

EXPERIMENTAL EVIDENCE FOR THE EFFECT OF BASALT  
ON RADIONUCLIDE LEVELS IN HOT GROUNDWATER\*

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ABSTRACT

Hydrothermal reaction experiments on supercalcine and supercalcine plus Umtanum basalt with Grande Ronde groundwater were run at 200° and 300°C and 300 bars total pressure. These experiments allow a comparison of element abundances in solutions reacting with a waste form with, and without the presence of basalt.

The experiments were done in Dickson-type rocker vessels which allowed solution samples to be taken at pressure and temperature. Solid:liquid mass ratios of 1:10 were used. Samples were taken at intervals over one month periods for 300°C runs and four month periods for 200°C runs. Solutions were analyzed for pH, B, Na, Si, Mo, Cr, Fe, Ni, Ba, Cl and F using a combination of ICP and ion specific electrodes. Solids recovered at the end of the runs were analyzed by SEM equipped with an energy dispersive system for qualitative elemental analysis.

Addition of basalt causes a significant decrease in Mo concentration, especially at 200°C. The most striking difference is in Cr abundance; addition of basalt quantitatively removes Cr from solution, and the removal occurs essentially immediately after the initiation of the run.

SEM observations of the solid material from the runs shows recrystallization of the titaniferous magnetite originally present in the basalt. The recrystallized magnetite would readily incorporate Cr, explaining the removal of Cr from the solutions in contact with basalt. More importantly, the recrystallization of magnetite suggests that it is acting to control oxygen fugacity in the system. The original magnetite in the basalt is titanium rich, so the oxidation reaction would initially produce magnetite progressively poorer in Ti and richer in ferric iron. Such a reaction would consume oxygen and also maintain a relatively low oxygen fugacity until a large proportion of the original magnetite

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was consumed. The prevailing oxygen fugacity in the system would probably be low enough to maintain U and Pu in tetravalent oxidation states in which they are much less soluble than when they are hexavalent.

## INTRODUCTION

For buried nuclear repositories the 'worst case' scenario involves failure of all of the canister materials and the resulting direct interaction of groundwater with the waste form. Alteration of the waste form by the groundwater could possibly allow transport of toxic radionuclides to the biosphere. However, the presence of surrounding rock, either as backfill material or local country rock may significantly change the levels of radionuclides in groundwater. In this paper we report experimental results which are directly applicable to the case of mined repositories in basaltic host rocks. The experimental results were obtained using a supercalcine waste form but our conclusions should be generally applicable to all waste forms.

The interaction of groundwater with country rock may change solute levels (compared to situations involving only waste form and groundwater) in at least four important ways. (1) The country rock may react to consume dissolved oxygen in groundwater. Thereby greatly lowering oxygen fugacity. This would lower the concentrations of many actinide elements in groundwater. (2) Phases in the country rock may react with the groundwater to precipitate radionuclide containing phases which could not form from the waste form alone. This would lower concentrations of the radionuclides involved. (3) The country rock might contribute solution components which would complex with radionuclides from the waste form, causing an increase in the solubility of some elements in groundwater. (4) The country rock may react with the groundwater to precipitate a phase or phases containing a complexing element from the waste form. This would indirectly lower the solubility of complex-forming radionuclides.

In this paper we show that our data confirm the importance of interactions of types (1) and (2), and suggest that types (3) and (4) may occur.

## EXPERIMENTAL

A detailed discussion of the experiments is given in Jenkins and others<sup>1</sup> and Holloway and others<sup>2</sup>; only a brief summary is given here. The experiments were done in Dickson-type rocker vessels in which the sample is enclosed in a gold and titanium sample bag.<sup>3</sup> The apparatus allowed solution samples to be taken during the course of an experiment. The experiments lasted for one month at 300°C and four or more months at 200°C. All experiments were run at 300 bars total pressure. Initial solid:liquid mass ratios of 1:10 were used. Synthetic Grande Ronde groundwater was prepared as described by Holloway and others.<sup>2</sup> Solid starting materials were Urtanum basalt and supercalcine SPC-4 supplied by Rockwell Hanford

Operations. The solid starting materials were ground and sieved to -100 + 200 (300°C) or -250 + 375 (200°C) mesh.

