria: Met ■ Not Met ☐ Software QA Assessment: Successful ■ Unsuccessful ☐

Code Custodian: T.J. Ratchford Date: 3/22/94

CNWRA Form TOP-4-1 (08/93)

```
login: tjr1
Password:
Last successful login was : Tue Mar 22 07:20:09 from mica
Service class changed to p2 from p2
news: mail_problems configuration abaqus4.9 abaqus5.2 FUNDING.OCT1 synpop
 IMWI_report zircon net.maint xwd tech_library billing spms_orps symposium
 udmp_change host_table tmpdir ov_mail HPforms atlas fortran_90 elm imagen
 NSF.access exit_status brackets
TERM = (vt100) vt100
gemstone.1 ~ => cd FITEQL2.0
gemstone.2 ~/FITEQL2.0 => ls -l
total 4
drwxr-x---   2 tjr1     tjr1         4096 Mar 22 07:40 CHECKO/
drwx------   2 tjr1     tjr1         4096 Jan 13 13:56 TEST/
drwx------   2 tjr1     tjr1         4096 Mar 22 07:40 VCS/
drwxr-x---   2 tjr1     tjr1         4096 Mar 22 07:39 WKDIR/
gemstone.3 ~/FITEQL2.0 => cd VCS
gemstone.4 ~/FITEQL2.0/VCS => ls -l
total 64
-rw-r-----   1 tjr1     tjr1           31 Mar 22 07:40 p.fit2.for
-rw-r-----   1 tjr1     tjr1           31 Mar 22 07:40 p.fit2dim.for
-r--r-----   1 tjr1     tjr1       124073 Mar 22 07:26 s.fit2.for
-r--r-----   1 tjr1     tjr1       124058 Mar 22 07:26 s.fit2dim.for
gemstone.5 ~/FITEQL2.0/VCS =>                          134.20.1.1 08:41:49
```

3/22/94 YJR

SOFTWARE RELEASE NOTICE

01. SRN Number: GHGC-SRN-039

02. Project Title:
FITEQL - Determination of Chemical Equilibrium Constants From Experimental Data

Project No.
20-5704-072

03. SRN Title: FITEQL Ver 2.0

04. Originator/Requester:
David Turner

Date:
9/28/95

05. Summary of Actions

- ■ Release of new code admitted to CM System
- □ Release of modified code:
  - □ Enhancements made
  - □ Corrections made
- □ Change of access code
- □ Software retirement

06. Persons Authorized Access

Name	RO/RW	A/C/D

07. Element Manager Approval: Date:

08. Remarks:

A copy of the software package FITEQL, Ver 2.0 was retained by the Principle Investigator for use in the CNWRA work center; therefore, a new release may not be necessary.

SOFTWARE SUMMARY FORM

01.Summary Date: 7/28/95	02. Summary prepared by(Name and Phone) David R. Turner 210-522-2139	03. Summary Action: NONE
04. Software Date: 12/12/87	05. Short Title: FITEQL, Version 2.0	
06. Software Title: FITEQL, Version 2.0: A Computer Code for Determination of Chemical Equilibrium Constants from Experimental Data		07. Internal Software ID: NONE

08. Software Type:	09.Processing Mode:	10. APPLICATION AREA
□ Automated Data System	□ Interactive	A. General: ■ Scientific/Engineering □ Auxiliary Analyses □ Total System PA
■ Computer Program	■ Batch	□ Subsystem PA □ Other
□ Subroutine/Module	□ Combination	b. Specific: Geochemical Calculations

11. Submitting Organization and Address:	12. Technical Contact(s) and Phone:
CNWRA, SwRI, San Antonio, Texas	Dr. John C. Westall, 503-737-2081

13. Narrative: FITEQL, version 2.0 is designed to determine chemical equilibrium constants. It was designed especially for consideration of surface complexation models of adsorption at electrastatically charged interface. The code includes four (4) surface complexation models, triple layer, double layer, constant capacitance, and Sterne models. The code was prepared by Dr. John C. Westall, of Ocean State University for the Dept. of Energy and Botelle Pacific Northwest Laboratory.

14. Computer Platform	15. Computer Operating System:	16. Programming Language(s):	17. Number of Source Program Statements:
IBM PC/XT/AT	DOS	Fortran 77	1558 lines of code
18. Computer Memory Requirements:	19. Tape Drives:	20. Disk/Drum Units:	21. Graphics:
640 kb	N/A	N/A	N/A

22. Other Operational Requirements

NONE

23. Software Availability:	24. Documentation Availability:
■ Available □ Limited □ In-House ONLY	■ Available □ Inadequate □ In-House ONLY

25. Submission Package Status:

Acceptance Criteria: Met ■ Not Met □ Software QA Assessment: Successful ■ Unsuccessful □

Code Custodian: T. J Ratliff Date: 9/28/95

CNWRA Form TOP-4-1 (08/93)

CNWRA INFORMATION PROCESSING STANDARD SOFTWARE SUMMARY

01. Summary Date	02. Summary prepared by *(Name and phone)*	03. Summary action
Yr. 04 Mo. 01 Day 02	David R. Turner 512-522-2139	New [x] Replacement [ ] Deletion [ ]
04. Software Date: Yr. 12 Mo. 12 Day 27	03. Software title: FITEQL Version 2.0: A Computer code for determination of chemical Equilibrium Constants from Experimental Data.	Previous Internal Software ID
06. Short title: FITEQL Version 2.0		07. Internal Software ID

08. Software type	09. Processing Mode	10. APPLICATION AREA — General		Specific
[ ] Automated Data System	[ ] Interactive	[ ] Computer Systems Support/Utility	[ ] Management/Business	Geochemistry
[x] Computer Program	[x] Batch	[x] Scientific/Engineering	[ ] Process Control	
[ ] Subroutine/Module	[ ] Combination	[ ] Bibliographic/Textual	[ ] Other	

11. Submitting organization and address	12. Technical contact(s) and phone
Dr. John C. Westall Department of Chemistry Oregon State University Corvallis, OR 97331	Dr. John C. Westall 503-737-2081

13. Narrative

FITEQL Version 2.0 is designed to determine chemical equilibrium constants. It was designed especially for consideration of surface complexation models of adsorption at charged interfaces. The code includes four electric double layer models and corrects for ionic strength effects on activity coefficents using the Davies equation. The code was preparedby Dr. John C. Westall of Oregon State University for the Department of Energy and Batelle Pacific Northwest Laboratory.

14. Keywords

FITEQL, Electrostatic, Double Layes, Surface Complexation, Equilibrium Constant, Adsorption

15. Computer manufacturer and model	16. Computer operating system	17. Programming language(s)	18. Number of source program statements
IBM PC/XT/AT	DOS	FORTRAN 777	
19. Computer memory requirements	**20. Tape drives**	**21. Disk/Drum units**	**22. Terminals**

23. Other operational requirements

24. Software availability			25. Documentation availability		
Available	Limited	In-house only	Available	Inadequate	In-house only
[x]	[ ]	[ ]	[x]	[ ]	[ ]

26. FOR SUBMITTING ORGANIZATION USE

CENTER FOR NUCLEAR WASTE REGULATORY ANALYSES

M E M O R A N D U M

September 25, 1995

TO: Bruce Mabrito
Director, Quality Assurance

FROM: David R. Turner
Senior Research Scientist

SUBJECT: Configuration management for the geochemical speciation codes FITEQL, Version 2.0 and MINTEQA2, Version 3.11

The original installation disks for FITEQL, Version 2.0 and MINTEQA2, Version 3.11 include sample input and output files to ensure that the codes have been installed and will run properly on different systems. I have followed instructions and installed both of these codes on an IBM 486 PC and run the test problems provided with the codes. The configuration managment package that I have submitted to T. Ratchford includes both the original ASCII input and output files, as well as the sample output files produced using the codes as installed on my system. In all cases, the run output on my system has matched the included output files.

To: File

FROM: T. J. Ratchford, Code custodian

SUBJECT: FORWARN Evaluation of an unmodified copy of FITEQL.

The following information is a summation of the testing of FITEQL using FORWARN. FITEQL is a unmodified, purchased program. There were no program limiting information uncovered by the test.

