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BACKFILL BARRIERS: THE USE OF ENGINEERED BARRIERS BASED ON GEOLOGIC MATERIALS TO ASSURE ISOLATION OF RADIOACTIVE WASTES IN A REPOSITORY

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INTRODUCTION

The disposal of high level radioactive wastes by deep geologic burial involves questions that cannot be answered on the basis of human experience. Assurance that an underground repository will provide adequate isolation of wastes from the biosphere for unprecedented periods of time will have to be based upon predictive modeling (NRC, 1979). Verification of the performance of a repository by in-situ measurement is not practicable over the long term (NRC, 1979). Geologic media are inherently variable and their properties can rarely be determined in-situ with the degree of certainty and confidence perceived to be necessary for disposal of wastes. Therefore, uncertainties must exist in the analysis and prediction of the performance of a repository, the magnitude of which increases with time. The practical and the theoretical difficulties in resolving this problem are very great; large amounts of time and effort could be devoted to improving methods for determining properties and conditions and their variability in-situ with no guarantee of success. Any other means by which uncertainties in the prediction of the performance of a repository may be diminished are, therefore, of great potential importance.

A means by which these uncertainties may be diminished is through the use of engineered barriers. Engineered barriers may be made from materials known to exist geologically, the properties of which are, or can be, fully understood in the long term. The control exercised over engineered barriers should resolve the questions of variability and uncertainty, so that these will be less than those inherent in the geologic media within which a repository is developed. Thus, predictions concerning the performance of engineered barriers should be relatively precise.

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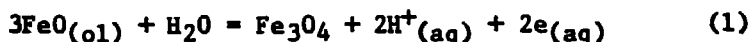
Accordingly, it becomes important to identify geologic analogs of materials that may be used as barriers, and to assess the potential of such materials to provide adequate assurance of the performance of a repository in the long term, regardless of the geologic media.

Ringwood (1978) and others already are addressing the concept of synthesizing waste forms consisting of minerals similar to those known to occur stably in nature. This concept can be expanded to include the canister, overpack and backfill. Copper, iron, nickel-iron alloys, and nickel-iron-cobalt alloys occur in nature. Fyfe (1977) has investigated copper as a canister material, and this has been incorporated in the design of a repository in Swedish bedrocks (KBS). Another canister material proposed by Fyfe (1977) is a nickel-iron alloy known to occur naturally in some ultrabasic rocks.

In this paper, a preliminary assessment is made to show that canisters fabricated of nickel-iron alloys, and surrounded by a suitable backfill, may produce an engineered barrier where the canister material is thermodynamically stable with respect to its environment. As similar conditions exist in nature, the performance of such systems as barriers to isolate radionuclides can be predicted over very long periods, of the order of 10^6 years.

ORIGIN AND OCCURRENCE OF IRON AND NICKEL-IRON ALLOYS IN NATURE

Iron and nickel-iron alloys have been observed on many occasions as secondary alteration products resulting from the serpentinization of ultrabasic rocks, particularly dunites and peridotites. These rocks consist primarily of olivine, $(Mg,Fe)_2SiO_4$ and enstatite, $MgSiO_3$. They alter in the presence of water to antigorite or chrysotile, $Mg_3Si_2O_5(OH)_4$, together with smaller amounts of tremolite, $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$, and occasional diopside, $CaMgSi_2O_6$. The range of temperatures over which these processes take place has been estimated to vary between $25^\circ C$ to $500^\circ C$ (Wenner and Taylor, 1973). During alteration of ultrabasic rocks, the coexisting aqueous phase becomes extremely alkaline, particularly in the absence of dissolved carbonates. The pH of groundwaters emanating from partially serpentinized bodies ranges from 11.2 to 12.0 (Barnes and O'Neil, 1969). In the presence of carbon dioxide, the pH is lowered, but is still alkaline (pH = 7.8-9.0), (Barnes and O'Neil, 1969). The ferrous iron released from the decomposing olivine under these conditions is immediately precipitated as an oxide, usually magnetite, driving down the oxidation potential:



Because the FeO component of the olivine and enstatite is usually less than 10 weight percent, the proton production is offset easily by hydroxyl ion production resulting from hydrolysis by the magnesia component of these two minerals:



The uptake of electrons can be accomplished only through the reduction of the metal ions, sulfur, carbon dioxide, nitrogen or water. Ultrabasic rocks contain between 5 and 10 weight percent FeO, and small amounts of nickel, (0.2 percent) (Nickel, 1959; Azais et al., 1968).

Field observations indicate that reduction of iron and nickel occurs with the formation of α Fe (kamacite), γ (Fe,Ni) (taenite) with a composition of approximately Ni_2Fe , and possibly Ni_3Fe , commonly referred to as awaruite. Associated with these metallic phases in serpentinite are native copper, pyrrhotite or troilite, FeS; heazlewoodite Ni_3S_2 ; millerite, NiS; and pentlandite, $(Ni,Fe)_9S_8$. Evidence for thermodynamic equilibrium among these phases is as usual, inconclusive.