A significant amount of very fine (<1 µm) particulate matter remained in the sieved material and could only be removed by repeated washing and ultrasonic cleaning. Chemical analysis of the unsieved, sieved, and sieved and washed fractions of basalt demonstrate the absence of compositional differences within analytical precision (1% RSD). Solutions were analyzed for pH, B, Na, Si, Mo, Cr, Fe, Ni, Ba, Ca, Cl and F using a combination of inductively coupled plasma spectroscopy and ion-specific electrodes. Solids recovered at the end of the experiments were characterized by optical microscopy, bulk x-ray diffraction and scanning electron microscopy with qualitative analysis.

## RESULTS

The results of the experiments are summarized in Figs. 1 - 4 and in Table I. We have demonstrated a high degree of reproducibility in the solution compositions as long as starting materials from run to run are treated identically.<sup>1</sup> As can be seen in the Figures and Table, Mo, Si, Na and Cl are present in relatively high concentrations, K, Al and F at moderate values, Fe, B, Cr, Ni, Sr and Ba at low, but measurable concentrations, and Ca, Mg, U and Qz were at or below detection limits. The pH is in the alkaline range for all experiments. There are small systematic differences observed between the 200° and 300°C experiments but with the possible exception of Fe and Ba the differences are not large compared to the differences caused by the presence or absence of basalt.

Table I. Solution Compositions<sup>†</sup>

Starting Material T°C	time*, hours	pH	Cr	Ni	Fe	Sr	Ba	B
SPC-4 300°C	2	11.2	4.4	.17	1.6	.04	.1	ND
	24	11.2	5.0	.17	1.5	.07	.1	ND
	300	10	4.7	.21	1.2	.07	.1	ND
	500	10.8	4.5	.22	1.2	.07	.2	ND
SPC-4 + Basalt 300°C	2	9.7	<.01	.12	.95	.02	.1	ND
	24	9.9	<.01	.13	.92	.05	2.	ND
	500	9.5	.05	.14	.70	.04	.5	ND
	800	9.4	.10	ND**	.44	.07	.1	ND
SPC-4 200°C	2	11.0	1.2	ND	1.1	0.1	0.8	.32
	24	11.4	1.3	ND	1.3	0.1	2.0	.42
	800	11.7	2.8	ND	0.9	0.2	0.8	3.2
	2000	11.7	2.9	ND	0.6	0.2	0.8	3.1