Local Diagnostics for Subroutine SUBMN File FIT2.FOR

Line	Severity	Message
91	I	(17) Local variable NDTDIM is assigned but never used
92	I	(17) Local variable NDXDIM is assigned but never used
104	I	(17) Local variable NT0DIM is assigned but never used
105	I	(17) Local variable NX0DIM is assigned but never used
106	I	(17) Local variable NUKDIM is assigned but never used
107	I	(17) Local variable NUTDIM is assigned but never used
108	I	(17) Local variable NUXDIM is assigned but never used

Local Diagnostics for Subroutine SURFIN File FIT2.FOR

Line	Severity	Message
1308	I	(17) Local variable AVNO is assigned but never used

Local Diagnostics for Subroutine ACT0 File FIT2.FOR

Line	Severity	Message
1524	I	(17) Local variable ZKFZKF is assigned but never used

Summary

File Name	Lines	Local I	Local W	Local E	Global I	Global W	Global E
FIT2.FOR	1558	9	0	0	0	0	0
Totals	1558	9	0	0	0	0	0

SOFTWARE RELEASE NOTICE

01. SRN Number: CHGC-SRN-128

02. Project Title: Radionuclide Transport	Project No. 20-5708-871

03. SRN Title: FITQL Version 2.0

04. Originator/Requestor: D. Turner	Date: 8/2/96

05. Summary of Actions

- ■ Release of new software
- □ Release of modified software:
  - □ Enhancements made
  - □ Corrections made
- □ Change of access software
- □ Software Retirement

06. Persons Authorized Access

Name	RO/RW	A/C/D
David Turner	RW	

07. Element Manager Approval: David R Turner for E C Pearcy Date: 8/2/96

08. Remarks:

CNWRA Form TOP-6 (06/95)

SOFTWARE RELEASE NOTICE

01. SRN Number: GHGC-SRN-106

02. Project Title:
FITEQL, Version 2.0: A computer Code for Determination of Chemical Equilibrium Constants from Experimental Data

Project No.
20-5702-424

03. SRN Title: FITEQL, Version 2.0 (Cray)

04. Originator/Requestor: Budhi Sagar

Date: 01/22/96

05. Summary of Actions

- ☐ Release of new software
- ☐ Release of modified software:
  - ☐ Enhancements made
  - ☐ Corrections made
- ☐ Change of access software
- ■ Software Retirement

06. Persons Authorized Access

Name	RO/RW	A/C/D
N/A		

07. Element Manager Approval: E.C. [signature] Date: 1/31/96

08. Remarks:

Not considered important to regulatory reviews in revised FY96 OPS Plans.

FIT2 Fortran Program
Static and Dynamic Analysis

March 10, 1994

Earl S. Marwil
John E. Tolli
Scientific Computing Unit
Idaho National Engineering Laboratory

1. Introduction

This analysis was performed on the Cray version of the software as provided by Southwest Research Institute (SwRI).

One sample problem was supplied along with the source code. The program was analyzed using the Craft (Cross Reference Analysis of Fortran) tool, FORWARN, the Fortran 77 analyzer, and PC-Metric. These tools provide static analysis, coverage analysis, and complexity analysis.

The sister program FIT2DIM was alao analyzed. Since the only difference between the two programs is in the size of some arrays, the information in this analysis is also applicable to FIT2DIM

2. References

[1] N.H. Marshall and E.S. Marwil, Cross Reference Analysis of Fortran (CRAFT), EG&G-CATT-9198, EG&G Idaho, Inc., July 1991.
[2] Fortran 77 Analyzer User's Manual, National Bureau of Standards, NBS GCR 81-359, 1981
[3] FORWARN User's Guide, Quibus Enterprises, Inc., July 1991.
[4] PC-Metric User's Guide, SET Laboratories, Inc., 1987.

3. Functions

The FIT2 program contains 20 Fortran routines.

There are 27 alternate entry points as follows:

Alternate entry	Module	Alternate entry	Module	Alternate entry	Module
actx	act0	oieql	oidat	setup	submn
actz	act0	outy	outx	sne	submn
adjktx	submn	outyab	outx	surf0	surfin
bldnm	submn	outz	outx	surfoi	surfin
ftfx	submn	preql	coeql	surfpx	surfin
incntl	submn	prktx	submn	surft	surfin
inda	submn	prnum	conum	surfx	surfin
ineql	submn	prsos	submn	surfy	surfin

```
init        submn   | prvar       covar   | surfz       surfin
```

4. Common Block Irregularities

There are 20 common blocks in the FIT2 program.

There are several instances of a common block not being used by a module in which it is declared:

Block name	Modules not using
/bfdim/	covar
/bfeql/	submn
/bfnumu/	submn
/bfvar/	submn
/bufnum/	submn
/data/	coeql, conum, covar, fiteql2, prktx0
/dy/	coeql, conum, fiteql2, oidat, prktx0
/n0/	fiteql2
/nin/	coeql, conum, covar, fiteql2, prktx0
/parm/	actpr, conum, covar, fiteql2, prktx0
/pow/	fiteql2, oidat
/sigma/	coeql, conum, covar, fiteql2, prktx0
/u/	coeql, conum, fiteql2
/var/	fiteql2
/wt/	covar, fiteql2, oidat, prktx0

5. Interface Irregularities

No Exceptions to report.

6. Local Variable Irregularities

Local variable exceptions are noted as follows:

Module	Variable	Exception
act0	zkfzkf	Defined, Unused
error	j	Defined, Unused
submn	ndtdim	Defined, Unused
submn	ndxdim	Defined, Unused
submn	nt0dim	Defined, Unused
submn	nukdim	Defined, Unused
submn	nutdim	Defined, Unused
submn	nuxdim	Defined, Unused
submn	nx0dim	Defined, Unused
surfin	avno	Defined, Unused

7. Fortran Extensions

Module "fiteql2" has a name which is longer than 6 characters.

8. Optimization

The following table summarizes the performance data gathered from execution of the sample problem. Only those routines exercised by the sample problem are shown

(see "Coverage Analysis" for a list of routines not exercised by the sample problem, i.e., coverage = 0%). The table lists all program modules in descending order according to CPU time. To optimize code execution time, emphasis should be placed on those modules which appear highest in the listing.

In order to obtain meaningful statistics for performance evaluation, the program should execute for a reasonable amount of time. Note that the execution time for this sample problem is short (<< 10 sec) and that the resulting statistics may therefore not accurately reflect program performance for more typical (possibly longer) runs.

The performance data show that a high percentage of the overall execution time (68.090%) is spent in the first 4 routines listed. This is due primarily to the following (applies to some or all of the 4 routines):

1) a low percentage of floating point operations which are performed in vector mode (%Vflops is small)

2) a high rate of instruction buffer fetches (IBFR > 1).

A detailed optimization analysis effort should focus on these 2 areas.

PERFORMANCE DATA FOR FIT2

ROUTINE NAME	Time	%ExTime	%AccumT	%Vflops	IFact	MC/MR	IBFR
SOLVEX	0.060	51.904	51.904	75.87965	0.00	0.386	0.488
MATPX	0.007	5.745	57.649	0.00000	0.00	0.813	1.002
FTFX	0.006	5.579	63.228	42.44306	0.02	0.869	0.915
PREQL	0.006	4.863	68.090	55.34537	0.00	0.768	0.940
SIMQ	0.004	3.732	71.823	15.70328	0.43	1.670	0.759
BLDNM	0.004	3.470	75.293	48.59813	0.02	1.171	0.829
SETUP	0.003	2.859	78.152	4.47761	0.04	1.625	1.060
INDA	0.003	2.537	80.690	0.00000	0.00	0.600	0.836
SURFX	0.003	2.504	83.194	0.00000	0.37	1.937	0.858
SURFPR	0.003	2.219	85.413	0.00000	0.00	0.879	0.966
OIEQL	0.002	2.072	87.485	0.00000	0.00	1.007	0.888
INPROX	0.002	1.898	89.383	0.00000	0.00	0.719	1.047
IADX	0.002	1.856	91.239	0.00000	2.23	6.168	1.046
FITEQL2	0.002	1.510	92.749	0.00000	0.00	1.678	1.649
IADY	0.002	1.458	94.207	0.00000	2.17	3.616	0.388
SURFZ	0.001	1.240	95.447	0.00000	1.37	5.583	1.004
SURFT	0.001	0.936	96.383	0.00000	1.82	6.607	0.444
SURFY	0.001	0.756	97.139	0.00000	2.25	25.323	0.549
PRKTX	0.001	0.604	97.743	0.00000	0.00	0.924	1.018
SURFO	0.001	0.546	98.290	0.00000	0.21	2.375	0.991
INCNTL	0.000	0.427	98.717	0.00000	0.00	0.820	0.821
PRSOS	0.000	0.290	99.007	0.00000	0.00	1.028	0.997
INEQL	0.000	0.249	99.256	0.00000	0.00	0.743	0.925
ADJKTX	0.000	0.176	99.431	1.91571	0.00	1.311	0.958
PRKTXO	0.000	0.149	99.581	0.00000	0.00	1.096	0.805
SURFOI	0.000	0.141	99.722	0.00000	0.00	1.136	0.867
SURFIN	0.000	0.129	99.851	0.00000	0.00	0.277	0.971
COEQL	0.000	0.099	99.949	100.00000	0.02	1.877	0.785
SNE	0.000	0.025	99.975	0.00000	0.01	1.259	1.027

