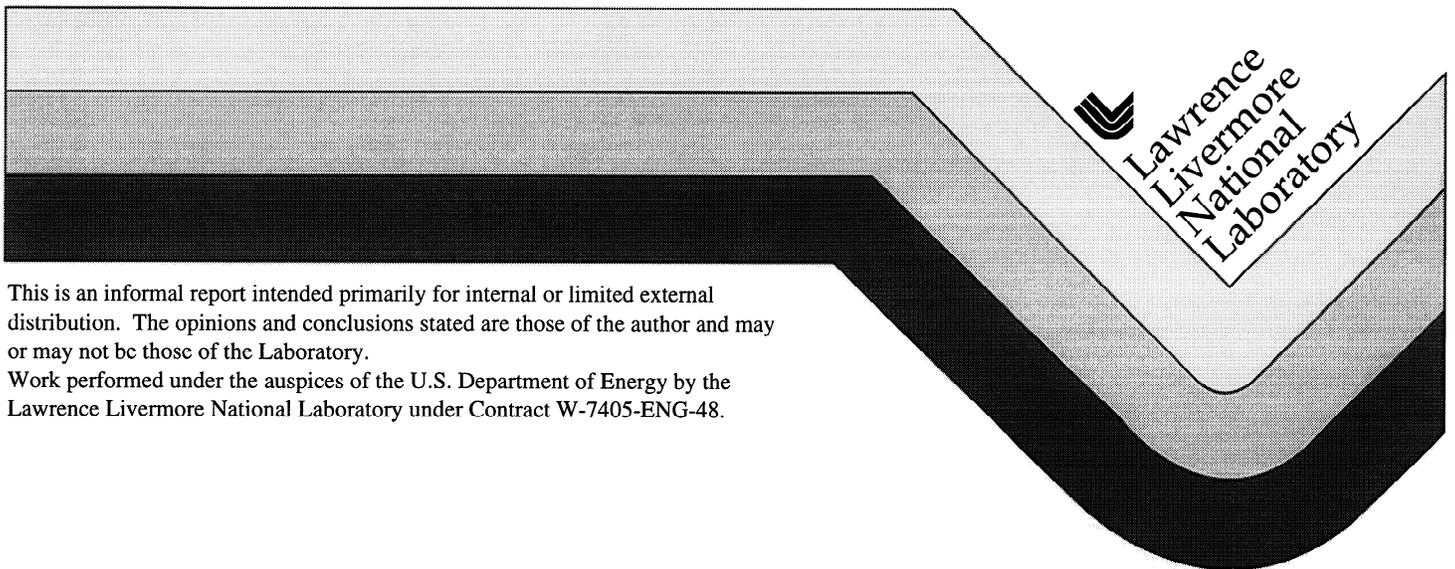


Formulation and Make-Up of Simulated Cement Modified Water

Greg Gdowski

September 12, 1997



This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.

Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This report has been reproduced
directly from the best available copy.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62, Oak Ridge, TN 37831
Prices available from (423) 576-8401

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Rd.,
Springfield, VA 22161

University of California



UNCONTROLLED

YUCCA MOUNTAIN PROJECT

Technical Implementing Procedure

No.: TIP-CM-11
Revision: 0
Effective Date:
Page: 1 of 9

Subject: Formulation and Make-Up of Simulated Cement Modified Water

AUTHOR: G. Gdowski

Training Required: Yes No

Comments: Training required for personnel performing work to this TIP

REVISION HISTORY

Rev. No.	CN No.	Effective Date	Description of Revision/CN
0		09/12/97	Initial Issue

Approved by: W. L. Lohme 9/12/97
CRWMS LLNL Manager Date

Approved by: Royce M. Jones 11 Sept '97
M&O LLNL Engineering Assurance Manager Date

Approved by: R. Daniel McGehee 11 Sept 1997
Technical Area Leader Date

No.:	Revision:	Date:	Page:
TIP-CM-11	0	09/12/97	2 of 9

1.0 PURPOSE

This procedure describes the formulation and make-up of Simulated Cement-Modified Waters (SCMW), which are aqueous solutions to be used for Activity E-20-50 "Long-Term Corrosion Studies." These solutions simulate the changes to "representative" Yucca Mountain water chemistry because of prolonged contact with "aged" cement. The "representative" water was chosen as J-13 well water [Harrar, 1990]. J-13 well water is obtained from ground water that is in contact with the Topopah Spring tuff, which is the repository horizon rock.

