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Hydrothermal Alteration of Concrete: Yucca Mountain Repository Analogues

K. B. Myers and A. Meike[1]

1. Introduction

Concrete could comprise a major share of construction materials present in the potential Yucca Mountain high-level radioactive waste repository. Concrete and shotcrete would be used as mechanical support (precast concrete liners), or road bed (invert) in repository emplacement drifts. These drifts could reach at least 150 to 200˚C for extended periods of time, possibly in the presence of fluids. This study characterizes chemical and structural transformations in concrete that may occur as a result of a repository hydrothermal cycle.

The specific concrete formulation to be used in the potential Yucca Mountain repository had not been determined at the time of the experiment. Invert and Fibercrete™ materials from the Exploratory Studies Facility (ESF) were chosen for these experiments as representatives of standard construction concrete used in this setting. This position is supported by a recent report by Tang (1997, pp. 48-49).

2. Work Description

Concrete from an ESF invert was cut into 3 mm ¥ 13 mm ¥ 25 mm coupons. Shotcrete (Fibercrete™) from the ESF North Portal was prepared similarly. Three batches of samples were hydrothermally treated at 200∞ C for one and a half (batch one), four (batch two), and nine (batch three) month durations. Three thermal treatments were represented in each batch; heat treatment in the presence of a 1 M $NaHCO_3$ solution, heat treatment in the presence of a 1 M NaCl solution, and heat treatment in a dry pressure vessel. The purpose was to investigate the consequences of varying the carbonate concentration at elevated temperature and the potential differences between aqueous and vapor phase alteration. Each treatment was conducted in a 125 ml pressure vessel. The design allowed for simultaneous vapor and aqueous

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treatment in the same vessel. A platform elevated two vapor treatment samples (one Fibercrete™ and one invert) above the fluid level. The third (invert) sample was submerged in solution at the bottom of the vessel.

After treatment, samples were analyzed for the effects of hydrothermal alteration. Analyses included: aqueous chemistry (pressure vessel fluid), petrology, scanning electron microscopy (SEM), glancing angle x-ray diffraction, and mechanical tests. Analyses and results are also described in Meike et al. (1997) and Myers and Meike (1997).

3. Results

3.1 Aqueous Chemistry

During the course of the experiments, the chemistry of the aqueous solution is expected to evolve, as represented by a comparison of the aqueous chemistries of the original solution to that at the end of each treatment duration (Table 1). The chemistry was analyzed with inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC). The pH of the $NaHCO_3$ solution increased with time, and stabilized at 9.5 after six weeks. The pH of the NaCl solution increases with time, near 11.5 within four months. Aqueous chemistry was not relevant to the “dry” samples from batch one or batch two. However, water added for the last two weeks of batch three yielded a pH of 11.84.

3.2 Thin Section Analysis

Aggregate mineralogy varies between invert and shotcrete samples, but is less variable within each sample type. Invert aggregate consists of 80-100% carbonate , 5-20% silicate minerals (quartz, quartz-bearing lithic fragments, and chert), and 1% or less of hematite and other opaque phases. Shotcrete aggregate mineralogy consists of 80-90% silicate minerals (SiO_2 phases and feldspar), 5-15% carbonate, 3-18% lithic fragments and biotite, and 1-10% accessory phases.

3.3 SEM

Secondary analcime and calcite are observed in the $NaHCO_3$ aqueous treated samples from all batches. Secondary calcite, two Ca-Si phases, and a SiO_2 phase are observed in treated samples from batches one and two.

The secondary mineralization in NaCl aqueous treated samples from all batches includes at least two Ca-Si phases, and at least two carbonate phases. Vapor treated samples from batches one and two contain at least four Ca-Si secondary phases morphologies, and at least one carbonate phase.

Dry samples from batches one and two show at least three morphologies of localized Ca-Si-hydrate rings around aggregate grains, as well as a secondary carbonate phase.