INIT	0.000	0.024	99.998	0.00000	0.01	1.580	0.652
SUBMN	0.000	0.002	100.000	0.00000	0.00	6.036	0.504
Totals (All Traced Routines)							
	0.116	100.000	100.000	69.99695	1.38	0.624	0.695

Key:

- %AccumT = accumulated percentage of total CPU time
- %ExTime = percentage of total CPU time
- %Vflops = percentage of floating point operations due to vector floating point operations
- IBFR = Instruction Buffer Fetch Rate (megafetches/sec)
- IFact = Inline Factor (total calls to routine / average time spent in routine for each call)
- MC = number of memory conflicts
- MR = number of memory references
- Time = total CPU time (sec)

9. Coverage Analysis

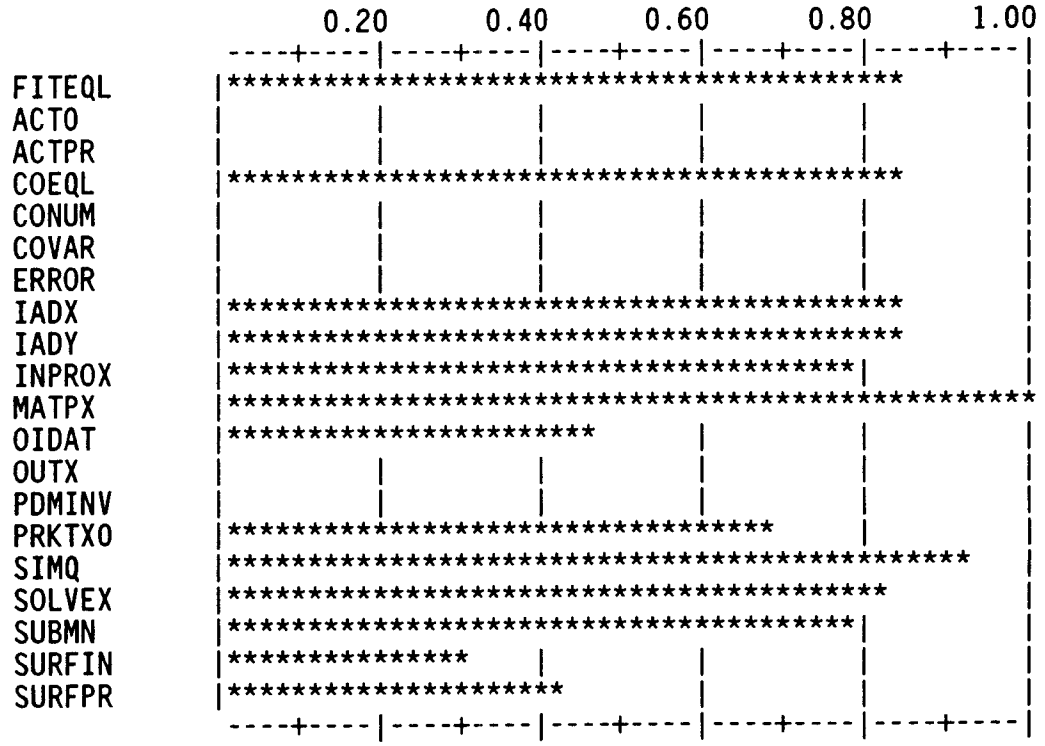
A coverage analysis shows that the sample problem yielded a 61% segment coverage of FIT2. Sample problems provided with simulation programs typically achieve only 35% to 50% coverage. A statement of software quality cannot be made for routines that have low coverage, i.e., large portions of the code are untested.

Note that 7 routines have 0% coverage. These routines are not tested with the supplied sample problem.

One routine achieves 20%-39% coverage, 2 routines achieve 40%-59% coverage, 3 routines achieve 60%-79% coverage, 6 routines achieve 80%-99% coverage, and 1 routine achieves 100% coverage.

Module Name	Number of Segments in module	Number of Segments Executed	Percent Segment Coverage
FITEQL	36	30	83.3
ACTO	9	0	0.0
ACTPR	3	0	0.0
COEQL	32	27	84.4
CONUM	10	0	0.0
COVAR	29	0	0.0
ERROR	3	0	0.0
IADX	6	5	83.3
IADY	6	5	83.3
INPROX	33	26	78.8
MATPX	3	3	100.0
OIDAT	45	21	46.7
OUTX	14	0	0.0
PDMINV	15	0	0.0
PRKTXO	25	17	68.0
SIMQ	27	25	92.6
SOLVEX	64	52	81.2
SUBMN	185	145	78.4
SURFIN	66	20	30.3

SURFPR	21	9	42.9
Totals	632	385	60.9



coverage = 0.	ACTO OUTX	ACTPR PDMINV	CONUM	COVAR	ERROR
0.20 <= coverage < 0.40	SURFIN				
0.40 <= coverage < 0.60	OIDAT	SURFPR			
0.60 <= coverage < 0.80	INPROX	PRKTXO	SUBMN		
0.80 <= coverage < 0.85	FITEQL	COEQL	IADX	IADY	SOLVEX
0.90 <= coverage < 0.95	SIMQ				
coverage = 1.00	MATPX				

Program coverage for this run =0.61

10. Complexity Analysis

Some key metrics are the number of executable statements (sloc), the number of non-blank comments (ncomt), McCabe's extended cyclomatic complexity (vg2), the number of branching statements (cgoto, ugoto, bIF, and lIF), and Halstead's predicted number of errors in (re)writing the code (bhat). Measures are normalized per 100 executable statements for ease of comparison and are listed in the table below.

The branching measures for this code indicate few unconditional GO TO statements and logical IFs for most program modules. There are, however, some notable exceptions (e.g. FITEQL2, SURFPR). This code appears to be fairly well structured.

Most routines have a low ratio of non-blank comments to source code. This code could probably benefit from more internal documentation.

McCabe's extended cyclomatic complexity (vg2), normalized per 100 lines of source code, indicates high values. Generally, the routines with the highest complexity are those most likely to have defects. As a guideline, normalized measures of 15 or greater should be considered complex. A software maintenance program should focus on those routines with the highest measures.

Complexity Report by Subprogram for FIT2

Name	loc	sloc	cmnt	ncomt	ncomt /sloc	vg2 /sloc	cgoto	cgoto /sloc	ugoto	ugoto /sloc	bIF	bif /sloc	lIF	lif /sloc	Bhat
FITEQL2	61	48	13	13	27.1	50.0	0	0.0	2	4.2	0	0.0	15	31.3	0
ACTO	32	26	1	1	3.8	15.4	0	0.0	1	3.8	0	0.0	2	7.7	0
ACTPR	21	10	1	1	10.0	20.0	0	0.0	0	0.0	0	0.0	0	0.0	0
COEQL	102	65	12	12	18.5	23.1	0	0.0	2	3.1	0	0.0	6	9.2	1
CONUM	92	44	13	13	29.5	11.4	0	0.0	0	0.0	0	0.0	0	0.0	1
COVAR	104	57	16	16	28.1	21.1	0	0.0	5	8.8	0	0.0	3	5.3	1
ERROR	9	5	2	2	40.0	40.0	0	0.0	0	0.0	0	0.0	0	0.0	0
IADX	15	10	1	1	10.0	30.0	0	0.0	1	10.0	0	0.0	1	10.0	0
IADY	15	10	1	1	10.0	30.0	0	0.0	1	10.0	0	0.0	1	10.0	0
INPROX	68	54	10	10	18.5	24.1	0	0.0	9	16.7	0	0.0	6	11.1	0
MATPX	8	5	0	0	0.0	40.0	0	0.0	0	0.0	0	0.0	0	0.0	0
OIDAT	120	80	10	10	12.5	27.5	0	0.0	8	10.0	0	0.0	12	15.0	1
OUTX	49	28	3	3	10.7	21.4	0	0.0	0	0.0	0	0.0	1	3.6	1
PDMINV	20	20	0	0	0.0	35.0	0	0.0	1	5.0	0	0.0	2	10.0	0
PRKTXO	55	41	3	3	7.3	29.3	0	0.0	6	14.6	0	0.0	6	14.6	0
SIMQ	55	50	7	7	14.0	24.0	0	0.0	4	8.0	0	0.0	4	8.0	1
SOLVEX	84	85	8	8	9.4	34.1	0	0.0	5	5.9	0	0.0	17	20.0	1
SUBMN	400	332	64	64	19.3	25.3	0	0.0	26	7.8	0	0.0	37	11.1	4
SURFIN	204	155	16	16	10.3	11.0	7	4.5	0	0.0	0	0.0	1	0.6	4
SURFPR	44	26	2	2	7.7	23.1	2	7.7	8	30.8	0	0.0	0	0.0	1