This summary description and interpretation of the genesis of nickel-iron alloys during the alteration of ultrabasic rocks must be followed by an evaluation of these natural alloys as a part of an engineered barrier for the isolation of wastes. The next step involves a closer examination to identify any deficiencies in knowledge that may hamper the adequate determination of the use of such an engineered barrier. Such an examination includes: a thermodynamic evaluation of the chemistry of the processes taking place; field studies to obtain estimates of the reaction rates and chemical fluxes in the system; field and laboratory studies to determine the physical properties of serpentinite, and design and testing to establish whether or not practicable barrier systems can be engineered replicating the natural analog.

THERMODYNAMIC ANALYSIS OF THE STABILITY OF NICKEL-IRON ALLOYS

The preliminary analysis presented below suggests that mineralogical and field observations published in the literature are essentially consistent with theoretical predictions, and that chemically, an engineered barrier could be constructed consisting of a nickel-iron canister surrounded by a backfill of olivine and serpentine.

Eh-pH Conditions Arising from the Alteration of Peridotite

To establish whether or not Eh-pH conditions could be attained that are compatible with the formation of iron-nickel alloys and consistent with field observations of groundwaters issuing from dunites and peridotites, the course of chemical reaction of a hypothetical ultrabasic rock (consisting of 40 mole percent olivine, 40 mole percent enstatite and 20 mole percent diopside, reacting with almost pure water at 25°C and one atmosphere pressure) has been simulated, Figures 1 and 2. Details of this type of simulation and the thermodynamic data used have been given by Helgeson et al., (1970).

The phases formed during the alteration of the ultrabasic rock are listed in Figure 1. All except talc and fayalite persist until native iron is formed at the termination of the simulation.

The phases produced are generally consistent with those observed in the field (Barnes and O'Neil, 1969). Figure 1 shows that the alteration leads to a pH of 11.25 and Eh of -700 millivolts S.H.E. upon formation of native iron. A dissolved hydrogen concentration of approximately 34 ppm is attained at that point.

Figure 2 illustrates the variation of the principal ions of magnesium, silica, calcium and iron in solution, as a function of pH. Comparisons are made with reported ranges of values of these elements in groundwaters of the Ca^{2+} - $(\text{OH})^-$ type issuing from dunitites and peridotites (Barnes and O'Neil, 1969). In general, the theoretical results compare favorably with chemical analyses of groundwaters.

The significance of this simulation is that the conditions of Eh-pH necessary for the formation of metallic iron can be achieved during the alteration of ultrabasic rocks.

Stability Relations Between Nickel-Iron Alloys and Coexisting Sulfides in the Presence of Water

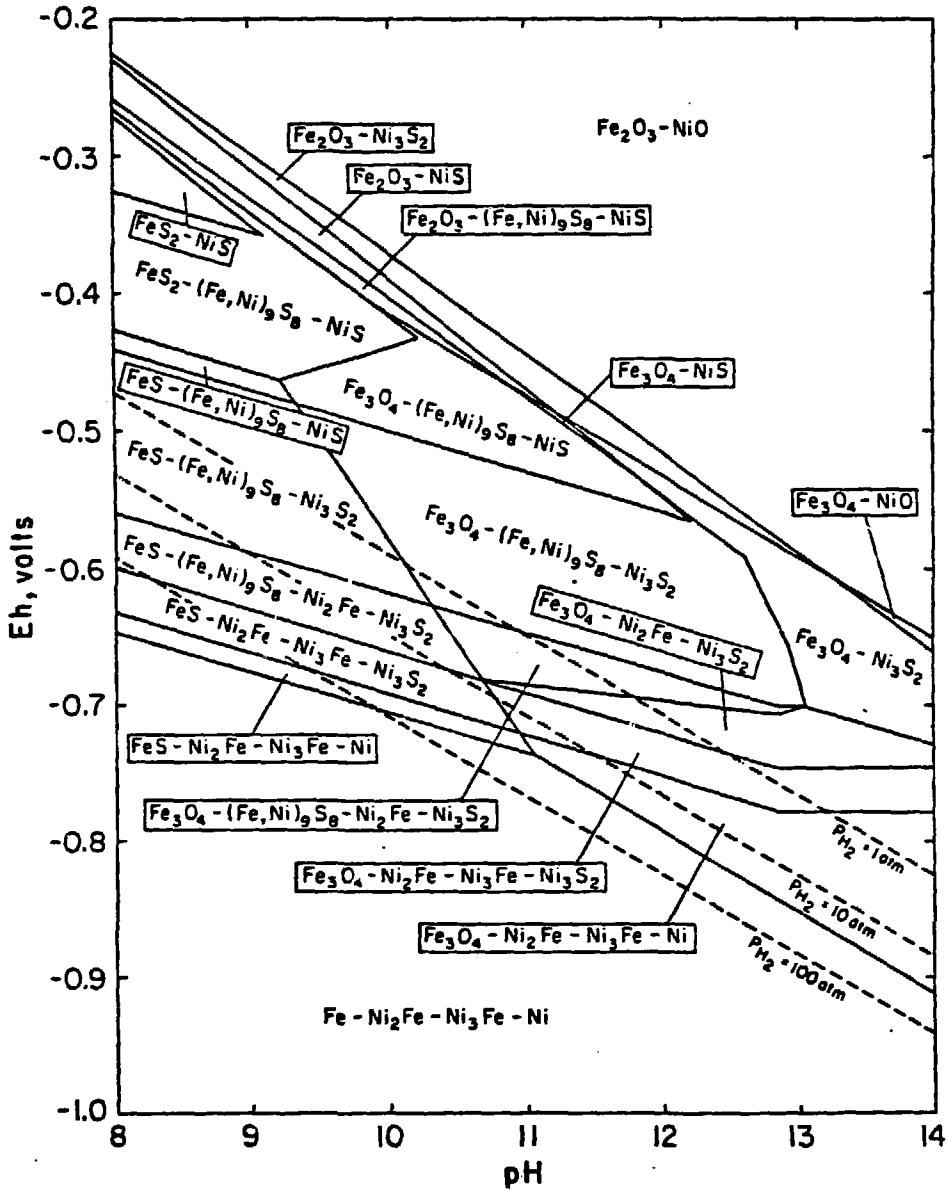
The free energy data needed to calculate the stability relations are incomplete so both estimates and approximations must be made through a graphical evaluation of phase relations in the system Fe-Ni-S at 25°C and one atmosphere using known thermochemical data (Garrels and Christ, 1965; Robie, *et al.*, 1978; Wagman *et al.*, 1969). Those phases for which free energy data are not known have been estimated from experimental and field information.