Water influx into the drifts and, hence, potential water contact with the waste packages is expected to occur a long time after the waste packages have been emplaced in the drifts. The cement in the drifts will "age" during this time at elevated temperatures. The chemical composition of the cement will change due the high temperatures and the exposure to gaseous carbon dioxide [Meike, 1997]. It is therefore assumed that if water does interact with the cement prior to contacting the waste packages it will contact "aged" cement rather than fresh "young" cement.

The composition of the SCMW was calculated by assuming that J-13 water was allowed to equilibrate with "aged" cement [Meike, 1997]. The calculations were performed with the EQ3/6 software program. (Results of the calculations are contained in Scientific Notebook #303 .)

The calculated compositions of the SCMW at 60 and 90°C are given in Table 1. It is anticipated that there will be some differences between the actual composition of test solutions and these calculated values. The pH of the solutions will initially be controlled to near the calculated value. The vessel to vessel variation of solution compositions is of limited significance to the testing, since similar type materials are to be tested in the same test vessel.

Two points are worth mentioning with regard to the choice of the aqueous solution chemistry. First, the fast transport of water through the cement obviously will not allow for much interaction / exchange between the cement and water, hence, the water chemistry will remain at or near to its original composition. Testing in aqueous solutions having dilute and concentrated ionic contents of Yucca Mountain waters (see TIP-CM-6 and TIP-CM-7) are also included in this activity. Second, the use of "aged" cement causes the pH of the resulting solutions to be lower than that which would result if "young" cement was used. The aqueous solutions that result from contact with "aged" cement expected to have pH 8-9, while those from "young" cement expected to have pH 11-12.

No.:	Revision:	Date:	Page:
TIP-CM-11	0	09/12/97	3 of 9

This aqueous solution is one of the aqueous test solutions to be used in the activity. The other aqueous solutions included a simulated dilute water (SDW), a simulated acidic concentrated water (SAW), and a simulated concentrated water (SCW).

This TIP documents the chemical reagents, reactant air, and the procedures used to make-up the aqueous solution for Activity E-20-50. More than 4,000 liters of simulated cement modified water solution are required for the test vessels for implementation of the test matrix of the activity plan.

2.0 SCOPE

This procedure applies to the Simulated Cement Modified Water solution, one of the aqueous solutions that are to be used in the test vessels for Activity E-20-50 "Long-Term Corrosion Studies."

3.0 RESPONSIBILITIES

The Principal Investigator (PI) or designee is responsible for:

- the conduct of the activities and methods described in this procedure, and
- maintaining laboratory scientific notebooks.

The Task Area Leader (TAL) is responsible for:

- ensuring that the requirements of this procedure are implemented,
- ensuring that personnel conducting the work are qualified and are trained to this procedure,
- verifying that this procedure meets the objectives of the Scientific Investigation Plan (SIP) "Metal Barrier Selection and Testing" (SIP-CM-01, Rev.3, WBS # 1.2.2.5.1) and Activity E-20-50 "Long-Term Corrosion Studies", and
- ensuring approval of this procedure.

The YMP Quality Assurance Manager (QA Manager) is responsible for:

- monitoring the work to assure proper implementation of this procedure, and
- assuring its continued effectiveness.

4.0 COMPOSITION OF SCW AND REACTANT AIR

4.1 Aqueous Solution Composition

The Simulated Cement Modified Water (SCMW) has a ionic composition that has been calculated to result from extended contact of J-13 well water with "aged" cement (see Scientific Notebook #303). J-13 well water is obtained from ground water that is in contact with the Topopah Spring tuff, which is the potential repository horizon rock.

The composition of J-13 well water is given in Table 1. Only ions with concentration greater than 0.5 ppm are included in this table. Minor constituents have been detected in J-13 well water; these include Li, B, Al, Mn, Fe, Sr, and PO₄ ions. These constituents have been reported in the 10-100 µg/liter concentration. The most consistently determined minor constituents are Li and B at mean (several studies) concentrations of 48 and 134 µg/liter, respectively. The minor constituents are not explicitly included in the SCW. However, the reagent chemicals have some impurities, which may include the above noted impurities. These minor constituents at the reported concentrations are not expected to significantly effect the corrosion of the test specimens.

Table 1. Compositions of "representative" Yucca Mountain waters J-13 well water and the theoretical composition of the simulated cement modified water.

