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## **TEST PLAN FOR LABORATORY AND MODELING STUDIES OF REPOSITORY AND RADIONUCLIDE CHEMISTRY FOR THE WASTE ISOLATION PILOT PLANT**

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### **ABSTRACT**

This Test Plan describes laboratory and modeling studies of: (1) the chemistry of brines that could enter WIPP disposal rooms; (2) the effects of anoxic corrosion of metals in steel containers and the waste on the gas and H<sub>2</sub>O budgets of the repository; (3) the effects of microbial degradation of cellulose in the waste on the gas and H<sub>2</sub>O budgets of the repository, the Eh and pH of any brine present, and the chemical behavior of radionuclides; (4) the effects of radiolysis on the gas and H<sub>2</sub>O budgets of the repository; (5) the efficacy and effects of backfill additives proposed to remove or prevent the production of some of the expected gases; (6) the chemical behavior of Pu, Am, Th, and U in WIPP brines; (7) additional development of the EQ3/6 geochemical software package for use in predicting the behavior of silicates and radionuclides in brines.

This Test Plan, current as of early 1990, describes studies of the chemical behavior of the repository as currently designed and the chemical behavior of radionuclides under these conditions. Addenda will discuss additional studies relevant to design modifications, especially reprocessed waste, and chemically hazardous waste constituents.

## CONTENTS

|         |  |    |
|---------|--|----|
| 1.0     | INTRODUCTION . . . . .   | 1  |
| 1.1     | Justification of Laboratory and Modeling Studies . . . . .                               | 1  |
| 1.2     | Brine Chemistry. . . . .   | 2  |
| 1.3     | Anoxic Corrosion . . . . .   | 2  |
| 1.4     | Microbial Activity . . . . .   | 3  |
| 1.5     | Radiolysis . . . . .   | 4  |
| 1.6     | Backfill Additives . . . . .   | 5  |
| 1.7     | Radionuclide Chemistry . . . . .   | 6  |
| 1.8     | Model Development. . . . .   | 7  |
| 1.9     | Hazardous-Waste Chemistry. . . . .   | 7  |
| 1.10    | Experimental Conditions for Laboratory Studies . . . . .                                 | 7  |
| 1.10.1  | Temperature. . . . .   | 8  |
| 1.10.2  | Pressure . . . . .   | 8  |
| 1.10.3  | Water Content. . . . .   | 9  |
| 1.10.4  | Eh and pH. . . . .   | 10 |
| 1.10.5  | Nonradioactive Constituents of TRU Waste . . . . .                                       | 11 |
| 2.0     | BRINE CHEMISTRY. . . . .   | 12 |
| 2.1     | Justification for Laboratory and Modeling Studies. . . . .                               | 12 |
| 2.2     | Sources of Fluids That Could Enter the Repository. . . . .                               | 12 |
| 2.2.1   | Salado-Fm. Brines. . . . .   | 12 |
| 2.2.2   | Castile-Fm. Brines . . . . .   | 13 |
| 2.2.3   | Fluids from Overlying Formations . . . . .   | 13 |
| 2.3     | Preliminary Definition of Standard Brine Compositions. . . . .                           | 13 |
| 2.3.1   | Salado-Fm. Brines. . . . .   | 13 |
| 2.3.1.1 | Chemical Variations in Salado-Fm. Brines. . . . .  | 14 |
| 2.3.1.2 | Collection of Salado-Fm. Brines and Minerals from the WIPP Underground Workings. . . . . | 15 |
| 2.3.1.3 | Preliminary Definition of a Standard Salado-Fm. Brine Composition . . . . .              | 17 |
| 2.3.2   | Castile-Fm. Brines . . . . .   | 21 |
| 2.3.3   | Fluids from Overlying Formations . . . . .   | 23 |
| 2.4     | Description of Laboratory, Modeling, and Field Studies . . . . .                         | 23 |
| 2.4.1   | Quantification of the Causes of Chemical Variations in Salado-Fm. Brines . . . . .       | 25 |
| 2.4.2   | Quantification of Spatial and Stratigraphic Variations in Salado-Fm. Brines. . . . .     | 26 |