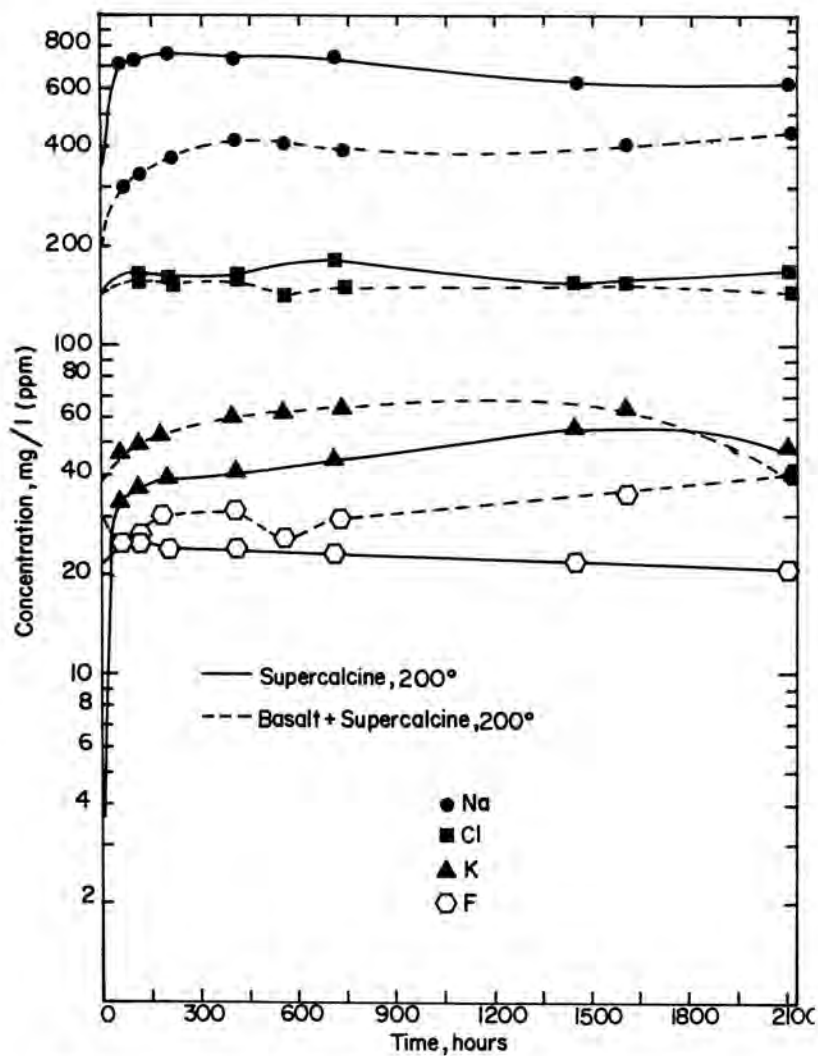


Fig. 1. Concentration of univalent ions in solution at 300 bars total pressure and 200°C.

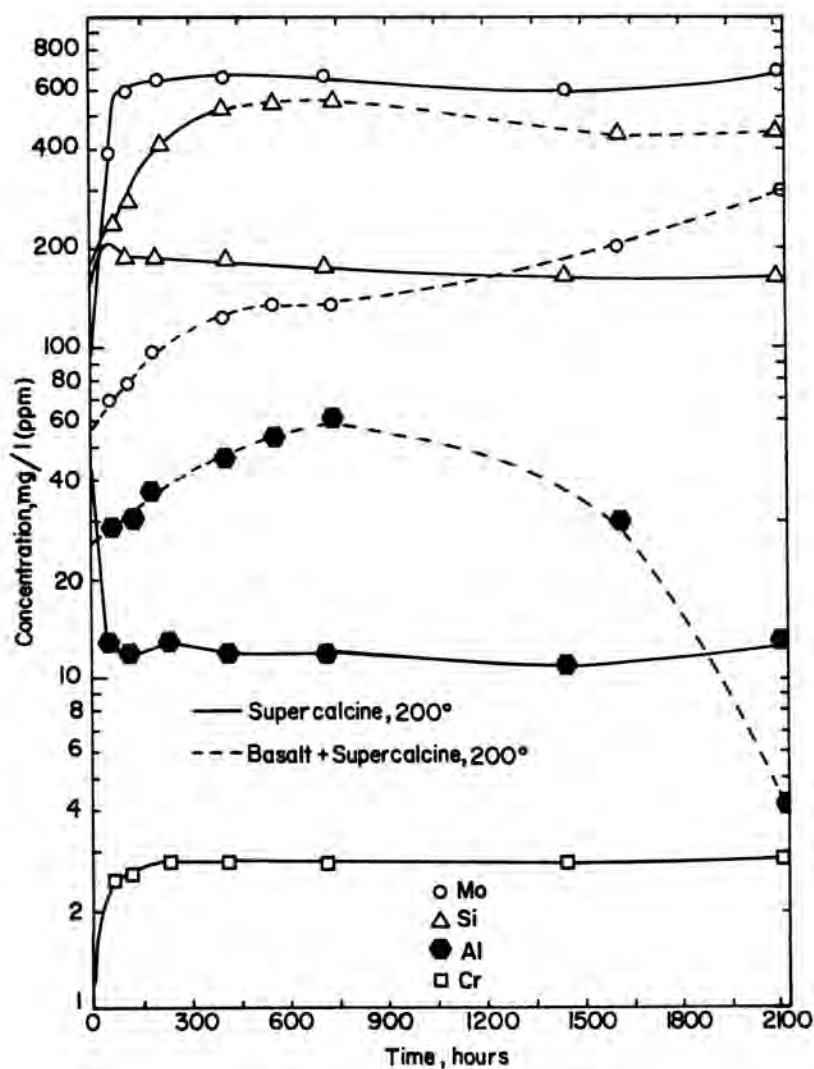


Fig. 2. Concentration of multivalent ions in solution at 300 bars total pressure and 200°C.