3.4 Glancing Angle X-Ray Diffraction.

Glancing angle XRD emphasizes the surface mineralogy, but does not distinguish between primary and secondary phases. The analyses are summarized (Table 2) with aggregate phases toward the top of the table, possible secondary phases clustered in the middle (including Ca-Si-hydrate phases), and phases associated with evaporated water droplets at the bottom. Thin section, SEM and untreated sample data clarify the distinction between aggregate and secondary phases.

Analcime and possibly killalaite and halite occur as a secondary phases in the aqueous $NaHCO_3$ treated samples. Scawtite and aragonite are possible secondary phases on the vapor treated samples. Secondary phases possibly occurring in the NaCl aqueous treated samples include scawtite, halite and killalaite. Secondary phases possibly occurring in the vapor treated samples include scawtite, tilleyite, tobermorite, killalaite, hillebrandite, gismondine, pectolite, plombierite, riversideite, and halite. Few secondary phases can be distinguished on dry treated samples. Tobermorite, ferdisilicate and halite may occur.

3.5 Mechanical Test

Results of compressional mechanical testing (Table 3) likely have a wide error due to sample size and heterogeneity. A simplified interpretation of the data suggests that the force required to cause brittle failure in the samples may be increasing, especially those samples subjected to $NaHCO_3$ treatment.

4. Conclusions and Discussion

Results of analyses completed thus far demonstrate that secondary mineralization increases with time and varies with sample treatment and concrete types (concrete vs. shotcrete). Secondary carbonate and Ca-Si phases formed in most of the samples. A greater variety of phases is observed in the vapor treated samples. A variety of both Ca-Si and carbonate secondary phases occur on NaCl aqueous treated samples, while only one carbonate phase and analcime occur on the $NaHCO_3$ aqueous treated samples. Dry treated samples contain the greatest variety of Ca-Si secondary phases, but few carbonates phases. Shotcrete samples (vapor treatment only) generally have the greatest variety and abundance of secondary phases, which is expected due to the localized nature of chemical interactions in these conditions. Carbonate aggregate is probably significantly involved in secondary mineralization; this relationship will be examined further via chemical modeling.

5. References

Meike, A., M. Spragge, and C. Aracne-Ruddle, (1997), *Hydrothermal Alteration of Cementitious Materials: First Batch of Samples,* Lawrence Livermore National Laboratory report. YMSCO Deliverable #SPLGBM4.

Myers, K. B., and A. Meike (1997),), *Hydrothermal Alteration of Cementitious Materials: Part II: Second and Third Batch of Samples,* Lawrence Livermore National Laboratory report. YMSCO Deliverable #SPLGDM4 and #SPLGEM4.

Tang, D. (1997) “Emplacement Drift Ground Support”, YMP Document BCAA00000-01717-0200-00003 Rev. 00B, May 23, 1997.

Table 1. Summary of aqueous chemistry results.

	NaCl treatment				NaHCO3 treatment				Dry
	Original solution	batch 1	batch 2	batch 3	Original solution	batch 1	batch 2	batch 3	batch 3
Ca (mcg/ml)	3.3	365	344	91	3.2	2	1.77	1	106
Na (mcg/ml)	23400	21500	23500	27000	22900	19000	24300	25000	25
Mg (mcg/ml)	n.m.	0.01	.04	0.11	n.m.	0.20	0.10	0.09	0.03
Al (mcg/ml)	n.d.	n.d.	n.d.	1.3	n.d.	n.d.	n.d.	n.d.	1.0
Si (mcg/ml)	4.81	n.d.	2.97	14.1	6.55	94	126	138	9.9
Cl (mg/l)	38100	38700	41100	47500	2.54	n.d.	8.50	9.80	15.7
NO3 (mg/l)	0.46	14.7	n.d.	n.d.	0.44	39.6	n.d.	3.55	0.55
PO4 (mg/l)	n.d.	n.d.	n.d.	n.d.	0.21	n.d.	n.d.	14.3	n.d.
SO4 (mg/l)	6.92	204	92.3	81.8	4.03	127	137	154	99.1
pH	6.35	n.m.	11.36	11.84	8.195	9.15	9.15	9.50	8.195

n.d. = none detected
n.m. = not measured
"Dry" treatment results include analyses of DI water added to pressure vessel during the last two weeks of the batch 3 treatment at 200°C.

