Conf,

SAND--90-2150C

DE90 016868

ESTIMATION OF GEOCHEMICAL BEHAVIOR OF CONCRETES PLACED AT YUCCA MOUNTAIN.*

Thomas E. Hinkebein, Sandia National Laboratories, Albuquerque, NM; and Mark A. Gardiner, IT Corporation, Albuquerque, NM.

INTRODUCTION

The prediction of the chemical alteration of cementitious sealing materials and other cementitious components such as liners in the tuffaceous environment of Yucca Mountain is an essential element in understanding the longevity of these materials. This study uses a chemical equilibrium model to obtain information about the chemical reaction of ground water with concretes. Because concretes, cements, and grouts are metastable assemblages, it is expected that these materials will dissolve, cause secondary precipitations and react with the environment. These reactions will alter the porosity and hydraulic conductivity of the concretes. While the importance of these chemical and conductivity changes has not been completely assessed, this study provides insight into the importance of this chemical alteration.

DESCRIPTION OF WORK

In order to study the chemical alteration of cementitious materials in a tuffaceous environment, simulated interactions of concretes with ground water were performed using the geochemical speciation/solubility/reaction path code EQ3NR/EQ6 (EQ3/6).[1] While other concretes, water compositions and temperatures were considered as part of a larger study, this paper discusses the equilibration of three candidate materials with J-13 water[2] at 25°C as representative of many other possible interactions. The assumptions used in these analyses will be discussed below. The amount of precipitate and dissolution are determined and reported graphically. These alterations are then interpreted as volumetric changes in the cementitious material from which alterations in the matrix permeability may be inferred. Because volumetric changes may also lead to crack formation, the bulk permeability changes in a cracked concrete will require further work.

ASSUMPTIONS USED IN DEFINING CANDIDATE CONCRETES

Three different candidate concretes were considered. Two of these were variations of an ordinary Portland cement (OPC) based concrete, proposed for use as liner and sealing elements, and one was a variation of an ettringite-rich, Portland cement based concrete (EPC), proposed for sealing applications. In order to run EQ3/6, the initial concrete mineralogy must be known. Hence, the composition and proportions of silicates, aluminates, and ferrites must be specified.

The main cement phase in Portland cement is C-S-H gel. In cement terminology C=CaO, S=SiO_2, A=Al_2O_3, and H=H_2O. C-S-H is a metastable, poorly crystalline material with variable composition and ill defined thermodynamic properties. Gartner and Jennings,[3] Taylor,[4] and Sarkar et al.[5] suggest that 14Å

---

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

---

tobermorite is a reasonable substitute for C-S-H gel. Further, Atkinson et al.[6] show that thermodynamic differences between the behavior of C-S-H gel and tobermorite are less than 1%. Hence, the mineral tobermorite was assumed as a surrogate for the C-S-H gel.

The sulfate bearing cement phase, ettringite, was chosen because it causes concrete to expand during setting and curing so that a tight bond may be formed with the host rock (tuff) and a low initial permeability may result. In addition to the hydrated sulfate phase, the hydrated aluminate phase, hydrogarnet, was chosen. Iron was assumed to follow aluminum in the hydrated cement such that the sum of available aluminum and iron was treated as if it were aluminum. While it was possible to incorporate iron into Al-Fe hydrogarnet and ettringite solid solutions, good thermodynamic data were not available for these phases, nor was their composition exactly known.

The Bogue[7] method was used to determine the relative proportions of the hydrated phases. The starting compositions of the three concretes are shown in Table 1. These are an OPC concrete with a balanced amount of silica and calcium (OPC-B), a calcium-rich OPC (OPC-C), and a silica-rich, ettringite-rich concrete (EPC-S). All of these concrete formulations were reacted with one pore volume of J-13 water. The initial porosity was assumed to be 30%.

TABLE 1. Cement Mineralogy per 3000 cc of Concrete

OPC-B Concrete
14 Å Tobermorite, $Ca_5Si_6O_{17}\cdot 10.5H_2O$ -- 2.102 moles
Ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$ -- 0.066 moles
Hydrogarnet, $Ca_3Al_2O_6\cdot 6H_2O$ -- 0.434 moles

EPC-S Concrete
14 Å Tobermorite -- 0.927 moles
Ettringite -- 0.143 moles
Hydrogarnet -- 0.960 moles
Silica (cristobalite), SiO_2 -- 1.140 moles
Active alkali, NaOH -- 0.018 moles
Active alkali, KOH -- 0.061 moles

OPC-C Concrete
14 Å Tobermorite -- 0.522 moles
Ettringite -- 0.068 moles
Hydrogarnet -- 0.605 moles
Portlandite, $Ca(OH)_2$ -- 5.150 moles
Active alkali, NaOH -- 0.033 moles
Active alkali, KOH -- 0.032 moles

ANALYSIS METHOD

The interaction of cementitious material with water was simulated using a closed system approach. The closed system approach models the behavior of the system where very slow water movement allows secondary minerals to exert a reverse equilibrium influence. In this approach two categories of minerals were suppressed from precipitating during these runs. The first category were those high-temperature igneous, and metamorphic or hydrothermal phases which could not form under the conditions of this study. The second category were those minerals which were kinetically or otherwise unreasonable. Specific minerals which were suppressed were low albite, K-feldspar, sanidine, kaolinite, chalcedony, quartz, and K-mordenite, and muscovite. Aqueous silica concentration was assumed to be controlled by cristobalite. Hence, the precipitation of other SiO_2 minerals, e.g., quartz, tridymite, chalcedony, and glass, were suppressed.