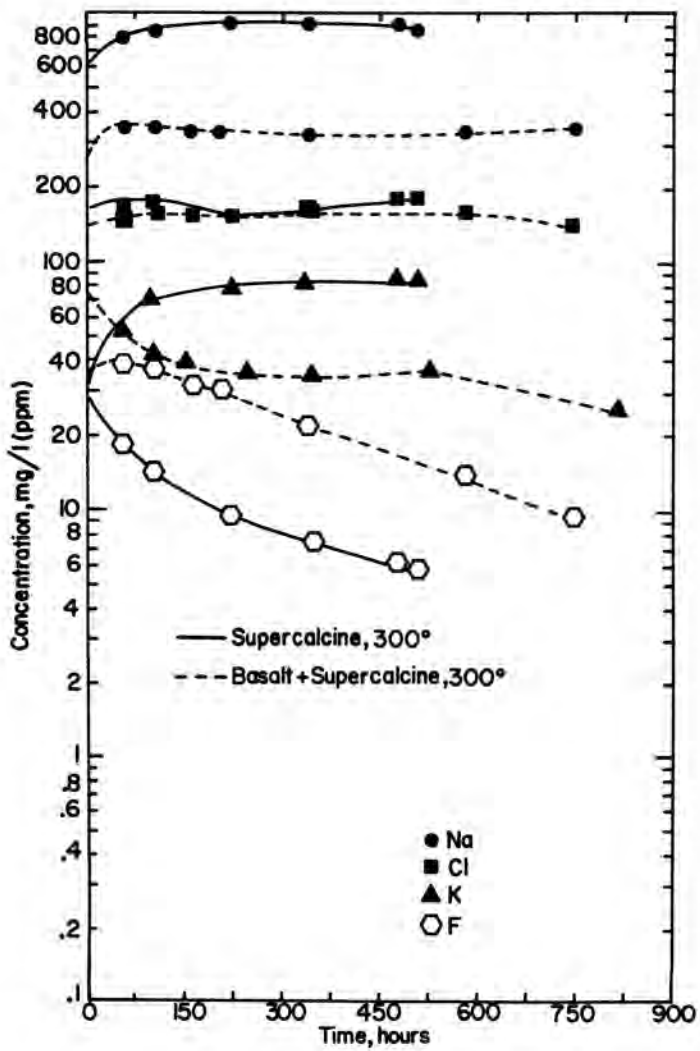


Fig. 3. Concentrations of univalent ions in solutions at 300 bars total pressure and 300°C.