CONTENTS  
(Continued)

|         |   |    |
|---------|---|----|
| 2.4.3   | Quantification of Variations in Analytical Techniques Used for Salado-Fm. Brines . . . . .                    | 27 |
| 2.4.4   | Quantification of the Effects of Sampling Artifacts on Variations in Salado-Fm. Brines . . . . .              | 27 |
| 2.4.5   | Simulation of Reactions between Castile-Fm. Brines and Salado-Fm. Brines and Minerals . . . . .               | 28 |
| 2.4.6   | Simulation of Reactions between Fluids from Overlying Formations and Salado-Fm. Brines and Minerals . . . . . | 28 |
| 2.4.7   | Quality Assurance and Safety . . . . .  | 29 |
| 2.5     | Results Expected from Bin-Scale and Alcove Tests . . . . .  | 29 |
| 2.6     | Schedules for Laboratory and Modeling Studies. . . . .  | 30 |
| 3.0     | ANOXIC CORROSION . . . . .  | 31 |
| 3.1     | Justification for Laboratory Studies . . . . .  | 31 |
| 3.2     | Evidence for Anoxic Corrosion. . . . .  | 32 |
| 3.2.1   | Thermodynamic Calculations . . . . .  | 32 |
| 3.2.1.1 | Calculations for Carbon-Dioxide- and Hydrogen-Sulfide-Free Systems . . . . .                                  | 32 |
| 3.2.1.2 | Calculations for Carbon-Dioxide-Bearing Systems . . . . .   | 34 |
| 3.2.1.3 | Calculations for Hydrogen-Sulfide-Bearing Systems . . . . .   | 35 |
| 3.2.1.4 | Calculations for Carbon-Dioxide- and Hydrogen-Sulfide-Bearing Systems. . . . .                                | 37 |
| 3.2.2   | Kinetic Data . . . . .  | 37 |
| 3.3     | Description of Laboratory Studies. . . . .  | 39 |
| 3.3.1   | Quantification of Anoxic Corrosion of Steels at Low Pressures . . . . .                                       | 40 |
| 3.3.2   | Quantification of Anoxic Corrosion of Steels at High Pressures. . . . .                                       | 43 |
| 3.3.3   | Additional Quantification of Anoxic Corrosion of Steels . . . . .   | 44 |
| 3.3.4   | Quantification of Anoxic Corrosion of Other Metals . . . . .  | 44 |
| 3.3.5   | Quality Assurance and Safety . . . . .  | 44 |
| 3.4     | Results Expected from Bin-Scale and Alcove Tests . . . . .  | 45 |
| 3.5     | Schedules for Laboratory Studies . . . . .  | 45 |

CONTENTS  
(Continued)

|         |  |    |
|---------|--|----|
| 4.0     | MICROBIAL ACTIVITY . . . . .   | 47 |
| 4.1     | Justification for Laboratory Studies . . . . .   | 47 |
| 4.2     | Identification of Potentially Significant Microbial Processes. . . . .   | 48 |
| 4.2.1   | Aerobic Respiration. . . . .   | 49 |
| 4.2.2   | Denitrification and Nitrate Reduction. . . . .   | 50 |
| 4.2.3   | Manganese Reduction. . . . .   | 51 |
| 4.2.4   | Iron Reduction . . . . .   | 51 |
| 4.2.5   | Sulfate Reduction. . . . .   | 52 |
| 4.2.6   | Fermentation and Methanogenesis. . . . .   | 53 |
| 4.3     | Estimates of Cellulosics in the WIPP Inventory . . . . .   | 53 |
| 4.4     | Description of Laboratory Studies. . . . .   | 54 |
| 4.4.1   | Stanford Batch Bioassay Procedure. . . . .   | 55 |
| 4.4.2   | Determination of Whether Potentially Significant Microbial Processes Occur. . . . .  | 57 |
| 4.4.3   | Quantification of the Effects of Potentially Significant Microbial Processes on Repository Gas and Water Budgets. . . . .                | 60 |
| 4.4.4   | Quantification of the Effects of Pressure on Microbial Processes That Affect the Repository Gas and Water Budgets Significantly. . . . . | 61 |
| 4.4.5   | Quantification of the Effects of Potentially Significant Microbial Processes on Radionuclide Chemistry. . . . .                          | 61 |
| 4.4.6   | Determination of Whether Microorganisms Are Likely to Survive for Long Periods . . . . .   | 61 |
| 4.4.7   | Quality Assurance and Safety . . . . .   | 62 |
| 4.5     | Results Expected from Bin-Scale and Alcove Tests . . . . .   | 62 |
| 4.6     | Schedules for Laboratory Studies . . . . .   | 62 |
| 5.0     | RADIOLYSIS . . . . .   | 64 |
| 5.1     | Justification for Laboratory Studies . . . . .   | 64 |
| 5.2     | Estimates of Plastics and Rubbers in the WIPP Inventory. . . . .   | 64 |
| 5.3     | Review of the Effects of Irradiation of Plastics . . . . .   | 65 |
| 5.4     | Additional Studies of Radiolysis . . . . .   | 67 |
| 5.5     | Description of Laboratory Studies. . . . .   | 68 |
| 5.5.1   | Quantification of the Effects of $\alpha$ Radiolysis on the Biodegradability of Plastics . . . . .                                       | 68 |
| 5.5.1.1 | Irradiation of Plastics . . . . .  | 68 |
| 5.5.1.2 | Bioassay of Irradiated Plastics . . . . .  | 73 |