Legend of Metrics in Report

loc -- lines of code
sloc -- number of executable statements
cmnt -- total number of commnts
ncomt -- number of non-blank COMMENT statements
100*ncomt/sloc -- percent, nonblank comments to number of executable statements
100*vg2/sloc -- percent, extended complexity of number of executable statements
cgoto -- number of COMPUTED GO TO statements
100*cgoto/sloc -- percent, computed GOTO's to number of executable statements
ugoto -- number of UNCONDITIONAL GO TO statements
100*ugoto/sloc -- percent, unconditional GOTO's to number of executable statements
bIF -- number of BLOCK IF statements
100*bif/sloc -- percent, Block IF statements to number of executable statements
lIF -- number of LOGICAL IF statements

100*lif/sloc -- percent, logical IF statements to number of executable statements
Bhat -- Halstead's predicted number of errors in writing code

SOFTWARE VALIDATION TEST PLAN FOR FITEQL, VERSION 2.0

Prepared for

U.S. Nuclear Regulatory Commission
Contract NRC–02–02–012

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English C. Pearcy — **Date**
Manager, Geohydrology and Geochemistry

CONTENTS

FIGURES

1 SCOPE OF THE VALIDATION

This document establishes the Software Validation Test Plan for validating the installation and functionality of the geochemical equilibrium speciation code FITEQL, Version 2.0 (Westall, 1982a,b). FITEQL, Version 2.0 is an acquired code, originally developed by John Westall in the Department of Chemistry at Oregon State University. It has been broadly used in the geochemical and chemical communities to derive parameters for sorption models (e.g., Dzombak and Morel, 1990). The software is used by staff at the Center for Nuclear Waste Regulatory Analyses (CNWRA) to provide technical assistance to the U.S. Nuclear Regulatory Commission (NRC) in its high-level waste program.

This Software Validation Test Plan applies to FITEQL, Version 2.0, and is intended to validate the software for use in modeling geochemical equilibrium reactions as identified in the test cases described in Section 6. FITEQL, Version 2.0 is currently under configuration control in accordance with Technical Operating Procedure (TOP)-018.

The CNWRA has extensive experience using FITEQL, Version 2.0 to simulate radionuclide sorption as a function of system chemistry (Turner, 1993; 1995). Current CNWRA plans for FITEQL, Version 2.0 continue to focus on using the code to interpret sorption experimental data and derive sorption model parameters. The sorption model most commonly used by CNWRA staff is the diffuse layer model. Other surface complexation models such as the constant capacitance and triple layer models are not commonly used and will therefore not be tested at this time. If a decision is made to use these models or other code capabilities, this software validation test plan will be modified as necessary.

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3 ENVIRONMENT

3.1 Software—Introduction

FITEQL, Version 2.0 (released October 1982, Westall, 1982b) is a FORTRAN IV nonlinear parameter optimization code designed to determine chemical equilibrium constants from experimental data. The code is especially intended to derive parameters for electrostatic surface complexation models of sorption at a charged mineral-water interface. It can be used to apply either a triple layer model, a constant capacitance model, or a diffuse layer model to

experimental sorption data. The code was written for a DOS-based operating system on personal computer compatible hardware. This Software Validation Test Plan is designed to evaluate installation and performance of FITEQL, Version 2.0 on a IBM Personal Computer, Windows NT platform (see Section 3.2).

3.2 Code Description

The following description of FITEQL, Version 2.0 is based on the source code and on the user's manuals for FITEQL, Version 1.2 (Westall, 1982a) and FITEQL, Version 2.0 file. As received, FITEQL consists of a single executable file (fit2.exe). At CNWRA, the source code was modified to enlarge the matrices considered by FITEQL, and allow a larger number of chemical components and experimental datapoints (fit2dim.exe). All data are entered as input, and FITEQL, Version 2.0 does not call any independent or compiled databases while running.

3.2.1 Input

A FITEQL, Version 2.0 user typically has a problem relevant to a laboratory experimental system, in particular batch sorption data. This system is described in terms of the physical conditions such as temperature, and the concentrations of chemical components, species, solids and gases that are present. FITEQL, Version 2.0 uses a formatted input file divided into three key parts. The first part sets flags to indicate what level of output is desired, establish limits on the number of iterations, indicate whether sorption is to be considered, and identify the chemical components to be considered in the system. The second part of the input file provides a description of the physical properties of the solid surface and the reactions for the chemical equilibrium model with corresponding equilibrium constant (Log K) values. Because FITEQL, Version 2.0 uses no standalone databases, all chemical reaction stoichiometries and thermodynamic data must be entered in the input file. The user also postulates one or more surface reactions and specifies the model parameter(s) intended for optimization. In the third part of the input file, the user enters serial sorption-pH or potentiometric titration data, along with some estimate of experimental uncertainty. Although there are preprocessors available for later versions of FITEQL (Herbelin and Westall, 1999), there is no preprocessor for FITEQL, Version 2.0. Input can be prepared using an ASCII text editor. A sample FITEQL, Version 2.0 input file is provided in Figure 3-1.

In calculating sorption model parameters, FITEQL seeks to minimize the difference between experimental values and those calculated based on mass action constraints for those components where both the free and total concentrations are known. The numerical procedures employed in FITEQL and the details of program input are described in more detail elsewhere (Westall, 1982a,b; Dzombak and Morel, 1990).

3.2.2 Output

The results from the equilibrium geochemical speciation calculation are written to an output file specified by the user. FITEQL, Version 2.0 will overwrite previously existing files with the same name. Depending on the level of detail chosen by the user, the output includes an echo of the input to verify that the input file was read correctly. FITEQL, Version 2.0 does not provide a time stamp in the output file to verify the time of the run. The output includes a "best-estimate" of the model parameters, along with a "goodness-of-fit" parameter and standard deviations for

```
         0                                                                  Neptunum
         1                                                                     on
         0                                                                  Hematite
         0                                                                  1.6s\nm2
         1                                                                  No CO2
        90                                                                  I=0.01
         3          1          3          1                                np=1e-7
00001  -4.412 3.87E-5   xoh                                               14.4m2/g
00160  -2.0   0.00E00   psi0                                              1 g/l
00031  -6.92  1.20E-7   npo2+                                             00000098
00032   0.0   0.00E00   npo2(ads)                                         00000100
00050   0.0   0.00E00   h+                                                00000102
00003  -2.00  0.00E00   na+                                               00000104
00005  -2.00  0.00E00   clo4-                                             00000106
                                                                          00000110
00001    0.00  001  1                                                     xoh
00050    0.00  050  1                                                     h+
00031    0.00  031  1                                                     npo2+
00003    0.00  003  1                                                     na+
00005    0.00  005  1                                                     clo4-
03100  -11.30  031  1 050 -1                                             npo2oh
03101  -23.50  031  1 050 -2                                             npo2oh2
00100  -13.90  050 -1                                                    h2o diss
01050    9.51  001  1 160  1 050  1                                      xoh2+
01100  -10.16  001  1 160 -1 050 -1                                      xo-
03201   -5.00  001  1 160  0 050 -1 031  1 032  1                        xonpo2
                                                                          00000174
                                                                          00000175
00002   014.4 1.000                                                       00000180
0.01   1.0                                                               00000185
         1                                                                00000190
       3201                                                               00000195
         6          1          1          0                             00000230
        32
3.00E-09
2.18E-08
4.53E-08
6.95E-08
7.37E-08
1.19E-07
        50
-5.802
-6.211
-6.697
-7.004
-7.251
-9.173
         1          1
        32       0.10    1.0E-10                                          10%error
        50       0.05    0.0E-00                                          +/- 0.02
```

Figure 3-1. Example Input File for FITEQL, Version 2.0 for Neptunium(V) Sorption on Hematite

the estimated parameters (Westall, 1982a,b). These values are determined based on the experimental error specified in the optimization run and the size of the data set. For example, goodness-of-fit and parameter uncertainty generally deteriorate for smaller data sets because the chemical system is not as well constrained (Dzombak and Morel, 1990). The goodness-of-fit parameter generated by FITEQL, Version 2.0 can be used as a measure of how well the experimental data are described by the assumed chemical and adsorption models. Additional

output includes equilibrium concentrations of the components and aqueous species that make up the geochemical equilibrium model.

3.3 System Requirements and Installation

3.3.1 System Requirements

FITEQL, Version 2.0 was programmed and compiled for the DOS-based IBM personal computer family or compatible systems. It is a very compact code and consists of a single stand alone executable file. It will run on almost any 386- or 486-based IBM personal computer with 640 Kb of available RAM.

3.3.2 Installing FITEQL, Version 2.0

Because it is a stand alone compiled executable, FITEQL, Version 2.0 requires no installation procedures.