Constituent	<u>Concentrations (mg/l)</u>		
	J-13	Simulated Cement Modified Water (theoretical)	
		60°C	90°C
Na ⁺	45.80	11	14.0
Si	28.5	12.8	22.7
Ca ²⁺	13.0	452.8	197.5
K ⁺	5.04	86.9	309
Mg ²⁺	2.01	3.6	0.3
F ⁻	2.18	1.3	1.3
Cl ⁻	7.14	4.1	4.3
NO ₃ ⁻	8.78	4.9	5.2
SO ₄ ²⁻	18.4	1201.6	864.7
HCO ₃ ⁻	128.9	9.0	6.4
pH	7.41	7.65	7.75

No.:	Revision:	Date:	Page:
TIP-CM-11	0	09/12/97	5 of 9

Simulations of equilibrium concentrations resulting from contact of J-13 well water with "aged" cement were run using EQ3/6 (see scientific notebook #303). The compositions of the SCMW at 60 and 90°C that result from the simulations are given in Table 1. Examples of the chemicals and their quantities used to prepare the solutions are given in Section 5.1. The actual compositions of the test solutions may vary somewhat from the simulations, however, it is the general composition of the solutions that determines the corrosive nature of the solutions. In addition similar type materials are tested in the same test vessel, so vessel-to-vessel variation of solution composition is of limited significance.

4.2 Reactant Air

Reactant air is compressed building air which has been purified to remove hydrocarbons and water. Air will be purified by flowing through a Whatman Zero Air Generator (see Section 6.0). Nominal flow rates through each test vessel will be 200 ml/min. Air will exit through a condenser to remove water; this greatly reduces the amount of water loss from the test vessels.

Reactant air serves two purposes: 1) it keeps the oxygen content of the vessels constant, and 2) the slightly pressurized test vessel will keep the potentially contaminated room air out of the test vessels.

5.0 REAGENTS AND FORMULATION

5.1 Reagent Chemicals

In order to obtain the solution composition given in Table 1, various combinations of chemicals can be used. A spreadsheet has been developed which calculates the composition of a solution based on the added chemicals. Copies of typical outputs of the spreadsheets are shown in Appendix A for 60 and 90°C solutions. Many of the chemicals listed in the spreadsheet are not used in this particular example. The inclusion of numerous chemicals in the spreadsheet allows the user the freedom to choose the needed chemicals based on availability, cost, and personal preference.

The algorithm to arrive at reagent concentrations was a trial and error method. The quantities of reagents required was estimated, and the spreadsheet calculated the total ionic content of the simulated solution. Iteration was continued until an acceptable match was achieved.

A few guidelines were used in choosing the reagents. The more soluble salts (minerals) were chosen. Also dissolved silica will be obtained by the addition of sodium silicate. (Calculations showed that dissolution of solid silica phases would take extended periods of time (>1000 days) in order for suffi-

cient amounts of silica to dissolve.) Using sodium silicate will result in the formation of hydroxyl ions equal to the number of moles of sodium atoms added. In order to neutralize the hydroxyl ions, an equal number of moles of hydrogen ions will be added as a strong acid (hydrochloric, nitric, or sulfuric). Note: dilute acid should be used to avoid forming locally very acidic solution during solution make-up (see section 7.0).

A word of caution in using the spreadsheet: the calculations assume that the chemicals dissolve completely and may therefore over estimate the composition of some species. The user must therefore be aware of potential solubility problems. A listing of the solubilities of various chemical is shown in Appendix B.

A typical example of chemicals used to make-up of the aqueous solution are listed in Table 2 along with the quantities required per 1000 l of solution.

Table 2. An example of the reagents and quantities required per 1000 liters of simulated aqueous solution.

Reagent	Quantity @ 60 C (gms / 1000 liters)	Quantity @ 90 C (gms / 1000 liters)
NaCl	5.2	—
NaF	2.9	2.9
Na ₂ SiO ₃ •5H ₂ O	20.1	35.8
MgSO ₄ •7H ₂ O	37.0	3.0
CaSO ₄ •2H ₂ O	1945.0	848.5
KCl	2.0	9.0
K ₂ SO ₄	171.5	661.5
KHCO ₃	14.8	10.5
KNO ₃	8.0	8.5
H ₂ SO ₄	7.6	26.0

The chemicals and the quantities used in making up the test solutions will be listed in the Scientific Notebook or electronic media.