For the purposes of this study the EQ3/6 computer code was operated in the equilibrium analysis mode. Because all reactions were assumed to be instantaneous, the results yielded conservative (maximum) estimates of both precipitation and dissolution.

For all of the reactions considered, individual phases were titrated into solution on an equal molar basis, i.e., for every mole of reaction progress, ζ, one mole of each reactant was added to the solution and equilibrated. When any one of the reactants was exhausted, no further additions of that component were made. While this equal molar assumption is not completely justifiable, the logic is that those cement phases present in the smallest amounts also happen to be the most reactive: the more reactive phases would be reacted before the more stable phases. Thus, in our particular case the equal molar approach is reasonable.

RESULTS

First run: J-13 + OPC-B

For the interaction of OPC-B concrete (see Table 1) with J-13 water, small amounts of the cement phases tobermorite, hydrogarnet, and ettringite were added sequentially to J-13 water. The precipitation of 17 different phases including clays, zeolites, silica and cement phases occurred during the course of this interaction. For very small additions of the cement phases, only minimal effects were noted on the water chemistry, as the natural buffering capacity of this ground water was evident. At a reaction progress of 10^{-5} moles (log ζ less than -5), the pH of this water was approximately 7 (results will be graphically presented). If the same amount of cement phases were added to deionized water the pH would have jumped to 10.5. In this dilute region, small amounts of cristobalite, clinoptilolite, nontronite and pyrite were precipitated, causing the J-13 water to become more reducing.

With the addition of larger amounts of the cement phases, additional clays and zeolites precipitated until at log ζ of -4.5, calcite formed. At log ζ of -3.5 the calcium silicate phase tobermorite first precipitated and from this stage forward controlled the solution silica concentration. At this point the silica concentration dropped by a factor of 2 to 5. Accompanying this drop in silica concentration, the zeolite clinoptilolite redissolved as the cement phases took control of the solution chemistry. The aluminum and hydroxide concentrations increased by 5 orders of magnitude at log ζ of -3. At log ζ of -2.8 hydrogarnet precipitated to control the pH and the aluminum concentration. With the addition of slightly more cement, gypsum precipitated to control the sulfate concentration.

The overall mass change for this series of reactions was principally described by the reaction of ettringite to form hydrogarnet and gypsum, i.e.,

$$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O \rightarrow Ca_3Al_2O_6\cdot 6H_2O + 3(CaSO_4\cdot 2H_2O) + 20H_2O \quad . \quad (1)$$

Ettringite is unstable and did not reach equilibrium during the course of this run. The hydration water lost in this reaction accounted for 86% of the total mass lost accompanying the interaction of this concrete with J-13 water. The additional mass change was caused by the formation of other less hydrated phases than the cement phases assumed at the start of the run. The total mass of the cement (6728 gm) was reduced by 0.41% (27.7 gm) during the course of this interaction.

Second run: J-13 + EPC-S

The addition of the expansive, silica-rich EPC-S concrete to J-13 water was very similar to that of the OPC-B concrete in terms of both solution chemistry and types of phases produced. One mole of reaction progress for the EPC-S concrete contains the same amount of calcium, aluminum, and sulfate, 16% more silica, and 6% more hydroxide derived from reactive alkalis than the OPC-B run did. For values of log ζ less than -2.8 the solution chemistry of the EPC-S run almost identically overlays that of the OPC-B run. At this point hydrogarnet started to precipitate as in the OPC-B run; however, the excess silica (cristobalite) reacted with this hydrogarnet to form gismondine and tobermorite, i.e.,

$$5(Ca_3Al_2O_6\cdot 6H_2O) + 22SiO_2 + 11H_2O \rightarrow$$
$$5Ca(Al_2Si_2O_8)\cdot 4H_2O + 2(Ca_5Si_6O_{17}\cdot 10.5H_2O) \quad . \quad (2)$$

This reaction terminated when all cristobalite was consumed. Since the same phases were present at the end of this run as were present at the end of the OPC-B run, the final solution concentrations were very similar.

The hydration water lost in reaction (1) plus that gained in reaction (2) accounted for 81% of the total mass lost accompanying the interaction of EPC-S concrete with J-13 water. The additional mass change was caused by the dissolution of the alkalis and the formation of other phases less hydrated than the cement phases. The total mass of the cement (6728 gm) was reduced by 0.76% (51.3 gm) during the course of this interaction.