CONTENTS  
(Continued)

|       |   |     |
|-------|---|-----|
| 5.5.2 | Determination of the Effects of Waste Compaction, Inundation, and Pressure on the Radiolytic Gas Production Rate. . . . .   | 74  |
| 5.5.3 | Quality Assurance and Safety . . . . .  | 75  |
| 5.6   | Results Expected from Bin-Scale and Alcove Tests . . . . .  | 75  |
| 5.7   | Schedules for Laboratory Studies . . . . .  | 75  |
| 6.0   | BACKFILL ADDITIVES . . . . .  | 76  |
| 6.1   | Justification for Laboratory and Modeling Studies. . . . .  | 76  |
| 6.2   | Description of Laboratory and Modeling Studies . . . . .  | 77  |
| 6.2.1 | Laboratory Study of Backfill Additives . . . . .  | 77  |
| 6.2.2 | Modeling Study of Backfill Additives . . . . .  | 80  |
| 6.2.3 | Quality Assurance and Safety . . . . .  | 81  |
| 6.3   | Results Expected from Bin-Scale and Alcove Tests . . . . .  | 81  |
| 6.4   | Schedules for Laboratory and Modeling Studies. . . . .  | 82  |
| 7.0   | RADIONUCLIDE CHEMISTRY . . . . .  | 83  |
| 7.1   | Justification for Laboratory Studies . . . . .  | 83  |
| 7.2   | Estimates of Radionuclide Speciation and Solubilities. . . . .  | 84  |
| 7.3   | Effects of Other Processes on the Source Term. . . . .  | 87  |
| 7.4   | Estimates of Ligand Concentrations in WIPP Brines. . . . .  | 87  |
| 7.5   | Identification of Potentially Significant Ligands. . . . .  | 92  |
| 7.6   | Description of Laboratory Studies. . . . .  | 93  |
| 7.6.1 | Quantification of the Speciation of Pu, Am, Th, and U in Neutral, Acidic, and Basic Solutions of High Ionic Strengths under Various Redox Conditions . . . . .                    | 94  |
| 7.6.2 | Determination of the Solubilities of Pu-, Am-, Th-, and U-Bearing Solids in Neutral, Acidic, and Basic Solutions of High Ionic Strengths under Various Redox Conditions . . . . . | 99  |
| 7.6.3 | Extension of the Speciation and Solubility Studies to Strongly Basic Conditions . . . . .   | 100 |
| 7.6.4 | Quality Assurance and Safety . . . . .  | 100 |
| 7.7   | Results Expected from Bin-Scale Tests. . . . .  | 100 |
| 7.8   | Schedules for Laboratory Studies . . . . .  | 101 |
| 8.0   | MODEL DEVELOPMENT. . . . .  | 102 |
| 8.1   | Justification for Model Development. . . . .  | 102 |

CONTENTS  
(Continued)

|       |  |     |
|-------|--|-----|
| 8.2   | Description of EQ3/6 . . . . .                                   | 102 |
| 8.2.1 | EQ3NR. . . . .   | 102 |
| 8.2.2 | EQ6. . . . .   | 104 |
| 8.2.3 | Thermodynamic Data and Other Supporting Files. . . . .           | 104 |
| 8.3   | Status of EQ3/6. . . . .   | 105 |
| 8.4   | Description of Additional Development of EQ3/6 . . . . .         | 106 |
| 8.4.1 | Extension of the Pitzer Model. . . . .                           | 107 |
| 8.4.2 | Additional Development of the Hydration-Theory<br>Model. . . . . | 107 |
| 8.4.3 | Quality Assurance. . . . .                                       | 113 |
| 8.5   | Schedules for Additional Development of EQ3/6. . . . .           | 114 |
| 9.0   | REFERENCES . . . . .   | 115 |