4 PREREQUISITES

Running FITEQL, Version 2.0 requires that the stand alone executable file (fit2dim.exe) be installed in the same directory as the input file created by the user. The input file must be formatted using the format described in Westall (1982a,b). The input file is submitted in batch mode to run with FITEQL, Version 2.0:

fit2dim<example.inp >example.out

where example.inp is the input file and example.out is the name of the file to be created for code output.

5 ASSUMPTIONS AND CONSTRAINTS

The results from geochemical equilibrium speciation codes are dependent on the type and quality of the data used in the simulation. Applications of FITEQL, Version 2.0 at the Center for Nuclear Waste Regulatory Analyses (CNWRA) have used thermodynamic data [equilibrium constants (log K)] for potentially important radioelements, including U, Pu, Th, Np, and Am. Thermodynamic data for U, Pu, Np, Am, and Tc are from the Nuclear Energy Agency Thermodynamic Database Project (Grenthe, et al., 1992; Silva, et al., 1995; Rard, et al., 1999; and Lemire, et al., 2001). These data are entered into the input file for appropriate geochemical equilibrium reactions.

6 TEST CASES

The purpose of FITEQL, Version 2.0 is to determine sorption parameters for different modeling approaches used to simulate experimental sorption data. FITEQL, Version 2.0 will be applied to a sorption data set and the model results compared against the experimental data.

In addition to testing code function against experimental data, another part of code validation is to test results from FITEQL, Version 2.0 against results from another geochemical speciation

code such as MINTEQA2, Version 4.02 (EPA, 1999a,b). If the results are in agreement, this will build some level of confidence in the capability of each code. MINTEQA2, Version 4.02 includes surface complexation modeling capabilities that have previously been validated for use in CNWRA technical assistance activities (Turner, 2002). To test FITEQL, Version 2.0 against MINTEQA2, Version 4.02, the same intensive properties (temperature, pressure) will be used and all chemical reactions will be written in terms of the same component species. Some differences in how ionic strength effects are handled in FITEQL, Version 2.0 and MINTEQA2, Version 4.02 may lead to differences in speciation that will be examined and resolved as necessary. The same thermodynamic data (e.g., log K at 298 K) will also be used to ensure consistency between calculational results.

6.1 Interpretation and Comparison to Experimental Sorption Data

Recently published data for Np(V) sorption on hematite (Kohler, et al., 1999) provides a good opportunity for testing the surface complexation modeling capabilities of FITEQL, Version 2.0. The modeling approach will be simplified to the extent possible, with a two-site model invoking strong ($>XOH_s^0$) and weak ($>XOH_w^0$) sorption sites as described in Dzombak and Morel (1990).

A single type of mononuclear, monodentate sorption reaction will be assumed for each sorption site:

$$>XOH_s^0 + NpO_2^+ = >XO_s\text{-}NpO_2^0 + H^+ \qquad \text{Log } K_{XOs\text{-}NpO2}$$

$$>XOH_w^0 + NpO_2^+ = >XO_w\text{-}NpO_2^0 + H^+ \qquad \text{Log } K_{XOw\text{-}NpO2}$$

FITEQL, Version 2.0 will be used to solve for the binding constants (Log $K_{XOs\text{-}NpO2}$ and Log $K_{XOs\text{-}NpO2}$) for the postulated sorption reactions. Additional input data include the surface protonation/deprotonation constants and total site concentration determined from the potentiometric titration data, and thermodynamic data for Np(V) from the NEA thermodynamic database (Lemire, et al., 2001). An additional adjustable parameter (for a total of three) will include the total concentration of the strong site type (T_{XOHs}).

Output from FITEQL, Version 2.0 will be compared to the experimental data of Kohler, et al. (1999). Output to be compared includes, but is not limited to:

- Total dissolved NpO_2^+ as a function of pH
- Total sorbed NpO_2^+ as a function of pH

6.2 Sorption—Surface Complexation Modeling

Turner (2002) has validated the diffuse-layer surface complexation model as implemented in MINTEQA2, Version 4.02. The Np(V)-hematite sorption data of Kohler, et al. (1999) interpreted using FITEQL, Version 2.0 (see Section 6.1) will provide the parameters necessary to implement a diffuse-layer surface complexation model in MINTEQA2, Version 4.02. These parameters will also be entered into a MINTEQA2, Version 4.02 input file, and the calculated sorption results for the Np(V)-hematite system compared to those produced by FITEQL, Version 2.0.

Output from FITEQL, Version 2.0 will be compared to the experimental data of Kohler, et al. (1999). Output to be compared includes, but is not limited to:

- Total dissolved NpO_2^+ as a function of pH
- Total sorbed NpO_2^+ as a function of pH
- Concentrations of different aqueous and surface species in the Np(V)-H_2O-CO_2 system

7 TEST INPUTS

In all test cases, the test inputs will consist of a batch input file created using the instructions contained in the user's manuals for FITEQL, Version 2.0 (Westall, 1982a,b) (see Figure 3-1). This input file will be prepared using an ASCII text editor. Chemical conditions in the FITEQL, Version 2.0 input file such as component concentration, surface area, and site concentration will be set at values consistent with the problems described in Section 6 of this software validation test plan. For test problems involving comparison to results from the geochemical speciation program MINTEQA2, Version 4.02, identical intensive parameters and thermodynamic data for Np(V) and other component species will be used to facilitate comparison of results. Differences will be evaluated and resolved as necessary.

8 TEST PROCEDURES

In all test cases, the input files described in Sections 6 and 7 will be submitted for batch run in FITEQL, Version 2.0 as described in Section 4 of this software validation test plan. Results contained in the output file created by each run will be evaluated as summarized in the following sections.

8.1 Installation Check

Because FITEQL, Version 2.0 is a stand alone code, there is no installation required other than to copy the executable (fit2dim.exe) to the same directory or subdirectory containing the input files.

8.2 Comparison with Experimental Data

The test problem described in Section 6.1 involves comparing FITEQL, Version 2.0 calculated sorption results against experimental data. The results, including component concentration and amount sorbed, will be compared in tabular and graphic form.

8.3 Comparison with MINTEQA2, Version 4.02 Simulations

For the test problem involving comparison against MINTEQA2, Version 4.02 simulations, output from the two computer programs will be compared in several ways:

- Comparison of component concentrations—This will be done in tabular form for the amount sorbed in the Np(V)-hematite system as a function of pH.

- Graphic comparison of aqueous and surface speciation—This is an effective means of comparing model results for speciation and sorption as a function of independent variables such as pH and P_{CO2}.

It is anticipated that results from the two codes will agree within a few percent, although there may be differences due to disparities between how ionic strength effects are calculated. Any differences resulting from these comparisons will be documented, evaluated, and resolved as necessary.

SOFTWARE VALIDATION REPORT FOR FITEQL, VERSION 2.0

Prepared for

U.S. Nuclear Regulatory Commission
Contract NRC–02–02–012

Prepared by

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Date

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FIGURES

TABLES

1 SCOPE OF THE VALIDATION

This report presents the results of validating the installation and functionality of the geochemical equilibrium speciation code FITEQL, Version 2.0 (Westall, 1982a,b) following the previously prepared validation test plan (Turner 2002a). FITEQL, Version 2.0 is an acquired code, originally developed by John Westall in the Department of Chemistry at Oregon State University. It has been broadly used in the geochemical and chemical communities to derive parameters for sorption models (e.g., Dzombak and Morel, 1990). The software is used by staff at the Center for Nuclear Waste Regulatory Analyses (CNWRA) to provide technical assistance to various U.S. Nuclear Regulatory Commission (NRC) programs.

This Software Validation Report applies to FITEQL, Version 2.0, and is intended to validate the software for use in modeling geochemical equilibrium reactions as identified in the test cases described in Section 2. FITEQL, Version 2.0 is currently under configuration control in accordance with Technical Operating Procedure (TOP)-018 (CNWRA, 2001). The validation tests described in this report were performed in a DOS environment on an IBM-compatible PC with a Windows NT, Version 4.0 Operating System and 256 MB RAM.

The CNWRA has extensive experience using FITEQL, Version 2.0 to simulate radionuclide sorption as a function of system chemistry (Turner, 1993, 1995, 2002b). Current CNWRA plans for FITEQL, Version 2.0 continue to focus on using the code to interpret sorption experimental data and derive sorption model parameters. The model most commonly used by CNWRA staff is the diffuse layer model. Because they require significantly more parameterization (Turner, 1993, 1995, other surface complexation models such as the constant capacitance and triple layer models are not commonly used by the CNWRA and will therefore not be tested at this time. If a decision is made to use these models or other code capabilities, the software validation test plan will be modified and the FITEQL software will be validated as necessary.