No.:	Revision:	Date:	Page:
TIP-CM-11	0	09/12/97	7 of 9

5.2 Purified Water

The make up of the test solutions requires large quantities of low ionic content water is required. The use of LLNL de-ionized water is acceptable. This water has an ionic content typically less than 1 ppm. The source of the water used in testing will be recorded in the scientific notebook.

5.3 Reactant Gas

The reactant air will be purified before entering the test vessels.

6.0 EQUIPMENT

A balance that can measure to 0.1 grams is acceptable for make-up of the test solutions. An acceptable balance is:

Mettler Balance Model # AT200
Serial Number 1114463500

Mettler Balance Model # PC16
Serial Number A51361

An air purifier for cleaning the building compressed air is required. The following unit or equivalent is acceptable:

Whatmann Type 76-818NA Zero Air Generator
Unit Serial Number 768180065B
Tower Module Serial Number 76811-10116B

This air purifier removes hydrocarbon to 0.1 ppm.

7.0 PROCEDURE

The following procedure will be followed in making-up of the Simulated Cement Modified Water solutions for the test vessels:

No.:	Revision:	Date:	Page:
TIP-CM-11	0	09/12/97	8 of 9

- 1) Purified water is emplaced in the cleaned vessel; the liquid level is slightly less than the required depth for testing. (Need to account for rise in water level due to the specimens and racks, and the density decrease due to raising the water temperature to the test temperature.)
- 2) The amount of purified water added to the test vessels is estimated.
- 3) The required amounts of reagent chemicals is determined and entered in the scientific notebook or electronic media.
- 4) The purified water is heated to a nominal temperature of 40°C. This will accelerate reactions that occur in solution.
- 5) The water will be stirred. The stirrer mounted on the vessel is sufficient.
- 6) Add chemicals to water. No particular order is required for chemical additions except that sulfuric acid will be the last chemical added to the test vessel.
- 7) Concentrated sulfuric acid shall be diluted 500-1000 times the required volume using deionized water and then added to the test vessel.
- 8) The vessel is sealed and brought to testing temperature for at least 24 hours.
- 9) The specimen racks are inserted into test vessel.
- 10) A sample of the test solution is withdrawn for analysis approximately a day after the level of water reaches the normal operation set point.

Note: The liquid level in the test vessels will self-adjust to the required level. If the liquid level is low, the liquid level control system will add purified water. If the liquid level is high, water removal by the air purge will occur; this may be slow but it will occur. It is preferable to add water rather than to remove water, since the control system shuts down the heaters when the liquid level is above a certain height.

No.:	Revision:	Date:	Page:
TIP-CM-11	0	09/12/97	9 of 9

8.0 QA RECORDS

Any data that is pertinent to this TIP shall be entered into the Scientific Notebook or electronic media for Activity E-20-50. This shall include, but is not be limited to the chemical used lot # manufacturer supplied analysis, and actual reagent chemical amounts used for make-up.

9.0 REFERENCES

J.E. Harrar, J.F. Carley, W.F. Isherwood, and E. Raber, "Report of the Committee to review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations," Lawrence Livermore National Laboratory report UCID-21867, Livermore California, January 1990.