Third run: J-13 + OPC-C

The addition of the calcium-rich concrete, OPC-C, to J-13 water yielded remarkably similar solution chemistry and phase equilibrium to the prior two runs. One mole of reaction progress yielded 12% more hydroxide and 7% more calcium, while other species were similar to the OPC-B run. As a consequence of these similarities, the titration curves were again very similar to those for the other two cements. The pH rise was a little quicker than for the balanced and silica rich concretes. Because of the large excess of portlandite, the cement mineral foshagite, $Ca_4Si_3O_{10}\cdot 1.5H_2O$, formed from tobermorite and portlandite at log ζ of -2.3 according to the reaction,

$$Ca_5Si_6O_{17}\cdot 10.5H_2O + 3Ca(OH)_2 \rightarrow 2(Ca_4Si_3O_{10}\cdot 1.5H_2O) + 10.5H_2O \quad . \qquad (3)$$

Concurrently, the zeolite gismondine disappeared. Once all of the tobermorite was consumed by this reaction the solution very rapidly equilibrated with the excess portlandite and the reaction was terminated at that point. The mineral brucite, $Mg(OH)_2$, replaced the 7Å clinochlore to control the solution magnesium concentration at log ζ of 0.19.

The hydration water lost by the sum of reactions (1) and (3) accounts for 93% of the total mass loss for the interaction of OPC-C with J-13 water. The total mass loss during this interaction is larger than that of the other two cements with 2.0% (131.9 gm) of the total mass of the concrete being lost during this interaction.

Porosity and Conductivity Change Projections

The interpretation of the mass change data as solid volume change information required specific density information on every phase that dissolves or is precipitated. This data was estimated for these phases and the resultant volume change computed. Because most of this mass change data represents the transfer of hydration water either into or out of the solid phase, the mass change versus reaction progress were composed of linear segments whose slopes were predominantly determined from the moles of water per mole of reaction progress. For small amounts of concrete addition, the water loss accompanying ettringite decomposition, Reaction (1), and alkali dissolution were most apparent. After ettringite was exhausted, OPC-B became stable with J-13 water, EPC-S porosity decreased as a result of Reaction (2), and the OPC-C porosity increased by Reaction (3).

These porosity changes were translated to permeability changes using the model of Alcorn et al.[8]. Alcorn et al. used nine sources of permeability-porosity data to develop a single empirical correlation for cementitious materials. This correlation represented the mean of the data sets while large deviations from the mean existed for individual data sets. For the limited conditions investigated in this study, these porosity changes corresponded to permeability changes of less than 12%.

CONCLUSIONS

Results of the modeling of concrete interactions with J-13 ground water suggested the following conclusions: (1) Solution chemistry for calcium-rich concretes was remarkably similar to that for silica-rich concretes. (2) Solution pH was strongly buffered by J-13 water at neutral values for small amounts of added concrete. For larger amounts of concrete the solution pH was approximately 12. (3) The overall mass and consequently volume change accompanying the aging of these three concretes was predominantly described by a few chemical reactions. If ettringite or excess portlandite were present, their decomposition opens the concrete structure. Excess silica reacted with hydrogarnet to tighten the concrete structure. (4) The permeability changes for the limited conditions discussed here were small.

REFERENCES

1. Wolery, T.J., 1983. "EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: User's Guide and Documentation," UCRL-53414, Lawrence Livermore Laboratory, Livermore, Ca, 191 pp.

2. DOE, U.S. Department of Energy, 1988. "Site Characterization Plan," DOE/RW-0199, Office of Civilian Radioactive Waste Management, Washington, DC, pp. 4-41 to 4-42.

3. Gartner, E.M., and H.M. Jennings, 1987. "Thermodynamics of Calcium Silicate Hydrates and Their Solutions," J. Am. Ceram. Soc., Vol. 70, No. 10, pp. 743-749.

4. Taylor, H.F.W., ed., 1964. The Chemistry of Cements, Vol. 1, Academic Press, New York, 460 pp.

5. Sarkar, A.K., K.W. Barnes, and D.M. Roy, 1982. "Longevity of Borehole and Shaft Sealing Materials: Thermodynamic Properties of Cements and Related Phases Applied to Repository Sealing," ONWI-201, prepared by the Pennsylvania State University for the Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus OH, 52 pp.

6. Atkinson, A., J.A. Hearne, and C.F. Knights, 1987. "Aqueous Chemistry and Thermodynamic Modeling of $CaO-SiO_2-H_2O$ gels," Report AERE-R12548, Materials Development Division, Harwell Laboratory, Oxfordshire, UK.

7. Bogue, R.H., 1955. The Chemistry of Portland Cement, 2nd Ed., Reinhold, New York, 793 pp.

8. Alcorn, S.R., W.E. Coons, and M.A. Gardiner, 1990. "Estimation of Longevity of Portland Cement Using Chemical Modeling Techniques," Mat. Res. Soc. Symp. Proc., Vol. 176, pp. 176-173.

Appendix

Information from the Reference Information Base
Used in this Report

This report contains no information from the Reference Information Base.

Candidate Information for the Reference Information Base

This report contains no candidate information for the Reference Information Base.

Candidate Information for the Site & Engineering Properties Data Base

This report contains no candidate information for the Site and Engineering Properties Data Base.