2 TEST CASES

FITEQL, Version 2.0 uses nonlinear optimization techniques to interpret experimental data and determine parameters for geochemical equilibria systems. It is particularly useful for deriving binding constants for different sorption modeling approaches. In this validation, FITEQL, Version 2.0 was used to interpret a sorption data set with an electrostatic diffuse layer model approach, and the model results were compared against the experimental data.

In addition to testing code function against experimental data, another part of the software validation is to test results from FITEQL, Version 2.0 against results from another geochemical speciation code such as MINTEQA2, Version 4.02 (EPA, 1999a,b). If the results are in agreement, this will build confidence in the capabilities of each code. MINTEQA2, Version 4.02 includes surface complexation modeling capabilities that have previously been validated for use in CNWRA technical assistance activities (Turner, 2002c). To test FITEQL, Version 2.0 against MINTEQA2, Version 4.02, the same intensive properties (temperature, pressure) were used, with chemical reactions written in terms of the same component species. The same thermodynamic data (e.g., log K at 298 K) from the Nuclear Energy Agency thermodynamic data base for neptunium (Lemire, et al., 2001) were used in each code to ensure consistency.

2.1 Interpretation and Comparison to Experimental Sorption Data

Recently published data for Np(V) sorption on hematite (Kohler, et al., 1999) provide a good opportunity for testing the surface complexation modeling capabilities of FITEQL, Version 2.0. For the purposes of validating FITEQL, Version 2.0, the modeling approach was simplified, to the extent possible, with a two-site electrostatic diffuse layer model invoking strong ($>XOH_s^0$) and weak ($>XOH_w^0$) sorption sites as described in Dzombak and Morel (1990). The sites were assumed to protonate and deprotonate according to the reactions:

$$>XOH^0 + H^+ = >XOH_2^+ \qquad \text{Log } K^+$$

$$>XOH^0 = >XO^- + H^+ \qquad \text{Log } K^-$$

Protonation (Log K^+) and deprotonation (log K^-) constants for both site types were assumed to be equal and set at values (Table 2-1) determined for the NEA sorption exercise, Test Case 1 (Turner, 2002b).

The Np(V)-hematite sorption data of Kohler, et al. (1999) for CO_2-free atmosphere, M/V = 0.1 g/L, I = 0.1 M $NaClO_4$, and $Np(V)_{total} = 1.24 \times 10^{-6}$ M was selected for optimization using FITEQL, Version 2.0 (Table 2-2). The reason for selecting this sorption data set is that it offers the highest sorption density (highest concentration, lowest M/V), and demonstrates behavior consistent with saturation of the $>XOH_s^0$ site type.

A single type of mononuclear, monodentate sorption reaction was assumed to form on both sorption sites:

$$>XOH_s^0 + NpO_2^+ = >XO_s\text{-}NpO_2^0 + H^+ \qquad \text{Log } K_{XOs\text{-}NpO2}$$

$$>XOH_w^0 + NpO_2^+ = >XO_w\text{-}NpO_2^0 + H^+ \qquad \text{Log } K_{XOw\text{-}NpO2}$$

FITEQL, Version 2.0 was used to solve for the binding constants (Log K values) for the postulated sorption reactions (Table 2-1). Additional input data (Table 2-1) include the surface protonation/deprotonation constants and site concentrations determined from the potentiometric titration data (Turner, 2002b). Thermodynamic data for Np(V) were taken from the Nuclear Energy Agency thermodynamic database (Lemire, et al., 2001). Also, because the FITEQL calculation is concentration-based rather than activity-based, the Log K values for the chemical equilibrium model have been adjusted to compensate for the ionic strength of the solution (0.1 M $NaClO_4$) using the Davies equation and methods presented in Dzombak and Morel (1990, Table 2.13). For this reason, the Log K values in the FITEQL, Version 2.0 input files differ slightly from those used in the MINTEQA2, Version 4.02 input and those values given in Table 2-1.

Results from the FITEQL, Version 2.0 simulation of the Kohler, et al. (1999) data are listed in Table 2-2 and a direct comparison to the experimental data is provided in Figure 2-1. The input file is included in the Appendix. The output file is quite extensive and is included in the electronic files accompanying this validation report.

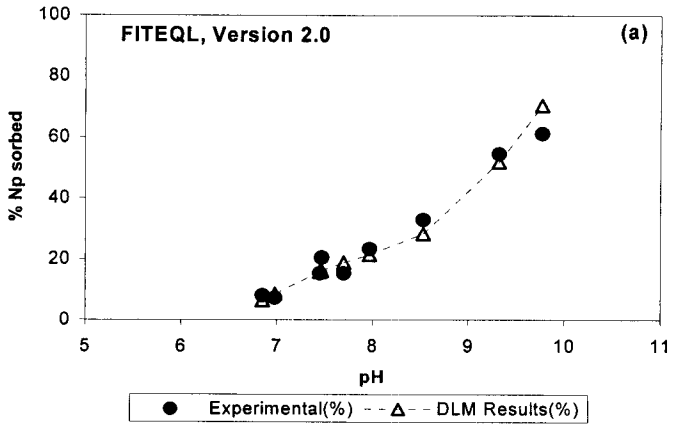
Table 2-1. Input Parameters for FITEQL, Version 2.0 and MINTEQA2, Version 4.02 Simulations for Np(V) Sorption on Hematite			
Surface Species	**Log K**	**T_{XOH} (mol sites/m^2)**	**Source**
$>XOH_s^0 + H^+ = >XOH_2^+$	9.56	—	*
$>XOH_s^0 = >XO^- + H^+$	-10.21	—	*
$>XOH_s^0$	—	1.81×10^{-07}	*
$>XOH_w^0 + H^+ = >XOH_2^+$	9.56	—	*
$>XOH_w^0 = >XO^- + H^+$	-10.21	—	*
$>XOH_w^0$	—	2.51×10^{-06}	*
$>XOH_s^0 + NpO_2^+ = >XO_s\text{-}NpO_2^0 + H^+$	-0.44	—	This study
$>XOH_w^0 + NpO_2^+ = >XO_w\text{-}NpO_2^0 + H^+$	-3.62	—	This study

*Turner, D.R. "Center for Nuclear Waste Regulatory Analyses (CNWRA) Input to the Nuclear Energy Agency Phase II Sorption Modeling Project." CNWRA Letter Report. San Antonio, Texas: CNWRA. September 2002b.

Table 2-2. Comparison of Sorption Results Calculated Using FITEQL, Version 2.0 with Np(V)-Hematite [Specific Area (A_{sp}) = 14.4 m^2/g] Sorption Data.* No CO_2, $Np(V)_{total}$ = 1.24×10^{-6} M, M/V = 0.1 g/L, I = 0.1 M $NaClO_4$.

pH	Np(V) dissolved Experiment (M)	Np(V) dissolved FITEQL, Version 2.0 (M)	Np(V) sorbed Experiment (percent)	Np(V) sorbed FITEQL, Version 2.0 (percent)
6.85	1.14×10^{-06}	1.16×10^{-06}	8.1	6.4
6.98	1.15×10^{-06}	1.13×10^{-06}	7.3	8.5
7.45	1.05×10^{-06}	1.04×10^{-06}	15.3	15.9
7.47	9.87×10^{-07}	1.04×10^{-06}	20.4	16.1
7.70	1.05×10^{-06}	1.01×10^{-06}	15.3	18.8
7.97	9.52×10^{-07}	9.76×10^{-07}	23.2	21.3
8.53	8.32×10^{-07}	8.90×10^{-07}	32.9	28.2
9.32	5.63×10^{-07}	5.98×10^{-07}	54.6	51.8
9.77	4.80×10^{-07}	3.67×10^{-07}	61.3	70.4

*Kohler, M., B.D. Honeyman, and J.O. Leckie. "Neptunium(V) Sorption on Hematite (α-Fe_2O_3) in Aqueous Suspension: The Effect of CO_2." *Radiochimica Acta.* Vol. 85: pp. 33–48. 1999.



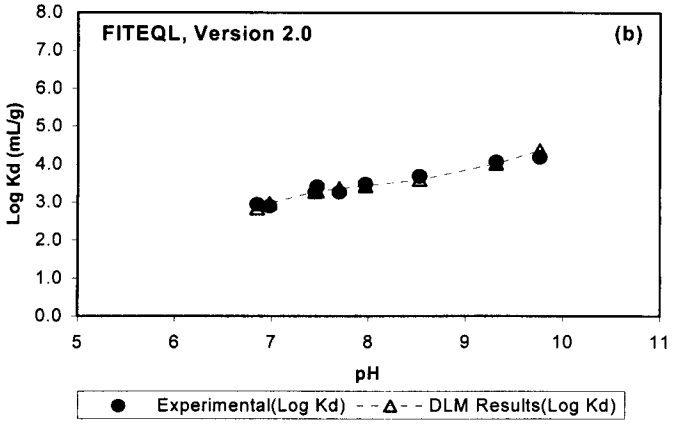


Figure 2-1. Comparison of Sorption Results Calculated Using FITEQL, Version 2.0 with Np(V)-Hematite Sorption Data of Kohler, et al. (1999). (a) Percent Np(V) Sorbed (b) Log K_d sorbed in mL/g.

