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Reduction of Sulfate by Hydrogen in Natural Systems: A Literature Review

J. J. Mahoney
D. M. Strachan

January 1987

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INTRODUCTION

The reduction of inorganic sulfate to sulfide in the near-field environment of a salt repository may be important because of the influence of the sulfide ions on the corrosion performance of the container material. Based solely upon thermodynamic arguments and the hydrogen fugacities anticipated in the vicinity of the waste package, inorganic sulfate should be reduced to sulfide by hydrogen gas. However, the kinetics of the sulfate reduction reaction appear to be sluggish in the absence of bacteria and may limit the sulfide concentrations to values that have an inconsequential effect on container corrosion. This report describes some of the literature related to the kinetics of this reaction, but does not review the literature concerning the bacterial reduction of sulfate. The annual report from Task 06 of the Waste Package Program will discuss the effect of microbial sulfate reduction on the corrosion of the container, but will not discuss the mechanisms or the kinetics involved. In general, the review presented here will concentrate on experimental studies that are related to geologic environments. Other reports related to non-geologic systems are discussed briefly.

A literature search was performed using the key words "sulfate", "sulfide" and "reduction". Although biological references were eliminated, the majority of the articles that were identified and were related to natural systems still described bacterially mediated near-surface reactions. Bacterially controlled reduction of sulfate appears to be better understood than inorganic reduction. The action of bacteria is generally much more rapid than the inorganic reaction. Westrich and Berner (1984) state that the reduction rate of seawater sulfate to sulfide by bacteria in marine sediments can vary over eight orders of magnitude. This large variation in rate is an indication of the importance of bacteria in the low-temperature reaction. Moreover, different pathways are available for this reduction reaction when sulfate reducing-bacteria are present.

Conditions anticipated in the waste package environment include a maximum temperature of around 150°C, reducing to less than 100°C after 100 years (ONWI 1986). Hydrogen pressures, though difficult to estimate because of diffusion into the surrounding salt, are not expected to exceed 100 atmospheres and values below 10 atmospheres may be more realistic. Solutions are basically high-ionic-strength brines. Based upon the composition of PBB1, a sulfate concentration of up to 3840 mg/L is possible. This solution is mainly a sodium and chloride dissolution brine. The inclusion brine, PBB3, has a sulfate concentration of 250 mg/L and contains more Mg, Ca, and K and much less Na than PBB1. however, the range in sulfate concentration for the inclusion brines is from 1 to 20,000 mg/kg of solution (Roedder 1984a, 1984b; U.S. Department of Energy 1984) These two brines , PBB1 and PBB3, bracket the expected range of sulfate concentrations. Sulfide concentrations in both of these brines are very low, probably less than 1 mg/L.

This work was conducted by the Pacific Northwest Laboratory (PNL) Waste Package Program (WPP) in support of the Salt Repository Project as part of the FY 1987 WPP Technical Program Plan (TPP), WBS 0803, "Hydrogen Effects on Near Field Environment".

SUMMARY OF RESULTS

The results of this literature search indicate that the reduction of sulfate by hydrogen gas can occur in nature, but that temperature appears to be a key factor in the rate of this reaction. At temperatures below 200°C, the rate of reaction appears to be extremely slow. This reaction is also influenced to some extent by pH. At low pH the rate of reaction is faster than at high pH. The solution composition also influences the reaction rate; the most recent research available (Yanisagawa 1983) suggests that the concentration of sulfide in solution influences the rate of this reaction. The reduction reaction appears to proceed through a thiosulfate intermediate, so the presence and distribution of other sulfur species will influence the reaction rate. If the reaction mechanism proposed by Yanisagawa is correct, then higher concentrations of sulfide will result in faster rates of sulfate reduction. In conclusion, the reduction of sulfate by hydrogen to form significant amounts of sulfide is a function of temperature, sulfate and sulfide concentration, pH, and solution composition. The rate of this reaction appears to be very slow under the conditions anticipated in the repository, but given the length of time required to maintain the integrity of the containers (300 to 1000 years) and the unusual solution compositions present, a better understanding of the reaction mechanism is needed.