The relations between metallic and sulfide phases, and coexisting oxides in the presence of water have been examined through construction of an Eh-pH diagram for the system Fe-Ni-S-O-H, at 25°C and one atmosphere, covering the region of interest, Figure 3. The stability fields of various metal alloys, sulfides and oxides are located within the ranges Eh -1000 to -200 millivolts S.H.E., and pH 8 to 14. The total sulfur activity has been set at 10^{-6} molal in concordance with field conditions (Barnes and O'Neil, 1969).

The stability fields of coexisting phases are largely consistent with both laboratory investigations and field observations by numerous investigators. However, taenite $\gamma(\text{Fe},\text{Ni})$ may be metastable below 350°C (Goldstein, 1973). They demonstrate further that regions can be attained where nickel-iron alloys are thermodynamically stable, particularly when: the pH is greater than 10; sufficient $\text{FeO}(\text{ol}), (\text{en})$ is present to produce the desired reducing conditions; total sulfur activity is below 10^{-6} molal, and relatively high concentrations of dissolved hydrogen, that is, up to 0.1 molal (200 ppm) exist.

FURTHER FIELD AND LABORATORY STUDIES

Field studies of nickel-iron alloys in altered ultrabasic rocks provide incidental observations that bear on their use as an engineered barrier, particularly as they relate to the thermodynamic stability of the metal canister, and the behavior of the backfill in the event that



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Figure 3. A preliminary Eh-pH diagram of part of the system Fe-Ni-S-O-H at 25°C and 1 atmosphere and $S = 10^{-6}\text{m}$.

a canister leaks. The geochemical environment within an altering ultrabasic rock is different usually from surrounding host rocks, causing chemical potential gradients to be set up. Petrological, geochemical and physical studies, conducted from the interior to exterior of an ultrabasic body to establish the extent of chemical migration and conditions of Eh-pH during alteration, yield semi-quantitative estimates of chemical migration rates over time spans up to millions of years (Chamberlain et al., 1965; Azais et al., 1968).

Several physical aspects to the use of altered ultrabasic rocks as an engineered barrier merit further study. The stoichiometry of reactions proceeding during serpentinization of ultrabasic rocks has not been resolved (Turner and Verhoogen, 1960), so that the volume change during alteration is not known. A backfill that swells during alteration would be advantageous. Little is known about the porosity, permeability or rheologic properties of partially or completely serpentinized rocks, but serpentine can flow plastically, a desirable property.

CHEMICAL BEHAVIOR OF ALTERING SERPENTINITE TO RADIONUCLIDE MIGRATION

Although canisters should not leak during the first 1000 years in consideration, the migration of radionuclides through the serpentinite matrix of the backfill must be examined. Cesium would be mobile, and unless either chrysotile or antigorite adsorb $\text{Cs}^+(\text{aq})$ a secondary barrier would be necessary to contain it, such as some natural zeolite that is stable under alkaline conditions.

It is clearly beyond the scope of this paper either to explore the many other fascinating concepts regarding a nickel-iron alloy canister - serpentinite backfill barrier system or to advocate it as the best system. However, further evaluation is merited if only because a clear connection exists with an engineered barrier system, and because this or some other system may provide predictable long term isolation of radionuclides.

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