2.2 Sorption—Surface Complexation Modeling

The parameters derived by optimizing the data of Kohler, et al. (1999) are suitable for use in the diffuse layer model model as implemented in MINTEQA2, Version 4.02. These FITEQL-derived parameters (Table 2-1) were entered into a MINTEQA2, Version 4.02 input file. The calculated sorption results and aqueous speciation for the Np(V)-H_2O-hematite system were compared to the experimental data and the model results produced using FITEQL, Version 2.0.

Results from the MINTEQA2, Version 4.02 simulation of the Kohler, et al. (1999) data using the FITEQL-derived parameters are listed in Table 2-3 and a direct comparison to the experimental data is provided in Figure 2-2. A comparison between the FITEQL and MINTEQA2 results is shown in Figure 2-3. The MINTEQA2, Version 4.02 input file is included in the Appendix. The extensive output file is included in the electronic files accompanying this validation report.

Table 2-3. Comparison of Np(V)-Hematite Sorption Results and Np(V) Aqueous Speciation Calculated Using FITEQL, Version 2.0 and MINTEQA2, Version 4.02. $Np(V)_{total}$ = 1.24 × 10^{-6} M, M/V = 0.1 g/L, I = 0.1 M $NaClO_4$, No CO_2.

	XO(s)-NpO_2^0		XO(w)-NpO_2^0		NpO_2^+		NpO_2OH^0		$NpO_2(OH)_2^-$		Goodness-of-Fit (Equation [1])	
pH	FITEQL (M)	MINTEQA2 (M)	FITEQL (M)	MINTEQA2 (M)	FITEQL (M)	MINTEQA2 (M)	FITEQL (M)	MINTEQA2 (M)	FITEQL (M)	MINTEQA2 (M)	FITEQL	MINTEQA2
6.85	7.89×10^{-08}	7.93×10^{-08}	1.05×10^{-09}	1.04×10^{-09}	1.16×10^{-06}	1.16×10^{-06}	3.20×10^{-11}	3.13×10^{-11}	1.46×10^{-16}	1.45×10^{-16}	1.10×10^{-02}	1.05×10^{-02}
6.98	1.04×10^{-07}	1.04×10^{-07}	1.60×10^{-09}	1.59×10^{-09}	1.13×10^{-06}	1.13×10^{-06}	4.22×10^{-11}	4.13×10^{-11}	2.60×10^{-16}	2.58×10^{-16}	5.70×10^{-03}	5.94×10^{-03}
7.45	1.90×10^{-07}	1.91×10^{-07}	6.48×10^{-09}	6.44×10^{-09}	1.04×10^{-06}	1.04×10^{-06}	1.14×10^{-10}	1.12×10^{-10}	2.08×10^{-15}	2.07×10^{-15}	3.19×10^{-04}	3.51×10^{-04}
7.47	1.93×10^{-07}	1.93×10^{-07}	6.86×10^{-09}	6.82×10^{-09}	1.04×10^{-06}	1.04×10^{-06}	1.19×10^{-10}	1.17×10^{-10}	2.28×10^{-15}	2.26×10^{-15}	1.56×10^{-02}	1.54×10^{-02}
7.70	2.20×10^{-07}	2.20×10^{-07}	1.28×10^{-08}	1.28×10^{-08}	1.01×10^{-06}	1.01×10^{-06}	1.96×10^{-10}	1.92×10^{-10}	6.36×10^{-15}	6.31×10^{-15}	1.12×10^{-02}	1.13×10^{-02}
7.97	2.39×10^{-07}	2.39×10^{-07}	2.58×10^{-08}	2.56×10^{-08}	9.75×10^{-07}	9.75×10^{-07}	3.54×10^{-10}	3.47×10^{-10}	2.13×10^{-14}	2.12×10^{-14}	2.25×10^{-03}	2.26×10^{-03}
8.53	2.55×10^{-07}	2.55×10^{-07}	9.53×10^{-08}	9.48×10^{-08}	8.89×10^{-07}	8.89×10^{-07}	1.17×10^{-09}	1.15×10^{-09}	2.56×10^{-13}	2.55×10^{-13}	9.21×10^{-03}	9.34×10^{-03}
9.32	2.60×10^{-07}	2.60×10^{-07}	3.83×10^{-07}	3.82×10^{-07}	5.93×10^{-07}	5.94×10^{-07}	4.82×10^{-09}	4.73×10^{-09}	6.50×10^{-12}	6.47×10^{-12}	2.36×10^{-03}	2.54×10^{-03}
9.77	2.60×10^{-07}	2.60×10^{-07}	6.13×10^{-07}	6.12×10^{-07}	3.59×10^{-07}	3.60×10^{-07}	8.22×10^{-09}	8.08×10^{-09}	3.13×10^{-11}	3.12×10^{-11}	3.12×10^{-02}	3.05×10^{-02}

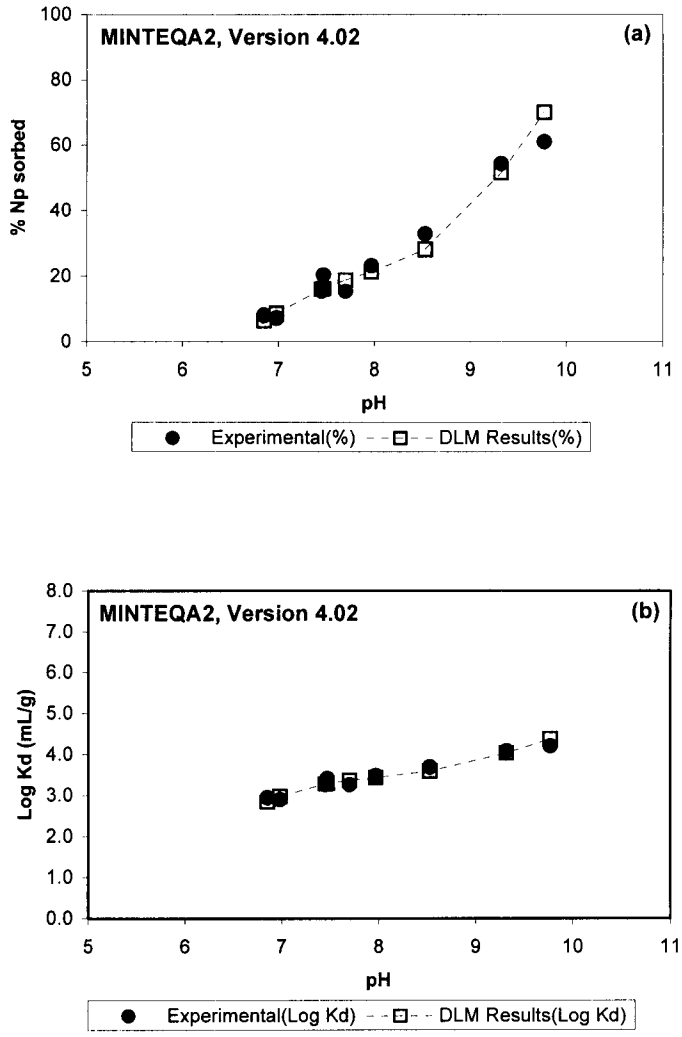
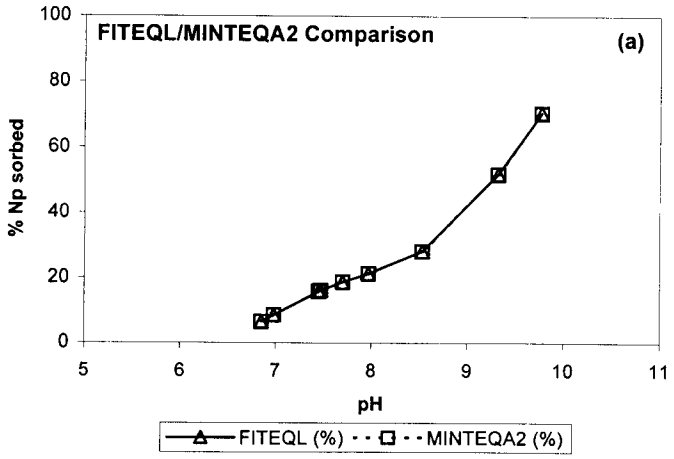


Figure 2-2. Comparison of Sorption Results Calculated Using MINTEQA2, Version 4.02 with Np(V)-Hematite Sorption Data of Kohler, et al. (1999). (a) Percent Np(V) Sorbed (b) Log K_d Sorbed in mL/g.