REVIEW OF SPECIFIC ARTICLES

REDUCTION OF SULFATE BY HYDROGEN

A paper by Malinin and Khitarov (1969) appears to be one of the earliest reports involving evaluation of sulfate reduction under hydrothermal conditions. The authors indicate that the reduction of sulfate in solutions of $ZnSO_4$ by H_2 to form ZnS can occur, but that the reaction is strongly influenced by temperature. They report that reduction occurred at temperatures above 250°C, and was very intense at 350°C. At temperatures of 200°C and below, no reaction was noted, even under high H_2 pressures.

In their research, testing involved placing solutions into chrome-nickel steel autoclaves lined with Teflon(a) or platinum. Hydrogen gas was then added to the head space in the vessel at a controlled pressure. The autoclaves were heated up to their operating temperature. At the end of the experiment, the autoclaves were then rapidly cooled and sampled. Experiment duration was up to 140 hours. Starting pressures of hydrogen varied from 0 atm to 185 atm of hydrogen. The concentration of $ZnSO_4$ varied from 0.003N to 1.38N. A table containing selected conditions and results from these experiments is included in the Appendix. The difference in sulfate concentration from the initial concentration was used as the main criterion to evaluate the extent of the reaction. Changes in the pressure of hydrogen and the presence of ZnS were also noted in those experiments where reduction was observed. These pressure changes provide additional evidence on the nature of the reaction.

The authors concluded that, "At temperatures below 200°C reduction of sulfates is extremely difficult and is probably not realized in nature, for it is not likely that either the concentration of the sulfate or the pressure of hydrogen can be as high under natural conditions as in our experiments. At temperatures above 200°C reduction occurs rather rapidly and may be quite intensive.... If sufficiently high temperatures are not reached, sulfates may

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(a) Teflon is a registered trademark of E.I. duPont de Nemours.

remain stable for long periods of time even if the partial pressure of hydrogen is considerable."

The Malinin and Khitarov paper is incomplete because it does not include any discussion of reaction mechanism or the role that the formation of ZnS may have on the reaction. The presence of Zn^{2+} in these solutions causes the precipitation of ZnS, which results in the nearly quantitative removal of sulfide from solution. This results in a different equilibrium concentration of sulfate and sulfide compared to an experiment in which sulfide did not precipitate. Thus, the presence of Zn^{2+} in these solutions would cause the reduction to proceed more toward completion. Although the reaction is favored by the addition of Zn^{2+} and should result in more sulfate reduction, its presence may slow the rate of reaction. Looking ahead to one of the reaction mechanisms proposed by other researchers, one finds that a low H_2S concentration should shift the first (fast) reaction to keep more reactants. This may result in a decrease in the reduction kinetics relative to an experiment in which there was no H_2S control. As described later, several researchers indicate that the initial reduction of sulfate is influenced by the initial concentration of H_2S; high concentrations of sulfide enhance the reaction rate. If the H_2S is removed by the formation of ZnS, then the reduction reaction may be retarded relative to an alternate method in which the H_2S was allowed to increase.

Another shortcoming in the Malinin and Khitarov paper is a result of the short duration of the experiments. The longest experiment ran for 140 hours. Most of the experiments that were performed at temperatures of 240°C or below operated for less than 70 hours. The combination of low temperatures and short experiments would result in less reaction. Longer reaction times may have helped to determine the rate at lower temperatures.

Spirakis (1981) uses the conclusions provided by Malinin and Khitarov (1969) to explain the formation of uranium deposits. Spirakis states that as sulfate-bearing solutions are cooled, they become more reducing because sulfide is an effective reducing agent at low temperatures, while the sluggish kinetics decrease the effectiveness of sulfate as an oxidant. At lower temperatures, these solutions are capable of reducing U species, which can then precipitate and form uranium deposits. The formation temperatures of these deposits is generally below 200°C. Although Spirakis does not provide any insight into the reaction mechanism of sulfate reduction, he does provide a temperature (200°C), based upon the formation temperature of certain uranium deposits, below which the reduction of sulfate is not considered important in this type of ore deposit environment. The author also states that below 200°C, disequilibrium among sulfur species becomes more evident. This evidence, primarily found in ore deposits, includes discrepancies between the formation temperatures of the ore body as determined from sulfur isotope ratios and from fluid inclusions.