TABLES

|     |  |    |
|-----|--|----|
| 2.1 | Comparison of the Compositions of Brines Collected from the WIPP Underground Workings and Preliminary, Standard Brines. . . . .            | 18 |
| 2.2 | Comparison of the Compositions of G-Seep, SB-3, and Previous Standard Brines. . . . .  | 20 |
| 2.3 | Comparison of the Average Compositions of Brines from Reservoirs in the Castile Fm. . . . .  | 22 |
| 2.4 | Comparison of the Compositions of Selected Fluids from Overlying Formations . . . . .  | 24 |
| 7.1 | Previous Estimates of the Concentrations of Four Organic Ligands in Any Brine Present in WIPP Disposal Rooms. . . . .                      | 86 |
| 7.2 | Organic Compounds Identified in the Preliminary Inventory of Nonradioactive Constituents of TRU Waste to Be Emplaced in the WIPP . . . . . | 88 |
| 7.3 | Current Estimates of the Concentrations of 13 Organic and Inorganic Ligands in Any Brine Present in WIPP Disposal Rooms. . .               | 92 |



# 1.0 INTRODUCTION

## 1.1 JUSTIFICATION OF LABORATORY AND MODELING STUDIES

Quantification of repository chemistry is essential for the long-term performance assessment (PA) of the Waste Isolation Pilot Plant (WIPP). Because chemical reactions can produce or consume large quantities of gas and H<sub>2</sub>O, studies of these reactions are necessary to predict their effects on the gas and H<sub>2</sub>O contents of WIPP disposal rooms. The gas and H<sub>2</sub>O budgets could in turn affect room closure rates, the geomechanical properties of their contents, and the likelihood of radionuclide release under undisturbed conditions or in the event of human intrusion. Lappin et al. (1989) provided a preliminary appraisal of the possible effects of gas production and brine inflow on the performance of the repository. Although our understanding is evolving rapidly, a discussion of these effects is beyond the scope of this Test Plan. Various chemical reactions could also affect the Eh and pH of any brine present in WIPP disposal rooms. These parameters in turn will affect: the solubilities of certain gases in the brine; the speciation, solubilities, and sorption of radionuclides; the extent to which radionuclides form colloids.

Predictions of the chemical behavior of the important radionuclides in transuranic (TRU) waste in WIPP brines are necessary to define the source term for radionuclide-transport calculations for the WIPP PA.

Laboratory studies with nonradioactive simulated waste and, in some cases, radioactive simulated waste provide a unique opportunity to develop a mechanistic understanding of repository and radionuclide chemistry. Laboratory studies facilitate quantification of the effects of significant chemical processes under experimental conditions that isolate each process from the effects of other processes, yet are nevertheless realistic. The studies also facilitate quantification of the effects of variations in physicochemical conditions on these processes. The use of simulated waste will greatly simplify quantification of significant chemical processes, but will yield results applicable, at least in most cases, to both contact-handled (CH) and remote-handled (RH) TRU waste.

Modeling studies are necessary to interpret the results of the laboratory studies described herein and the planned bin-scale and alcove tests with CH TRU waste described by Molecke (1990a, 1990b). They are also necessary to extend the results of these laboratory, bin-scale, and alcove tests to other possible repository conditions. If successful, modeling studies would reduce the number of experiments required to quantify the effects of variations in chemical conditions on repository gas and H<sub>2</sub>O budgets, and the chemical behavior of radionuclides.

This Test Plan describes studies of the chemical behavior of the repository as currently designed and the chemical behavior of radionuclides under these conditions. It is current as of early 1990. Addenda and revised versions will discuss: (1) modifications of ongoing studies or additional studies relevant to design-basis conditions; (2) extensions of ongoing studies or additional studies pertinent to design modifications, especially reprocessed waste; (3) extensions of ongoing studies or additional studies applicable to chemically hazardous waste constituents.

Comparison of results from these studies of repository and radionuclide chemistry to results from bin-scale and alcove tests with CH TRU waste (Molecke, 1990a; 1990b) will in many cases provide a test of laboratory and modeling data. Agreement between these results would validate the use of laboratory and modeling data for the WIPP PA. Any significant disagreement would indicate a need for additional studies of repository and radionuclide chemistry, unless modifications to the WIPP design eliminate that need.

## **1.2 BRINE CHEMISTRY**

Laboratory and modeling studies of repository and radionuclide chemistry and bin-scale tests with CH TRU waste (Molecke, 1990a) require the use of realistic WIPP brines of standard composition to reduce the number of experiments and ensure the comparability of experimental results (2.1).

Because the extent to which compositional variations in WIPP brines will affect various chemical processes is still unknown, it is difficult to specify the level of understanding of brine chemistry necessary to predict the long-term performance of the repository.

Brush has identified the fluids that could enter WIPP disposal rooms after they are filled and sealed (2.2), but various studies are necessary to predict the most likely compositions and expected variability of these brines as they enter the repository (2.4).

