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POST EMLACEMENT ENVIRONMENT OF WASTE PACKAGES

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ABSTRACT

Experiments have been conducted as part of the Nevada Nuclear Waste Storage Investigations Project to determine the changes in water chemistry due to reaction of the Topopah Spring tuff with natural groundwater at temperatures up to 150°C. The reaction extent has been investigated as a function of rock-to-water ratio, temperature, reaction time, physical state of the samples, and geographic location of the samples within the tuff unit. Results of these experiments will be used to provide information on the water chemistry to be expected if a high level waste repository were to be constructed in the Topopah Spring tuff.

INTRODUCTION

The initial response of the near field environment to the heat generated by the emplacement of nuclear waste packages is an increase in temperature which causes the partially saturated country rock to dry out. Following the initial thermal pulse the rock will cool and liquid water will gradually return to the vicinity of the waste packages. As the water passes through heated rock it will react with the rock and change in chemical composition. To determine the chemistry of the water which will be available for interaction with the waste packages we have investigated the changes in chemistry resulting from the equilibration of J-13 well water with Topopah Spring tuff as a function of rock-to-water ratio, temperature, reaction time, physical state of the samples, and geographic location of the rock within the prospective repository location. Results of the experiments have been compared with predictions based on the EQ3/6 geochemical modeling code [1].

EXPERIMENTS USING CRUSHED TUFF

Two matrix experiments were conducted using Topopah Spring tuff crushed to less than 100 mesh and J-13 well water. Detailed experimental procedures and results are given in Oversby [2]. The tests were conducted in teflon containers (Parr acid digestion bombs). The test matrix at 150°C used sample weights of 0.2, 0.4, and 0.8 g of rock equilibrated with 12 ml of J-13 water for 1, 2, 4, 8, 16, 31 and 48 days. The 90°C matrix used larger reaction vessels, so sample sizes were scaled up to duplicate the surface area of rock to solution volume ratios used in the 150°C matrix. The 90°C matrix used rock weights of 0.4, 0.8, 1.6, and 3.2 g equilibrated for 1, 3, 6, 12, 24, 36, 48, 60 and 72 days with 48 ml of J-13 water.

The rock samples which were used were obtained from a surface outcrop at Fran Ridge, slightly east of Yucca Mountain. Previous experience with rock-water hydrothermal experiments using Bullfrog tuff showed that surface outcrop samples contain easily soluble material which should be removed before conducting the equilibration experiments [3]. All samples used in this study were pretreated by shaking for two minutes at room temperature with J-13 water. Figure 1 shows data for SO_4^{2-} , NO_3^- , and Cl^- for solutions from this rinse (RTS). To ensure that all easily

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soluble material had been removed, the samples were equilibrated overnight at the reaction temperature with fresh J-13 water (Sample number 0-1, Figure 1). This two step pretreatment was applied to all samples; thus, data for 4 days at 150°C means pretreatment followed by four days of equilibration with fresh J-13 water.

Fig. 1. Data for pretreatment solutions and four day and 48 day equilibration of Topopah Spring tuff with J-13 water at 150°C. Data for pretreatment solutions are the average of analyses for all samples of the given sample weight.

Under expected repository conditions in the unsaturated zone, liquid water will not generally exist at temperatures higher than 95°C, the unconfined boiling point of water at the repository level. Thus, the 90°C data discussed below are the most relevant to general repository conditions. The 150°C data were collected to obtain information on reaction kinetics. They are also relevant to small amounts of water held in pores by capillary forces; this water could be liquid at somewhat higher temperatures than the unconfined boiling point.

Concentrations of F⁻, Cl⁻, NO₃⁻, SO₄²⁻ and carbonate alkalinity were measured on all samples. There were no significant changes in concentration due to reaction of J-13 water with the rock except in the case of alkalinity. J-13 carbonate alkalinity is 2.16 meq/l, which corresponds to 132 ppm when calculated as HCO₃⁻. Reaction at 90°C reduced alkalinity to approximately 1.8 meq/l (110 ppm)

and reaction at 150°C reduced alkalinity to approximately 1.5 meq/l (92 ppm). Samples of J-13 water heated without rock (J-13 blanks) showed somewhat greater reduction in alkalinity. Most of the reduction in alkalinity can be correlated with a decrease in Ca and Mg; however, especially in the case of the blanks, there must also be some loss of CO₂ to the teflon container.

Figure 2 shows some of the experimental data for Ca and Al at 90°C and 150°C. The decrease in Ca is greater at the higher temperature, as would be expected from the retrograde solubility of CaCO₃. The precipitation reaction is slow, especially at 90°C. Magnesium, which is 1.8 ppm in J-13 water, precipitates faster than Ca, and is enriched in the centers of the euhedral calcite crystals which are found on the surface of reacted core wafers. Aluminum concentrations at 150°C rise on reaction with the tuff and then slowly decrease. This appears to be supersaturation due to colloid formation, followed by slow coagulation. The degree of supersaturation at 90°C is much less than at 150°C, suggesting reduced importance of colloids at the lower temperature.

Fig. 2 Calcium and aluminum concentrations versus reaction time for reaction of pretreated Topopan Spring tuff with J-13 water.