The disequilibrium of sulfur isotopes among the sulfur species, described above, is one of the reasons that ore deposit geochemists have studied the kinetics of sulfate reduction. A thesis by Yanisagawa (1983), Inorganic Sulfate Reduction by Hydrogen and Behavior of Sulfur Isotopes Under Hydrothermal Conditions, provides the most recent results on the reduction of sulfate by hydrogen, and also provides some data on the isotope equilibrium reaction. All experiments were performed at 300°C and at 100 MPa (1000 atm) pressure in Dickson autoclaves. The results indicate that the reaction can be divided into three periods: a waiting (induction) period, a period of rapid reaction, and a final period where the reaction occurs at a slower rate. Experiments to evaluate the influence of pH were also conducted. The results indicate that the reduction reaction proceeds faster when the pH is below 3.

The author suggests that a model that utilizes thiosulfate as an intermediate reaction product appears to fit the results. Because the reduction rate is governed by H_2S concentration during the initial induction period and by H^+ concentration in the later stages of the reaction, the author states that HSO_4^- and H_2S react to produce $HS_2O_3^-$. Hence the induction period is needed to build up the concentration of the reaction intermediate, thiosulfate, and this requires a significant sulfide concentration. The thiosulfate species is subsequently reduced by H_2 to form H_2S and HSO_3^-, and the hydrogen sulfite,

(HSO_3^-) molecules combine to form sulfate and HS^-. The three reactions in this model are

$$HSO_4^- + H_2S \xrightleftharpoons{K} HS_2O_3^- + H_2O \qquad \text{(fast)} \tag{1}$$

$$HS_2O_3^- + H_2 \xrightarrow{k} HSO_3^- + H_2S \qquad \text{(slow)} \tag{2}$$

$$4HSO_3^- \rightarrow 3HSO_4^- + HS^- \qquad \text{(fast)} \tag{3}$$

The first and last reactions are believed to be extremely fast while the second reaction, the reduction, is believed to be very slow and therefore is the rate determining step.

Yanisagàwa then provides a general form for the rate law that agrees with this model:

$$\frac{d(\Sigma SO_4^{2-})}{dt} = k(HS_2O_3^-)^n\ (H_2)^m \tag{4}$$

This rate law is then rewritten to show the dependence of this rate on the HSO_4^- concentration:

$$\frac{d(\Sigma SO_4^{2-})}{dt} = k'(HSO_4^-)^n\ (H_2S)^n\ (H_2)^m \tag{5}$$

where n = 0.6 and m = 0. The author provides values for the rate constant, k, as a function of pH. The significance of the value of n is not explained in the thesis except that it appears to be similar to the value obtained from an evaluation of pH and the half-life of the reaction. The value of m appears to be zero in the range of conditions (0.2-0.4 moles/L of H_2) used for these specific experiments. Calculations with m = 1 were also performed; the results appear to be similar to the m = 0 calculations. The discussion in the thesis is vague about this point. The reasons why a zero order was finally selected for H_2 dependence are not clear because the author apparently used m = 1 when calculating the curves of Figure 21 in his paper.

The concentration of H_2S controls the change from the waiting period to the rapid reaction period. At levels below 2 mmole/L H_2S, the reaction is slow; at higher concentrations, the reaction proceeds at the fast rate. The pH dependence of the faster rate can be related to the concentration of HSO_4^- ions, which are directly related to pH. The author also states that, because the concentration of S^{2-} in nature tends to be very low because of pyrite formation and because levels above 2 mmole/L H_2S are required to initiate significant amounts of sulfate reduction, reduction of sulfate to sulfide by H_2 is not likely in natural systems. The addition of Zn^{2+} in the experiments performed by Malinin and Khitarov (1969) would control the total sulfide level by the precipitation of ZnS in a manner analogous to the formation of pyrite described by Yanisagawa.