A. Meike, Scientific Notebook # 303 and personal communication, 1997.

Compound	Mol Wt.	g/1000 l	K	Na	Mg	Ca	Cl	F	HCO3	CO3	SO4
NaCl	58.44	0.0		0.0			0.0				
NaOH	40.00	0.0		0.0							
NaHCO3	84.01	0.0		0.0					0.0		
Na2CO3	105.99	0.0		0.0						0.0	
Na2SO4	142.04	0.0		0.0							
NaNO3	84.99	0.0		0.0							
Na2CO3	105.99	0.0		0.0						0.0	
NaF	41.99	2.9		1.6				1.3			
Na2SiO3	126.04	35.8		13.1							
Na2SiO3•9H2O	288.18	0.0		0.0							
SiO2 (colloidal)	64.06										
MgCl2•6H2O	203.31	0.0			0.0		0.0				
MgF2	62.31	0.0			0.0			0.0			
(MgCO3)4•Mg(OH)2•5H2O	485.69	0.0			0.0					0.0	
MgCO3	84.32	0.0			0.0					0.0	
MgSO4	120.37	0.0			0.0						
MgSO4•7H2O	246.48	3.0			0.3						
Mg(NO3)2•6H2O	256.41	0.0			0.0						
CaCl2	110.99	0.0				0.0	0.0				
CaCl2•2H2O	147.02	0.0				0.0	0.0				
CaF2	78.08	0.0				0.0		0.0			
CaCO3	100.09	0.0				0.0				0.0	
CaSO4•2H2O	172.17	848.5				197.5					47.0
Ca(NO3)2•4H2O	236.15	0.0				0.0					
H2SO4	98.08	27.6									2.7
HCl	36.46	0.0					0.0				
KF•2H2O	94.13	0.0	0.0					0.0			
KCl	74.56	9.0	4.7				4.3				
K2SO4	174.27	658.7	295.6								36.0
KNO3	101.11	8.5	3.3								
KHCO3	100.12	10.5	4.1						6.4		
K2CO3	138.21	0.0	0.0							0.0	
KOH	56.11	0.0	0.0								
Totals			307.7	14.6	0.3	197.5	4.3	1.3	6.4	0.0	86.4
Target @90°C			309.0	14.0	0.3	197.5	4.3	1.3	6.4	0.0	86.4
										6.4	

Appendix B. Solubilities in Water

Compound	Formula		Mol Wt.	Solubility gms/100cc	Solubility mg / l	T(°C)
Calcium sulfate	CaSO ₄	nat anhydrite	136.14	0.2090	2090	3
Calcium sulfate dihydrate	CaSO ₄ •H ₂ O	nat gypsum	172.17	0.2410	2410	
Calcium nitrate	Ca(NO ₃) ₂		164.09	121.2000	1E+06	1
Calcium Chloride	CaCl ₂		110.99	74.5000	745000	2
Calcium Fluoride	CaF ₂	nat flouride	78.08	0.0016	16	1
Calcium Carbonate	CaCO ₃	calcite	100.09	0.0014	14	2
Calcium hydroxide	Ca(OH) ₂		74.09	0.1850	1850	
Sodium sulfate	Na ₂ SO ₄	nat thenardite	142.04	4.7600	47600	
Sodium nitrate	NaNO ₃	soda niter	84.99	92.1000	921000	2
Sodium Chloride	NaCl	halite	58.44	35.7000	357000	
Sodium Fluoride	NaF	nat villiaumite	41.99	4.2200	42200	1
Sodium carbonate	Na ₂ CO ₃		105.99	7.1000	71000	
Sodium Bicarbonate	NaHCO ₃		84	6.9000	69000	
Sodium hydroxide	NaOH		40	42.0000	420000	
Sodium Silicate	Na ₂ SiO ₃	metasilicate	122.06	soluble		-
Magnesium sulfate	MgSO ₄		120.37	26.0000	260000	
Magnesium nitrate	Mg(NO ₃) ₂ •6H ₂ O		256.41	124.0000	1E+06	
Magnesium chloride	MgCl ₂		95.22	54.2500	542500	2
Magnesium flouride	MgF ₂	nat sellaite	62.31	0.0076	76	1
Magnesium carbonate	MgCO ₃	nat magnesite	84.32	0.0106	106	
Magnesium carbonate trihydrate	3MgCO ₃ •Mg(OH) ₂	nat hydromag	365.34	0.0400	400	
Magnesium carbonate basic	MgCO ₃ •3H ₂ O	nat nesqueho	138.37	0.179	1790	1
Magnesium hydroxide	Mg(OH) ₂	nat brucite	58.33	0.0009	9	1
Potassium sulfate	K ₂ SO ₄	nat arcanite	174.27	12	120000	2
Potassium sulfate, hydrogen	KHSO ₄	nat mercurite	136.17	36.3	363000	
Potassium nitrate	KNO ₃	salt peter	101.11	13.3	133000	
Potassium chloride	KCl	nat sylvite	74.56	23.8	238000	2
Potassium flouride	KF		58.1	92.3	923000	1
Potassium carbonate	K ₂ CO ₃		138.21	112	1E+06	2
Potassium Carbonate, hydrogen	KHCO ₃		100.12	22.4	224000	
Potassium Hydroxide	KOH		56.11	107	1E+06	1

Page 1 of 1

Appendix B
TIP-CM-11, Rev. 0

Source: CRC Handbook of Chemistry and Physics, R.C. Weast, M.J. Astle, eds., CRC Press, Inc., Boca Raton