SAND--91-2685C

DEC 27 1991

DE92 004480

(SAND91-2685C)

THE HYDROTHERMAL STABILITY OF CEMENT SEALING MATERIALS IN THE POTENTIAL YUCCA MOUNTAIN HIGH LEVEL NUCLEAR WASTE REPOSITORY.**J. L. Krumhansl***, **T. E. Hinkebein***, and **J. Myers****

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ABSTRACT

Cementitious materials, together with other materials, are being considered to seal a potential repository at Yucca Mountain. A concern with cementitious materials is the chemical and mineralogic changes that may occur as these materials age while in contact with local ground waters. A combined theoretical and experimental approach was taken to determine the ability to theoretically predict mineralogic changes. The cementitious material selected for study has a relatively low Ca:Si ratio approaching that of the mineral tobermorite. Samples were treated hydrothermally at 200°C with water similar to that obtained from the J-13 well on the Nevada Test Site. Post-test solutions were analyzed for pH as well as dissolved K, Na, Ca, Al, and Si. Solid phases formed during these experiments were characterized by scanning electron microscopy and X-ray diffraction. These findings were compared with predictions made by the geochemical modeling code EQ3NR/EQ6. It was generally found that there was good agreement between predicted and experimental results.

INTRODUCTION

Planning for the safe isolation of nuclear wastes at Yucca Mountain involves assessing the chemical stability of construction materials such as grout for far longer than can be addressed by direct observation or historical records. To meet this need one must resort to indirect methods. Two typical methods employed are (a) "accelerated tests" carried out at elevated temperatures, and (b) computational models that predict final stable phase assemblages assuming that cement-groundwater systems reach thermodynamic equilibrium.

Because both assessment methods are developmental, it is important to determine the extent to which they give consistent results. This was done by comparing the results of the geochemical solubility/speciation/reaction

This work performed under the auspices of the U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Yucca Mountain Site Characterization Project, under Contract DE-AC04-76DP00789.

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path code EQ3NR/EQ6 (EQ3/6; Version 3245, Release 1090 [1]) with autoclave experiments allowing for the interaction of cement + water ± tuff. The comparison was carried out at 200°C, where cement-solution interactions proceed rapidly while still approximating conditions that would be relevant to the repository at Yucca Mountain.

EXPERIMENTAL METHODS AND MATERIALS

To minimize the possibility of unfavorable tuff-cement interactions at Yucca Mountain, high-silica cements are favored over those with compositions resulting in normative portlandite. Two materials were tested: a grout containing only the cement paste and a concrete containing chips of Topapah Spring tuff from Busted Butte, Nevada, as aggregate (Table I).

Table I
Cement Compositions
(Weight Percent)

	<u>Grout</u>	<u>Concrete</u>
Class H Cement	18.6	11.9
Water	15.5	8.7
Silica Fume	4.2	3.4
Silica Flour	12.9	7.9
Slag	21.6	13.4
Silica Sand	26.7	----
Concrete Sand	----	18.1
Tuff Chips	----	36.2
Dispersant	0.5	0.4
Defoamer	0.02	0.02
Ca:Si Molar Ratio	0.39	0.22

Dry Bulk Composition

	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Fe ₂ O ₃	SO ₃
Grout	65.5	3.4	24.3	3.9	0.8	0.25	1.1	0.75
Concrete	70.9	6.9	14.6	2.4	1.6	2.2	1.0	0.45

Past EQ3NR/EQ6 computations [2], as well as experimental studies [3], demonstrated that cement-water interactions generally can be classified as "rock-dominated" systems. That is, within rather broad limits solution compositions will be governed by the solid phases present provided that relatively dilute starting solutions are used. Consequently, the starting solution used in these experiments was only an approximation to actual J-13 well water (Table II).

Table II
Fluid Compositions

	<u>Experimental Fluid</u>		<u>Well J-13 Water(Ref. 2)</u>	
	millimoles/liter	ppm	millimoles /liter	ppm
Potassium	0.133	5.2	0.133	5.2
Chloride	0.133	4.7	-----	---
Calcium	0.194	7.8	0.388	15.5
Sulfate	0.194	18.6	0.201	21
Sodium	2.03	46.7	1.61	37
Bicarbonate	2.03	123.8	0.714	43.7

To provide a test case for comparisons between modeled and experimental results the first experiment performed was carried out in a Dickson Hydrothermal System [4]. This apparatus withdraws the fluid at temperature and pressure, thus eliminating the possibility that the fluid could interact with the cement while cooling. It also allows sequential samples to be taken without disassembling the experiment. Thus, it is possible to tell when the cement-fluid interactions have stabilized. The grout sample used in this experiment was sawed into thin wafers with a thickness of between 0.5 and 1.0 mm. This precaution was taken to minimize concentration gradients between the fluid outside the sample and the pore fluid within the sample.

In the second type of experiment the reactivity of grout (no tuff) was compared with that of concrete (tuff present as chips). In these runs prisms of grout or concrete (1-2 cm long and roughly 0.4 cm on a side) were placed in small sealed titanium autoclaves that were heated to 200° C in an oven. The small size of these autoclaves precluded using thin wafers such as were used in the Dickson System experiment. At various times autoclaves were removed from the oven, quenched to below 100°C, and opened. The fluid was then withdrawn, filtered through a 0.4 micron Acrodisc filter, and diluted for analysis. Elapsed time from when an autoclave was cooled until the sample was filtered was typically less than three minutes. The solids produced during these experiments were analyzed by XRD and SEM and compared with those predicted by EQ3NR/EQ6.