Because all of the experiments by Yanisagawa were performed at 300°C, there is no information as to the importance of temperature in these experiments. But based on his Table 2, up to 185 hours were required for reduction of half of the sulfate (50 mmole/L to ≈25 mmole/L). Another 2000 hours were required for the remaining sulfate to change its concentration by half again (from 25 mmole/L to ≈13 mmole/L). This later reduction reaction occurred in solutions with much higher pH values (calculated to be around 7 at 300°C) than during the first 200 hours. These great differences in half-lives are probably not caused by changes in the abundance of sulfur species resulting from the reduction reaction as much as by the change in the distribution of these sulfur species as a result of the change in pH.

This research appears to be incomplete and raises more questions than it answers. One example is in the way the author used several additional models to fit his results from experiment one. These models are:

$$\frac{d(\Sigma SO_4^{2-})}{dt} = k\ (HSO_4^-)^n\ (H_2S)^n\ (H_2)^n \qquad \text{(model 2)} \qquad (6)$$

$$\frac{d(\Sigma SO_4^{2-})}{dt} = k\ (HSO_4^-)^n \qquad \text{(model 3)} \qquad (7)$$

$$\frac{d(\Sigma SO_4^{2-})}{dt} = k(H^+)^n \qquad \text{(model 4)} \qquad (8)$$

$$\frac{d(\Sigma SO_4^{2-})}{dt} = k\ (\Sigma SO_4^{2-})^\alpha\ (\Sigma S^{2-})^b\ (H^+)^{0.6} \qquad \text{(model 5)} \qquad (9)$$

The author states that the results from these models had the same tendency as those obtained with model 1. No additional information was provided about the values used as exponents to obtain these fits. We assume that n maintains its value around 0.6 for models 2 through 4. The values of α and b in model 5 are not given. The fact that several models all fit the results indicates that the author does not have any model that uniquely fits the data from this experiment. At best, all of the models appear to describe the distribution of sulfur species as a function of pH. The significance of the rate constants in the later models is not discussed. Thus, we are forced to assume that the same rate constants are used in all five of the models. Another problem is that H_2 does not appear explicitly in any of the rate expressions. We suggest that this may be the result of buffering caused by the gas phase, which may also result in the narrow range of values for the amount of gas dissolved in the test solutions throughout the experiments.

If this is the case, then a series of experiments over a wider range of gas concentrations would resolve this issue.

The problems with the rate laws and the lack of apparent reasons for the non-integral orders (except for some pH relationships) may stem from the selection of one experiment upon which most of this model is based. This particular experiment covered a pH range from 3 to 7 over the first 200 hours. Changes in the rate of reaction are a function of pH, and the model used may not have been sensitive enough to correctly factor this dependence out of the rate law. The method used to perform the calculations was not described. Another shortcoming with the report is the apparent use of a set of rate constants that were tabulated as a function of pH. The author's Table 15 contains these constants but how they were incorporated into the calculations is unknown. Overall, conclusions drawn from this paper, and in particular those conclusions related to rate laws and reaction mechanisms, should be used with some caution.

REDUCTION OF SULFATE IN SEAWATER

Shanks, Bischoff and Rosenbauer (1981) describe seawater sulfate reduction under hydrothermal conditions. The reductant in this case was Fe^{2+} from iron-bearing minerals, mainly fayalite. The authors indicate that reduction was rapid at temperatures of 350°C, and that at 250°C the reduction was detectable and produced dissolved amounts of H_2S, but solid reactions were slight. At 200°C, dissolved H_2S was not detected even in experiments that were operated for up to 219 days ($\approx$ 5200 hours), but mass balance calculations suggested that a small amount of pyrite may have formed.

Similar experiments by Mottl, Holland and Corr (1979) indicated that "the proportion of seawater sulfate which was reduced in the experiments with a water/rock ratio of one varied from 5-10% at 300°C to >95% at 500°C." Experiments lasting in excess of 200 days were performed. Although these temperatures are well above anticipated repository temperatures, the paper does indicate the significance of temperature effects on this reaction.