Silicon in solution increases slowly due to dissolution of quartz and cristobalite. Data are shown in Fig. 3 for a single rock/water ratio vs. reaction time. The solubility of silica is much higher at 150°C than at 90°C, and appears to be controlled by cristobalite rather than by quartz. The pH of the solutions, 8.5 at 90°C and 9.0 at 150°C, is somewhat higher than that predicted based on modeling calculations for the observed silica. This is especially true in the case of J-13 blanks which have only 20 to 25 ppm Si. The high pH is attributed to loss of CO₂ to the teflon. This is confirmed by the results of gold bag autoclave experiments (discussed below) which give final pH at 150°C of approximately 7.

Fig. 3 Silicon concentration in solution for reaction of pretreated Topopah Spring tuff with J-13 water.

Sodium concentrations in solution after reaction are essentially the same as the J-13 starting values at both temperatures. Potassium shows an increase from 5.3 ppm to values between 7 and 10 ppm; the value depends on the ratio of rock to water which suggests that the increase is due to the incomplete removal of the original soluble phase.

In order to estimate the degree of variability of solution chemistry as a function of position at Yucca Mountain we have used Topopah Spring tuff samples selected from the appropriate depth interval from three vertical drill holes (G1, G4 and GU3) and one horizontal air drilled hole (H1) at Fran Ridge. The solution concentrations after reaction for 64 days at 150°C are given in Figure 4. The sample number gives the distance in feet from the surface at which the sample existed in situ. None of these samples showed the presence of any readily soluble salt material. This is especially significant in the case of the air drilled Fran Ridge samples. As a result of this data, we do not expect that we will encounter large amounts of soluble anion material at the repository horizon. Solution data for these samples is very similar for all samples except for GU3-1072 Ft. which shows clear evidence of precipitation of a silicate phase (Na is also low for this sample) and for two samples which are somewhat low in Si. The main difference between these samples and those discussed previously is in the K concentrations. Other data for shorter reaction times is similar to that for the Fran Ridge outcrop material which indicates the slow precipitation of K from solution in the case of the G4 day reaction times.

EXPERIMENTS USING CORE WAFERS

In order to investigate the water chemistry changes due to surface area variation and to sample preparation effects, as well as to determine the changes in primary solid phase chemistry and the distribution and chemistry of secondary phases, polished core wafers of Topopah Spring tuff were reacted with J-13 water. Detailed experimental procedures are given in Knauss and Beiriger [4]. The tests were run at 150°C in large Parr bombs for periods of up to 4 months. The samples were not pretreated to remove soluble material; however, large amounts of water were used in the

Fig. 4. Solution concentrations for drill core samples of Topopah Spring tuff reacted with J-13 water for 64 days at 150°C.

preparation of the wafers which effectively removes most of the readily soluble material. Experiments were run with wafers fully submerged in J-13 water (samples 1-4) and with wafers subjected to water saturated air (using J-13 water in limited quantities to produce the saturation). Samples 5-8 were the water saturated air runs.

Table I gives data for cations in solution, weight loss by the core wafer, and pH as well as initial concentrations in J-13 water. The data for submerged samples are in excellent agreement with the results on crushed tuff samples except for Al and Si. The crushed tuff experiments gave higher Al; these samples were rolled during the reaction period, which may have stabilized colloidal material in suspension. The higher Si concentrations in the core wafers is due to the longer reaction time; there may also be a small amount of "glassy" material formed during the polishing of the core wafers prior to reaction [3].

Table I Solution data for core wafer experiments at 150°C in ppm

CW#	Time(d)	Al	Si	Ca	K	Mg	Na	pH	Wt. loss (%)
1	13.8	0.54	87.2	4.14	11.9	0.03	46.5	7.52	1.16
2	27.8	0.44	102.	3.84	9.0	0.05	47.5	8.06	1.38
3	55.8	0.37	119.	3.36	8.3	0.01	47.6	8.51	1.40
4	112.7	0.36	132.	4.24	7.1	0.01	61.0	8.70	1.44
5	13.8	0.00	25.2	7.10	4.8	0.29	44.3	7.35	0.09
6	27.8	0.00	28.5	6.27	7.6	0.26	49.7	7.35	0.11
7	54.8	0.02	27.7	5.68	6.4	0.17	48.9	7.40	0.10
8	111.7	0.00	35.7	6.16	7.0	0.04	58.5	8.50	0.12
J-13	0	0.05	25.7	10.7	4.9	1.91	37.0	7.56	0
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The SEM and electron microprobe analyses of reacted wafers showed no difference in the chemistry of major phenocrysts (plagioclase, sanidine and biotite) or the matrix assemblage due to hydrothermal reaction.

However, abundant discrete calcite crystals were formed on all submerged samples. The calcite crystals were found to have Mg enriched cores.

Data for samples run in water saturated air at 150°C show similar trends to the fully submerged samples, but all reaction rates appear to be slower.

EXPERIMENTS USING DICKSON ROCKING AUTOCLAVES

Fig. 5. Solution concentrations and pH data for Topopah Spring tuff reacted with J-13 water at 150°C in Dickson-type rocking autoclaves.