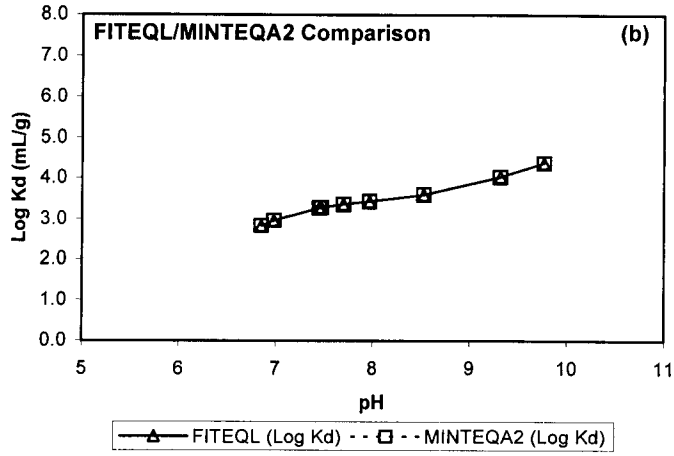


Figure 2-3. Comparison of Np(V)-Hematite Sorption Results Calculated Using FITEQL, Version 2.0 and MINTEQA2, Version 4.02. (a) Percent Np(V) Sorbed (b) Log K_d Sorbed in mL/g.

3 DISCUSSION AND SUMMARY

FITEQL, Version 2.0 does a good job of matching the experimental data of Kohler, et al. (1999) over most of the observed pH range (Figure 2-1). There is some variability in the experimental data that is not captured by the smooth curve calculated by FITEQL, Version 2.0. Results from FITEQL, Version 2.0 also match well with the sorption behavior calculated using MINTEQA2, Version 4.02 (Figures 2-2 and 2-3). Small differences are likely due to differences in how the two codes calculate activity coefficients for the aqueous solution (0.1 M $NaClO_4$). A quantitative measure of goodness-of-fit that compares the predicted sorption coefficient (K_d, in mL/g) with the experimental distribution coefficient R_d (mL/g) is:

$$\text{Goodness-of-Fit} = [\text{Log}\ (K_{d,model}/R_{d,experiment})]^2 \quad [1]$$

Smaller values indicate a better prediction of the observed sorption behavior. The goodness-of-fit calculated using this measure for both FITEQL and MINTEQA2 results is typically small, in most cases ranging from 10^{-4} to 10^{-2} (Table 2-3). The goodness-of-fit parameters also compare well between the two codes, providing confidence that they are handling the geochemical and sorption equilibria in a comparable manner.

The model is chemically plausible with regard to Np(V) speciation. The dominant Np species is NpO_2^+ for pH up to about 8, and continues to be a significant species over the range of experimental conditions (Turner, et al., 1998). The postulated surface reactions are consistent with Extended X-Ray Absorption Fine Structure data on Np(V)-sorption on goethite (Combes, et al., 1992). The model parameters also provide good prediction of the effect of CO_2 on Np(V) sorption (Turner, 2002b).

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APPENDIX

Validation Np(V)-hematite sorption. FITEQL, Version 2.0 input file for Np(V) sorption on hematite.

```
         1                                                                  Neptunum
         1                                                                     on
         1                                                                  Hematite
         1                                                                  1.6s\nm2
         1                                                                  No CO2
        90                                                                  I=0.10
         4          1          3          1                                np=1e-6
00001   -6.584 2.61E-7    xoh(str)                                         14.4m2/g
00002   -4.440 3.61E-6    xoh(weak)                                        0.1 g/l
00160   -2.0   0.00E00    psi0                                             00000095
00031   -5.91  1.24E-6    npo2+                                            00000098
00032    0.0   0.00E00    npo2(ads)                                        00000100
00050    0.0   0.00E00    h+                                               00000102
00003   -1.00  0.00E00    na+                                              00000104
00005   -1.00  0.00E00    clo4-                                            00000106
                                                                           00000110
00001    0.00  001  1                                                      xoh(s)
00002    0.00  002  1                                                      xoh(w)
00050    0.00  050  1                                                      h+
00031    0.00  031  1                                                      npo2+
00003    0.00  003  1                                                      na+
00005    0.00  005  1                                                      clo4-
03100  -11.30  031  1 050 -1                                              npo2oh
03101  -23.38  031  1 050 -2                                              npo2oh2
00100  -13.78  050 -1                                                      h2o diss
01050    9.45  001  1 160  1 050  1                                       xoh2+(s)
01100  -10.10  001  1 160 -1 050 -1                                       xo-(s)
02050    9.45  002  1 160  1 050  1                                       xoh2+(w)
02100  -10.10  002  1 160 -1 050 -1                                       xo-(w)
03201    0.500 001  1 160  0 050 -1 031  1 032  1                          xos-npo2
03202   -3.250 002  1 160  0 050 -1 031  1 032  1                          xow-npo2
                                                                           00000174
00002   014.4 0.100                                                        00000175
0.10   1.0                                                                00000180
         2         1                                                       00000185
       3201                                                              00000190
       3202                                                              00000195
        001                                                              00000195
         9         1         1         0                                00000195
        32                                                               00000230
1.00E-07
9.00E-08
1.90E-07
2.53E-07
1.90E-07
2.88E-07
4.08E-07
6.77E-07
7.60E-07
        50
-6.740
-6.870
-7.340
-7.360
-7.590
-7.860
-8.42-0
-9.210
-9.660
         1         1
```

```
32      0.10    1.0E-09                                    10%error
50      0.05    0.0E-00                                    +/- 0.02
```

Note: For this input file, the input file is constructed to optimize on the experimental data and derive binding constants (log K) for the formation of XO(s)-NpO_2^0 (Species 3201) and XO(w)-NpO_2^0 (Species 3202). The numbers in the input file are seed values, not the final values determined by the optimization. Also, because the FITEQL calculation is concentration-based rather than activity-based, the Log K values for the chemical equilibrium model have been adjusted to compensate for the ionic strength of the solution (0.1 M $NaClO_4$) using the methods presented in Dzombak and Morel (1990, Table 2.13). For this reason, the Log K values in the FITEQL, Version 2.0 input files differ slightly from those used in the MINTEQA2, Version 4.02 input and those values given in Table 2.1.

Validation Np(V)-hematite sorption. MINTEQA2, Version 4.02 input file for Np(V) sorption on hematite. Sorption parameters from FITEQL, Version 2.0 optimization.

```
Np-Hematite Sorption Exp. 6: 0.1 g/L; I=0.1 M NaClO4
No CO2; Np=1.2E-6 M; 2-site model
25.00 MOLAL  0.000  0.00000E+00
0 0 1 0 1 0 0 0 1 1 2 5 3
 9 H+1                    ACTIVITY   mol/L
1 330   1.000
   6.85   6.98   7.45   7.47   7.70   7.97
   8.53   9.32   9.77
kohler99.123 8115520 8125520     552 5523300 5523301
4   1   7
1.000E-01   14.40 0.000 0.000 81
    330  0.000E+00   -5.00 y                    /H+1
    500  1.000E-01   -1.00 y                    /Na+1
    181  1.000E-01   -1.00 y                    /ClO4-
    552  1.240E-06   -5.91 y                    /NpO2+1
    813  0.000E+00    0.00 y                    /ADS1PSIo
    811  2.610E-07   -5.58 y                    /ADS1TYP1
    812  3.610E-06   -4.44 y                    /ADS1TYP2

  3   1
    330     5.0000     0.0000                   /H+1
  6   1
    813     0.0000     0.0000                   /ADS1PSIo

  2   6
8113300 xo(s)-          0.0000  -10.2100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811  -1.000 330  -1.000 813   0.000   0   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8113301 xoh2+(s)        0.0000    9.5600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 811   1.000 330   1.000 813   0.000   0   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8115520 xo(s)-npo2      0.0000   -0.4400   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 4   1.000 811   1.000 552  -1.000 330   0.000 813   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8123300 xo(w)-          0.0000  -10.2100   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 812  -1.000 330  -1.000 813   0.000   0   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8123301 xoh2(w)+        0.0000    9.5600   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 3   1.000 812   1.000 330   1.000 813   0.000   0   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
8125520 xo(w)-npo2      0.0000   -3.6200   0.000   0.000 0.00 0.00 0.00   0.0000
 0.00 4   1.000 812   1.000 552  -1.000 330   0.000 813   0.000   0   0.000   0
  0.000   0   0.000   0   0.000   0   0.000   0   0.000   0   0.000   0
0  0.000   0   0.000   0   0.000   0
```