In both of these papers, pyrite was identified as a product, but sulfate was also reduced. This suggests that the conclusion by Yanisagawa -- the lack of significant sulfate reduction caused by the low concentrations of sulfide, as a result of pyrite formation -- may require additional evaluation. This evidence could even be used to suggest that the model proposed by Yanisagawa is incorrect, particularly about the role of sulfide in the reaction mechanism.

Another important aspect of this area of research related to the reduction of sulfate involves work described briefly by Yanisagawa (1983). He states that work performed by Takenaka (1981) indicates that ferrous iron from minerals can reduce H_2O to produce hydrogen. This hydrogen is then capable of reducing the sulfate. The specific details, such as temperature and solution composition, are lacking but Yanisagawa indicates that in Takenaka's experiments, hydrogen was observed. The works of Mottl, Holland and Corr (1979) and Shanks, Bischoff and Rosenbauer (1981) do not suggest that the reaction between Fe^{2+} and water has been observed directly in their experiments, but their discussion of mechanisms is limited.

REDUCTION OF SULFATE BY ORGANICS

The use of sulfate to oxidize organic molecules such as p-xylene is discussed in a paper by Toland (1960). The author reports that temperatures between 300 and 350°C were necessary to obtain significant reaction rates. Below 300°C, sulfate reactions were extremely slow "even though the organic compound may be capable of oxidation by other forms of sulfur under milder conditions." Reaction between H_2SO_4 and H_2S to form thiosulfate appears to be required prior to the reduction. This reaction is similar to that suggested by Yanisagawa (1983). This paper is not directly relevant to a salt repository, but it provides additional support of the temperature dependence of sulfate reduction and some insight into the "history" of the reaction mechanism. The mechanism described by Yanisagawa (1983), which uses a thiosulfate intermediate was probably derived from Ohmoto and Lasaga (1982), and both mechanisms appear to be related to the mechanism used by Toland in this paper.

A paper by Kiyosu (1980) describes results of reactions between dextrose and sulfate under hydrothermal conditions. This research was conducted to evaluate the role of organic substances in the reduction of sulfate. The author reported that, at temperatures above 250°C, reduction of sulfuric acid was observed. Temperatures greater than 300°C were required before the reduction of sodium bisulfate and sodium sulfate occurred. The author concluded that the reduction rate depends upon temperature, pH, and sulfate species. He also observed that the reduction of sulfate "seems to be a first-order reaction."

The paper by Kiyosu was unclear on whether the rate dependence caused by the variation in species was real or was actually caused by the differences in pH. Also, the author should have stated that the rate is first order in sulfate. By not specifying whether the rate is first order overall or only first order with respect to sulfate, and by using different rate constants for the three different experiments some confusion resulted. The rate constants for the three different experiments were different. This is probably a result of a pH effect on the rate law. If the pH effect is factored out of the rate constant, the overall reaction order would be greater than first order because the rate law would contain H^+ to some power. Under these conditions ($\approx$0.19 mole/L of sulfate), no evidence of an induction period was noted. The paper also provided some additional information about reactions with H_2. The author stated, "Although molecular H_2 was formed by thermal decomposition of dextrose at temperatures lower than 300°C, reduction of sodium sulfate solution did not occur." No additional discussion on this topic was provided. It should be remembered that this experiment was performed at the highest pH of the three experiments. The rate of reaction, in this high pH experiment, was significantly slower than in the other two experiments.

DISCUSSION OF PAPERS RELATED TO SULFATE REDUCTION

All of the papers previously discussed collectively indicate that there is a significant temperature dependence in the reduction of sulfate by a variety of reductants. Most of the researchers indicate that temperatures in excess of 250°C are required for the reaction to proceed at measurable rates.

Barton (1984) discusses inorganic sulfate reduction in a very simple manner. Because the sulfur atom in a sulfate molecule is shielded from its environment by four tetrahedrally coordinated oxygen atoms, the sulfur does not "see" the redox conditions as easily as a more poorly shielded redox species. Bacteria can open up the tetrahedra by means of specific enzymes, but for inorganic reactions, the rates become significant only at temperatures above 300°C. This simple explanation provides a plausible reason for the strong temperature dependence of the reduction of sulfate.