In order to run experiments at temperature and pressure limits beyond those where teflon can be used and to allow samples to be taken without quenching we have run experiments in Dickson-type gold cell rocking autoclaves. These autoclaves provide a chemically inert, gas tight reaction vessel. Detailed experimental procedures are given in Knauss and Peifer [5]. Pretreated crushed Topopah Spring tuff and J-13 water were reacted at 150°C for 32 days in duplicate experiments.

Figure 5 shows data for Si, Ca, Al, K and pH. Agreement between the crushed tuff results run in teflon with those run in the gold bag is excellent for Si, Ca and Al, indicating that quenching is not a problem in the teflon container runs. Potassium is higher in the gold cell runs. This may be due to incomplete removal of soluble K during the pretreatment steps. The pH differs markedly between the teflon runs and the gold autoclave runs. The pH in autoclave runs drops initially due to carbonate precipitation and then slowly rises. The solutions remain essentially neutral for the entire test period rather than rising as seen in the teflon capsule experiments. Alkalinity remains relatively constant in the gold cells, while alkalinity in the teflon containers decreased. This suggests that CO₂ is lost to the teflon and causes the change in pH seen in those experiments. New long term experiments in the Dickson autoclave systems are in progress and will extend for periods of up to one year.

The solution chemistry data taken as a whole shows that the changes in chemistry due to

hydrothermal reaction between the Topopah Spring tuff and J-13 water are very small except for the dissolution of silica.

EQ6 MODELS OF THE DICKSON AUTOCLAVE EXPERIMENTS

The EQ6 computer code (1) was used to generate several kinetic reaction path models for the previously described Dickson autoclave experiments. Briefly, the code provides for aqueous speciation equilibria, solubility equilibria for secondary solids, and rate laws for the dissolution of primary solids. It has no capability now to model precipitation kinetics. The user can, however, choose which potential secondary minerals are allowed to precipitate. The EQ6 models generated in this study differed in the set of such allowed phases.

The tuff was represented as a suite of dissolving minerals, whose surface areas were presumed proportional to their volume percentages. The rate laws and rate constants are described elsewhere [6]. The tuff was assumed to be free of soluble salts.

All reasonable models showed that the water becomes saturated with respect to cristobalite and, to varying degrees, supersaturated with all of the other original tuff minerals except biotite. These minerals stop dissolving upon reaching saturation. The supersaturations result from common ion effects driven by primary minerals that are still dissolving. This puts the water in a metastable state, in which it is also supersaturated with respect to numerous potential secondary phases. The problem of finding a model that was a good match to the experiment lay largely in trying to determine which secondary phases were actually forming.

The best match was generated by model H, in which the allowed secondary phases were iron oxide (hematite), magnesian calcite, and gibbsite. This model is shown in the curves in Figure 5. It gives an excellent match to the data for pH. It gives an equally good match in the case of magnesium (not shown in Figure 5), which drops from about 1.9 ppm to about 0.01-0.4 ppm after one day of reaction. It yields results for Na (not shown) and K that are less than the experimental data. However, it appears likely that close matches would have been obtained if the leaching pretreatment of this batch of tuff had effectively removed the soluble salt component. The predicted Si concentration is somewhat high, perhaps because the model does not take into account kinetically controlled growth of quartz, a process which should be occurring because the water is supersaturated with it and it is present in the tuff as a major primary mineral. The data for Al and Ca show a kinetically controlled approach to equilibrium assumed in the model. Encouragingly, model I (not shown on Figure 5, the same as model H, but without gibbsite) predicted the maximum in Al concentration within a ppm.

These results are very encouraging with respect to the question of the feasibility of this type of modeling. The inclusion of precipitation kinetics in the code will obviously lead to better kinetic models of short-term and longer experiments, and will be a necessary step to making long-term extrapolations.

CONCLUSIONS

The results from the three types of rock-water interaction tests can be summarized to show that there will be very little change in water chemistry due to interaction of vadose water with the rock on the path

through the repository before contact with waste packages. We see no significant increase in anion concentration in the water due to interaction with the rock and there is no evidence to suggest that the readily soluble component found on surface outcrop samples will be present at depth. This is important because some anions such as fluoride and chloride can cause enhanced localized corrosion of canister materials. Other anions might act as complexing agents and enhance the solubility or mobility of radionuclides. The absence of a source of anions is, therefore, of assistance to the performance of the waste package. The pH of the solutions when runs are conducted in vessels that do not absorb CO₂ remains nearly neutral. This will enhance the durability of borosilicate glass which shows higher dissolution rates at pH less than 5 or greater than 9. The increase in silica concentration of the water as a result of reaction with the rock will also assist the durability of borosilicate glass since the dissolution rate of such glasses decreases as the silica content of the solution increases. The lack of detectable alteration of the primary mineral phases of the rock suggests that the long term behavior of the rock should be similar to that observed in the short term laboratory experiments. Finally, the success in modeling the system using a geochemical modeling code (EQ3/6) shows that we have sufficient understanding of the processes involved so that long term prediction of the water chemistry should be possible.

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