MODELING

The model employed in this study, EQ3NR/EQ6, is essentially the same as that used to model cement - J-13 water interactions at room temperature [1]. It is assumed that tobermorite would proxy for CSH gel. A normative procedure was used to determine relative proportions of all phases in the starting mixture and resulted in an initial assemblages of: ettringite + hydrogarnet + tobermorite + NaOH + KOH + cristobalite. In constructing the model both sand and tuff were removed from the bulk compositions given in

Table I. This change was made because these components proved to be largely unreactive during the experiments.

The model was also modified from that used previously [1] to accommodate the presence of silicon metal in the fume used in the mixtures. The importance of this trace component became apparent when a strong odor of hydrogen sulfide was noted during sampling. Evidently, the silicon metal reduced a part of the sulfate according to the reaction:

The computational procedure followed was to initially speciate the aqueous solution from Table II at 200°C. It was then allowed to react incrementally with the materials in the cement. During each increment an equal proportion of each phase present was brought in contact with the solution and a new equilibrium condition was established reflecting the bulk composition achieved by this incremental addition. Thus, some phases may dissolve completely while new phases precipitate.

RESULTS: SOLID PHASES

The code indicates that there should be substantial alteration of the cement. The initial phase assemblage used to model the cement (ettringite, hydrogarnet, tobermorite, sodium and potassium hydroxide, and cristobalite) should have changed to the assemblage: anhydrite, calcite, chalcedony, gyrolite and stilbite. With concrete the presence of potassium feldspar was also predicted.

In reality, the situation proved to be more complex. Prior to heating the grout actually contained an amorphous CSH gel, quartz, potassium feldspar (both from the sand used in mixing the grout), and traces of brownmillerite, calcite, and portlandite. In the concrete the initial phase inventory also contained the minerals indigenous to tuff (quartz, cristobalite, potassium feldspar and sodic plagioclase).

Neither the tuff nor the sand grains visibly interacted with the cementitious matrix surrounding them. The X-ray diffraction pattern of the bulk grout, however, indicated formation of tobermorite. SEM examinations of sample surfaces revealed that both concrete and grout samples were covered with a layer of well-crystallized material. EDS analyses of these materials showed the bulk of the material to be a calcium-aluminum-silicate. A trace amount of calcite was also observed. X-ray diffraction patterns of material scraped from the surfaces revealed the presence of both tobermorite and gyrolite.

RESULTS: SOLUTION COMPOSITIONS

The solution composition data permit two types of comparisons. Table III presents results from the sealed tube experiments where concrete and grout were treated at 200°C. Although the the results were similar, it is evident that systematic differences exist between the two types of experiments. Thus, the tuff was probably not as inert as the visual evidence suggests. Secondly, it is possible to compare results of the Dickson System experiment with the theoretical predictions from the EQ3NR/EQ6 modeling effort. Considering the large number of assumptions needed to make this comparison possible, the results of this exercise were very encouraging. In fact, with the exception of solution pH and dissolved Al, there is almost exact agreement between modeled and experimental values (see Fig. 1).

Table III
Solution Compositions From 200°C Tuff-Water Interactions

	<u>10 Days</u>		<u>44 Days</u>		<u>95 Days</u>	
	Grout	Concrete	Grout	Concrete	Grout	Concrete
Na (ppm)	230	310	181	320	178	280
Al (ppm)	1.0	2.1	0.4	3.9	0.2	0.8
Si (ppm)	37	53	96	100	78	110
K (ppm)	269	125	169	80	172	31
Ca (ppm)	24	16	18	32	24	31
pH (ppm)	10.2	9.9	9.7	9.7	9.7	9.6

DISCUSSION

The remaining disagreements between modeled and experimental values can be shown to be the artifacts of disequilibrium in the Dickson System and the effects of quenching the sample to room temperature. This was demonstrated by modeling the changes in solution chemistry that occur as a sample is quenched. When the temperature of a solution with the bulk composition of the last sample taken from the Dickson System is restored to 200°C using EQ3NR/EQ6, it is found that the calculated in situ pH is 7.9. This value is quite close to that predicted by the theoretical grout-water interaction model (predicted pH is 7.74). Thus, the pH difference between the experiments and the model predictions is a result of having quenching the samples to room temperature during sampling.

From this computation it also became apparent that the sample solution was probably supersaturated with respect to anhydrite, calcite, and mesolite (a hydrated sodium-calcium-aluminosilicate). Figure 1 clearly illustrates that the Dickson system had not achieved a steady state. Consequently, a minor amount of silicate disequilibrium would be expected. A supersaturated condition for calcite and anhydrite is more problematical as these components usually equilibrate rapidly. Possible causes for such a prediction are defects in the thermodynamic data base, the presence of

colloidal particles in the fluid samples, or analytic error. At this time it is not possible to isolate a single cause.

Finally, EQ6NR/EQ3 was used to evaluate the changes in solution composition that would occur when the supersaturated phases precipitated. When this is done it was found that all the concentrations in the experimental solution, including aluminum, were in good agreement with the equilibrium composition predicted by the initial grout-water interaction model.

CONCLUSIONS

Fortunately, the two techniques gave answers that were in close agreement. It follows that experimental studies combined with theoretical calculations can provide an effective tool in predicting the long-term stability of cementitious materials. It is necessary to stress, however, that the model can only yield useful long-term predictions if the scenario modeled is realistic. Hence, experiments are required to identify mechanisms that may have been missed in formulating the conceptual model.

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Fig. 1 COMPARISON BETWEEN MODELED (LEFT) AND EXPERIMENTAL (RIGHT) RESULTS

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