These papers also indicate that some confusion still exists about the exact nature of this reaction. The fractional orders obtained by Yanisagawa (1983) in his proposed rate law do not agree with the rate law obtained by Kiyosu (1980). Another flaw is the failure of Yanisagawa's mechanism to take into account the role of hydrogen.

SULFATE - SULFIDE EQUILIBRIA

A paper by Ohmoto and Lasaga (1982) does not specifically address the reduction of sulfate by hydrogen; but rather, it examines the equilibrium between sulfate and sulfide. The authors were specifically interested in equilibration of the isotopes of sulfur under hydrothermal conditions. The reaction studied involves the mutual oxidation and reduction of two identifiable sulfur atoms. A rate law to determine the extent of equilibration between the two isotopes was derived from the principles of isotope exchange. The rate constant in this equation can be obtained from the rate constant for the chemical equilibration between sulfate and sulfide. A general rate law for this reaction was found to be

$$R = k\ [\Sigma SO_4^-]\ [\Sigma S^{2-}] \qquad (10)$$

where R is the overall rate, k is the rate constant, and the concentrations of sulfide and sulfate are in molal units. The reaction was determined to be strongly dependent upon temperature and pH. The reaction mechanism involved three steps:

$$HSO_4^- + H_2{}^{*}S + H^+ \rightleftarrows H_2{}^{*}S\text{-}SO_3 + H_2O \qquad \text{(fast)} \qquad (11)$$

$$H_2O + H_2{}^{*}S\text{-}SO_3 \rightarrow H_2S\text{-}{}^{*}SO_3 \qquad \text{(slow)} \qquad \text{(sic)} \qquad (12)$$

$$H_2O + H_2S\text{-}{}^{*}SO_3 \rightleftarrows H^+ + H_2S + H^{*}SO_4{}^- \qquad \text{(fast)} \qquad (13)$$

where the sulfur with the asterisk represents the ^{34}S isotope and the other sulfur is the ^{32}S isotope.

The rate of this reaction was found to be strongly dependent upon temperature and pH. An Arrhenius plot of the authors' data indicates that different activation energies are present over different pH conditions. This indicates that several different reaction mechanisms are present over this range of pH. These different reaction mechanisms and, hence, rate laws, are directly related to the distribution of species. These species include the Na-containing ion pairs as well as the species shown above. This influence explains the pH dependence and a dependence on the concentration of Na^+ ions. Because the rate-determining step is unimolecular and basically involves a rearrangement of the thiosulfate molecule, the rate of this reaction is independent of ionic strength (basically activity coefficients). This does not contradict the previous statement about the influence of the Na^+ ion concentration. Rather, the Na^+ ion concentration affects the distribution of sulfate, thiosulfate, and sulfide species and, hence, their concentrations. The ionic strength effects discussed later in the paper apparently deal with the primary salt effect (Gardiner 1969). Because there is no change in the charge of the species involved in the rate-determining step, the activity coefficients of the reactants and the activated complex cancel. Therefore, there is no ionic strength effect.

The Na^+ concentration dependence on the rate law is caused by the existence of a series of parallel reaction paths for the rate-determining step. Each of these steps is controlled by the concentration of a specific thiosulfate species and should have a specific rate constant for that species. Because, in parallel reactions, the rate is determined by the fastest elementary reaction, and because the rate constants should be relatively similar, the rate is governed by the concentration of the dominant thiosulfate species. The nature of this species depends upon temperature, pH, and concentration of other cations in that solution.

Ohmoto and Lasaga provided a table of the minimum time required to reach 90% equilibrium between sulfate and sulfide at a total sulfur concentration of 0.01 mole/kg H_2O. A portion of that table is reproduced below.