Table 2. Summary of x-ray diffraction results

	PRE-CAST INVERT																		SHOTCRETE								
Treatment	Dry						NaCl						NaHCO3						Dry			NaCl			NaHCO3		
							aqueous			vapor			aqueous			vapor						vapor			vapor		
Batch	1		2		3		1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3	1	2	3
Sample No.	24	25	37	38	30	31	17	21	32	18	36	33	26	23a	28	27	23b	29	1	9	6	5	13	4	2	10	3
Quartz			x	x	x	x		x	•		x	•		x	•		x	x		s	x		p	p	x	x	x
Albite																				s	s		•			s	x
Sanidine																				s	s					•	
Anorthite																				s	s		•			•	s
Taramite																				p							
Pyrophyllite	s				•	•		•						•								p	s	•			
Margarite																				p		p		•			
Phlogopite																				p			p	•			
Dolomite	x		x	x	x	x		•	•		•	•	p	•	●	x	x	x		•			•				•
Calcite	x		x	x	x	x	x	x	x		x	s	x	x	✠	x	x	x	x	•	x		•		x	x	x
Hi-Mg Cal					•	•			•			s			⊠			•		x	•		x	•			•
Aragonite																										s	•
Portlandite	•		p	•	•	•	•	•	•	•	•	•	p	p	✍	•	•	•	•	p	•	•	•	•	•	•	•
Scawtite								s	x		•	•											s	•		p	•
Tilleyite								•			s	•															
Tobermorite11a			•	•	•	•		•	•	x	•	•		•	✍		•	•		•	p	x	s	s		•	•
Killalaite			•	•	•	•		p	s		•	•		p	✍		•	•		•	•		p	s		•	•
Hillebrandite			•	•	•	•		•	•	x	•	•		•	✍		•	•		•	•		•	s		•	•
Wollastonite			•	•	•	•		•	•		•	•		•	✍		•	•		•	•		•	x		•	•
Gismondine					p	•		•						•				p					p	•		•	•
Foshagite																				p							
Pectolite			•	•	•	•		•	•	x	•	s		•	•		•	•		•	•		•	•		•	•
Plombierite								•		p		•													p	•	•
Riversideite								•		p		p								•			•			•	
Analcime			•	•	•	•		•	•		•	•	x	x	x		•	•		•	•		•	•		•	•
Ferdisilicate																			s							•	
Halite							x	x	x		•	x		p	•			•			x	p	•	p			

• indicates that the phase is not detectable in the sample, according to the glancing angle technique.
x=definite, s=strong possibility, p=possibly. Blank spaces indicate work in progress, i.e., that the phase has not been reviewed.

Ferdisilicate																			s							·	
Halite							x	x	x		·	x		⚐	•			✍			x	⚐	•	P			

• indicates that the phase is not detectable in the sample, according to the glancing angle technique.
x=definite, s=strong possibility, p=possibly. Blank spaces indicate work in progress, i.e., that the phase has not been reviewed.

Table 3. Mechanical tests. Batch 1 and Batch 2 compared. Failure load is in lbf.

Treatment		**Failure load batch 1**	**Failure load batch 2**
Untreated	Invert	234	
	Shotcrete	80	
Dry	Inv Vapor	90	258
	Inv Vapor	65	248
	SH Vapor	75	137
NaHC03	Inv Aqueous	87	390
	Inv Vapor	174	709
	SH Vapor	258	446
NaCl	Inv Aqueous	137	264
	Inv Vapor	122	145
	SH Vapor	78	*

*Broken during handling

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