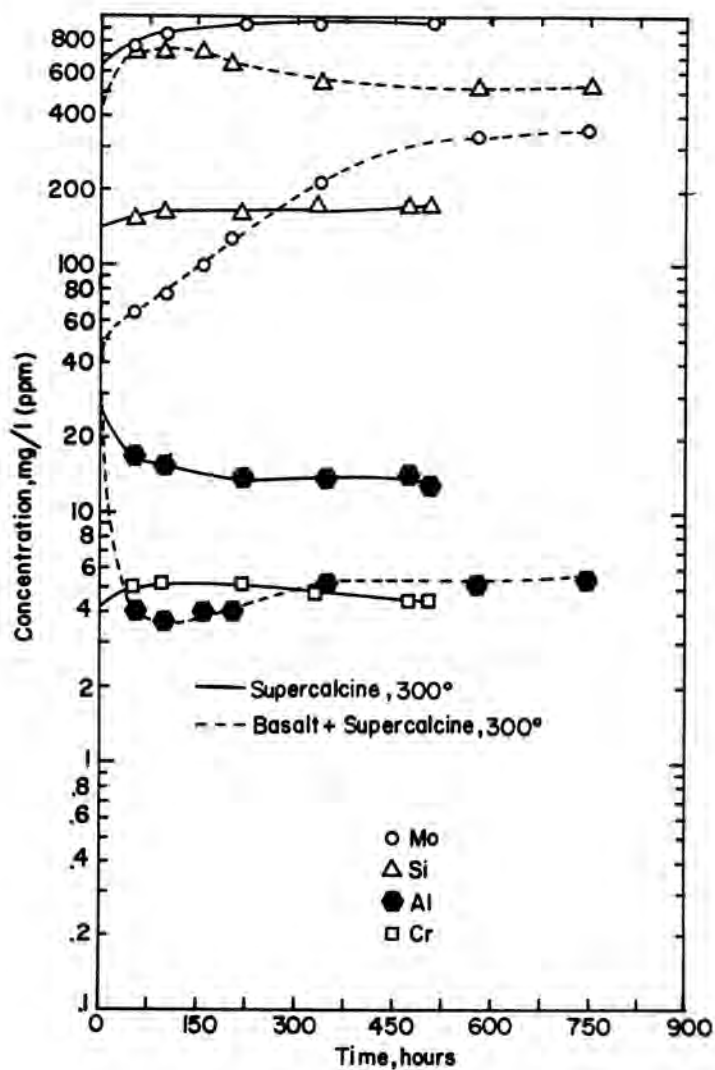


Fig. 4. Concentrations of multivalent ions in solution at 300 bars total pressure and 300°C.

Table I. Continued

Starting Material T°C	time*, hours	pH	Cr	Ni	Fe	Sr	Ba	B
SPC-4	2	9.9	0.60	ND	5.7	0.8	1.1	.08
+ Basalt	24	10.4	<0.01	ND	6.7	0.2	0.7	.09
200°C	800	10.2	<0.01	ND	40	0.7	6.0	.50
	2000	10.1	<0.01	ND	0.2	0.1	0.2	.81

† In ppm by weight except for pH. Precision is  $\pm 1\%$  RSD for pH,  $\pm 2\%$  RSD for B, Cr, Ni and Fe and  $\pm 10\%$  RSD for Sr and Ba.

\*Time rounded to  $\pm 10\%$ .

\*\*ND = not measured.

#### DISCUSSION

Comparison of solution compositions at both 200° and 300°C shows several important differences between those in contact with supercalcin and those in contact with basalt plus supercalcin. The levels of Si and F are significantly higher in the basalt experiments while Na, Mb, B, Ni, and especially Cr are lower. The increase in Si is almost certainly due to its much greater concentration in basalt compared to the supercalcin. The same explanation may hold for F, but its concentration has not been determined in either starting material. The increase in F abundance may be an example of a type (3) interaction because F is known to form soluble species with U, so the increase in its abundance caused by addition of basalt would tend to increase the solubility of uranium-like actinide elements (although the effect of F is only important at values of  $\text{pH} < 4$ ).<sup>4</sup>

The decreases in Na, Mb and B in the presence of basalt have not been fully explained but probably result from relatively complex solution/precipitation reactions, as suggested by the much slower changes in concentration in the basalt-containing compared to the basalt-free experiments. This would then be an example of a type (2) reaction in the case of Mb, which may be a geochemical analogue for Tc. In this case the precipitated phase is probably Sr-powellite  $[(\text{Sr}, \text{Ca})\text{MoO}_4]$ . The decrease in B is an example of a type (4) interaction. In as much as B is commonly a complexing agent and decreasing its abundance will decrease the solubility of any metal complexed by B.

The most dramatic effect of the addition of basalt is on the Cr abundance. At 300°C Cr decreases from 4-5 ppm to less than 0.1 ppm; at 200°C it decreases from 2-3 ppm to less than 0.01 ppm and in each case the change occurs within the first few hours of the experiment. Based on the behavior of Cr in natural geochemical systems, its behavior in these experiments suggests that Cr in solution was reacting with magnetite in the basalt. Alternatively basalt may have been controlling the oxygen fugacity so that Cr was in the +3 oxidation state in the basalt-containing experiments and



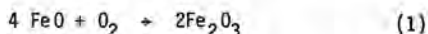
the +6 state in the basalt-free experiments. Both of these mechanisms may have operated to produce the observed Cr behavior.

Examination of the solid materials at the end of each basalt experiment showed the presence of small, elongate crystallites of an iron-titanium oxide phase. Semi-quantitative analyses of this phase strongly suggest that it is magnetite-ulvöspinel, but it could possibly be hematite-ilmenite. In either case its crystal form is unlike that of the iron-titanium oxides originally present in the basalt, so this phase was almost certainly precipitated from the solution during the course of the experiments.  $\text{Cr}^{+3}$  has a strong affinity for iron-titanium oxides and would readily be incorporated to the precipitating crystals. Using visible absorption spectroscopy we were able to demonstrate the existence of  $\text{Cr}^{+6}$  in solutions from some of the basalt-free experiments. We could not detect a  $\text{Cr}^{+6}$  absorption in any of the basalt-containing experiments. This suggests that basalt was indeed controlling oxygen fugacity in the solutions at a relatively low value. This is an example of a type (1) interaction and has important consequences for radionuclide migration as we show below.