Table 1: Length of Time to Reach 90% of Equilibrium

	pH		
T(°C)	≈2	4-7	≈9
350	4.2h	17d	100y
300	15h	140d	1000y
250	3d	4.4y	1.0E+5y
200	20d	90y	1.0E+7y
150	200d	4000y	1.0E+9y
100	10y	4.0E+5y	1.0E+12y
50	500y	2.0E+8y	1.0E+16y

(h = hour, d = day, y = year)

It should be remembered that this table is for the reaction involving the equilibration of the two isotopes of sulfur and is not for the reduction of sulfate. The table demonstrates how temperature and pH can influence the rate of this equilibration reaction.

Ohmoto and Lasaga also discuss the rates of sulfate reduction: "The rates of sulfate reduction or of sulfide oxidation are not the same as the rates of chemical reactions between aqueous sulfates and sulfides which have been discussed in this paper, although they are related to each other." They go on to state that the rate of reaction for this reduction will depend upon three factors: 1) the concentrations of ΣSO_4^{2-} and of the reducing compounds, 2) the temperature, and 3) the pH. The pH dependence is caused by the need to form intermediate valence state compounds such as thiosulfate; the speciation of these compounds depends upon pH. Low pH favors faster rates of sulfate reduction. Temperature effects were also discussed: the authors conclude that the reduction of sulfates may become important in natural systems at temperatures above 200°C. These constraints are very similar to the constraints present in the equilibration of sulfate and sulfide.

LABORATORY PROGRAM

To address the issue of sulfate reduction in a salt repository, a series of experiments has been developed to determine whether the sulfate reduction kinetics are as slow as those found for the low ionic strength solutions discussed above. Once the relative kinetics have been determined in brine both with and without iron and gamma radiation present, a test plan will be developed and used to determine the rate law for sulfate reduction in the salt repository brines. This rate law will be useful in assessing potential container corrosion effects and subsequent performance assessment calculations.

Although a complete test matrix has not been developed, a general approach to the problem has. The program that will be carried out will first address the issue of the SO_4^{2-} reduction kinetics in the solutions of interest to the Salt Repository Project. To accomplish this end, several tests will be performed to demonstrate that the sluggish sulfate reduction kinetics that are reported in the literature are also found for studies conducted in PBB1 and PBB3. These tests will be performed in autoclaves using H_2 gas both with and without metal present. In parallel to the autoclave experiments, similar experiments will be carried out in the presence of gamma radiation. These tests will be used to determine whether there is any increase or decrease in the reduction kinetics due to the presence of a radiation field. Once these initial tests are complete, a more complete set of tests will be designed to determine the correct kinetic rate law for use in the Salt Repository Project. The actual test matrices will be the subject of a future report.

CONCLUSIONS

The general conclusion drawn from this review is that the inorganic reduction of sulfate by hydrogen is strongly temperature dependent, and that the reaction appears to be of little geologic importance below 200°C. The reaction also appears to be influenced by the pH and the concentration of H_2S in the solution. Most of the models that involve reduction of sulfate or sulfate-sulfide equilibrium also appear to involve thiosulfate or other intermediates.

This review has demonstrated several important concepts that need further examination. First is the important role that temperature will play to retard the reduction reaction at the conditions anticipated in the repository. Secondly, how important is the variability in the sulfide and sulfate content in the brines? The reduction reaction as described by Yanisagawa (1983) appears to depend on sulfide concentrations. If the amount of sulfide is very small in the initial composition of the brine, the rate of the reaction will remain slow, but if the concentration of sulfide increases, it will catalyze the reaction.

Thirdly, if the reduction reaction resembles the equilibration reaction as described by Ohmoto and Lasaga (1981), and given the apparent similarity of the mechanisms, particularly the role of thiosulfate, then the concentration of the brine with respect to cations that can complex with sulfide, sulfate, and thiosulfate may be very important. These cations would then influence the rate of sulfate reduction. It is apparent from the current literature that the reduction of SO_4^{2-} by H_2 is extremely sluggish at temperatures less than 200°C. The issue that must be addressed relates to the reduction of SO_4^{2-} by H_2 in highly saline solutions. None of the experiments performed yet are directly relevant to a nuclear repository in salt. This environment will be addressed in the laboratory program.

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