#### Oxygen Buffering by Basalt

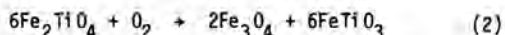
The above evidence strongly suggests that one or more components of the basalt are sufficiently reactive to participate in reactions that produce an iron-titanium oxide phase in a short time at 200° to 300°C. The most probable reactive phases in the basalt are the magnetite-ulvöspinel and the interstitial glass. The magnetite is 85 mole% ulvöspinel and contains about 59 wt% FeO. The glass contains about 1.2 wt% FeO. Modal abundances are 40-60% for glass and 1-10% for magnetite.<sup>5</sup>

Choosing intermediate values of 50% glass and 5% magnetite would result in a basalt containing about 3.5 wt% FeO available for reaction. The FeO contained in pyroxene crystals is probably not available for reaction over short time spans as evidenced by the observed lack of reaction in our experiments. The maximum amount of dissolved oxygen in groundwater may be taken as the value for air-saturated surface water. This value, about 7.5 ppm by weight at 25°C, is undoubtedly a 'worst-case' estimate as subsurface water is seldom air-saturated. The total reducing capacity in the basalt is given by the conversion of FeO in glass and magnetite to hematite ( $\text{Fe}_2\text{O}_3$ ):



From that reaction we calculate that 1 kg of basalt could reduce 4g of dissolved oxygen, equivalent to 500 kg of air-saturated groundwater. However, some of the reduction process results in the formation of hematite and in that case the oxygen fugacity would be fixed near the magnetite-hematite buffer, a relatively high value. Much lower values of oxygen fugacity would occur before hematite was formed. This situation would be approximated by the

reaction:<sup>6</sup>



which requires four times as much basalt to reduce the same amount of oxygen. In this case 1 kg of basalt would reduce 1g of dissolved oxygen, equivalent to about 130 kg of air-saturated groundwater. The original magnetite-ulvöspinel in the basalt was probably formed under conditions where the oxygen fugacity was near quartz-fayalite-magnetite (QFM) or Ni-NiO. Thus during the initial stages of interaction of groundwater with basalt in a mined repository, the oxygen fugacity of the system would be at similar values (QFM or NNO). However, because the silicate minerals in the basalt do not appear to be reacting at 200° or 300°C, the oxygen fugacity will not be 'buffered' in a strict sense and will rise gradually as ulvöspinel is converted to magnetite and ilmenite by reaction with circulating groundwater. The ambient oxygen fugacity would then depend on the amount of dissolved oxygen in the circulating groundwater and on the rock:water ratio, but would remain at values within an order of magnitude of NiNiO until the ulvöspinel content of magnetite falls below 10 to 20 mole%.<sup>7</sup> At this point magnetite (containing 10 to 20% ulvöspinel) probably oxidizes to rutile plus a titanium-poor magnetite and oxygen fugacity lies mid-way between the NiNiO and hematite-magnetite buffers. Finally magnetite oxidizes to rutile plus hematite.<sup>8</sup>

In the worst case situation of air-saturated groundwater, oxygen fugacity will remain within an order of magnitude of the Ni-NiO buffer until a water:rock ratio of 100:1 (by mass) has been exceeded. At lower water:rock ratios the ambient oxygen fugacity will be low enough to keep uranium in the relatively insoluble tetravalent oxidation state.

Jacobs and Apted<sup>9</sup> have proposed that oxygen fugacity in groundwater is controlled primarily by reaction with the interstitial glass in basalt. Our data are consistent with their hypothesis, but reaction with magnetite-ulvöspinel is also indicated by our experiments, and provides a greater capacity to control oxygen fugacity.

From the data and discussion presented in this paper, we conclude that the best type of basalt for use both as back-fill and country rock in a repository will be one with a high modal amount of titanium-rich magnetite and interstitial glass.

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