In lieu of the studies described below, most investigators are using brines collected from the WIPP underground workings (2.3.1.2) for their initial laboratory studies of repository and radionuclide chemistry. Brush has defined preliminary, standard compositions (2.3.1.3) for synthetic Salado- and Castile-Fm. brines for Molecke's (1990a) bin-scale tests with CH TRU waste.

The specific objectives of these laboratory, modeling, and field studies are to: (1) quantify the causes of chemical variations in brines from the Salado Fm. (2.4.1); (2) quantify any spatial or stratigraphic variations in Salado-Fm. brines (2.4.2); (3) quantify the variations caused by differences in the analytical techniques used by the three laboratories analyzing Salado-Fm. brines (2.4.3); (4) quantify the effects of sampling artifacts described in 2.3.1.1 on variations in Salado-Fm. brines (2.4.4); (5) simulate reactions between fluids from the Castile Fm. or overlying formations and Salado-Fm. brines and minerals (2.4.5 and 2.4.6).

Bin-scale tests with CH TRU waste (Molecke, 1990a) will provide information on the chemistry of synthetic Salado- and Castile-Fm. brines after reactions with the contents of the bins (2.5).

## **1.3 ANOXIC CORROSION**

Lappin et al. (1989) estimated that if brine were present in WIPP disposal rooms, anoxic corrosion of steel containers (drums and boxes) and Fe and Fe-base alloys in the waste would produce about 2 moles of H<sub>2</sub> per drum of waste per year for 400 to 500 years, or a total of 900 moles per drum (3.1). Anoxic corrosion is the process of greatest concern from the

standpoint of the gas budget of the repository. It could also consume as much as 200 m<sup>3</sup> of brine per room.

The quantity of H<sub>2</sub>O in the disturbed rock zone (DRZ) available for transport to the waste, either by brine inflow or vapor-phase transport, may prevent the production of 900 moles of H<sub>2</sub> per drum. Absorption of H<sub>2</sub>O by crushed salt and bentonite in the backfill and the possible consumption of H<sub>2</sub>O by microbial activity (4.1) may limit the extent of anoxic corrosion of metals.

Brush has reviewed the evidence for anoxic corrosion (3.2), but it is still unknown whether anoxic corrosion of steels would occur if H<sub>2</sub>O vapor or H<sub>2</sub>O absorbed by backfill materials, but not brine, were present in the repository. The extent to which microbially produced CO<sub>2</sub> will accelerate anoxic corrosion and previously produced H<sub>2</sub> will decelerate anoxic corrosion are also unknown. Finally, the anoxic corrosion rates of other metals are unclear.

The objectives of these laboratory studies are to: (1) quantify anoxic corrosion of steels by brine, H<sub>2</sub>O vapor, and H<sub>2</sub>O absorbed by backfill materials in the presence of N<sub>2</sub> or CO<sub>2</sub> at low pressure (3.3.1); (2) quantify anoxic corrosion of steels by brine, H<sub>2</sub>O vapor, and H<sub>2</sub>O absorbed by backfill materials in the presence of CO<sub>2</sub> or H<sub>2</sub> at high pressures (3.3.2); (3) determine the effects of other factors, such as basic conditions, O<sub>2</sub> concentration, and the presence of the proposed backfill additive CuSO<sub>4</sub> (6.1) on anoxic corrosion of steels (3.3.3); (4) quantify anoxic corrosion of other metals, especially Al and Al-base alloys (3.3.4).

Bin-scale and alcove tests with CH TRU waste (Molecke, 1990a; 1990b) will also provide information relevant to anoxic corrosion (3.4).

## 1.4 MICROBIAL ACTIVITY

Lappin et al. (1989) estimated that if brine or H<sub>2</sub>O vapor were present in WIPP disposal rooms, microbial degradation of cellulose in the waste would produce about 1 mole of various gases per drum of waste per year for 600 years, or a total of 600 moles per drum (4.1). These gases could include CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S, N<sub>2</sub>, and NH<sub>3</sub>, but the relative proportions are unknown. Microbial activity is the process of second greatest concern from the standpoint of the gas budget of the repository. It could also affect the H<sub>2</sub>O budget, but the net effect is still unknown.

The quantity of H<sub>2</sub>O in the DRZ available for transport to the waste may prevent the production of 600 moles of gas per drum, especially if absorption of H<sub>2</sub>O by the backfill and anoxic corrosion of metals consume significant quantities of H<sub>2</sub>O (3.1). The quantities of nutrients in WIPP brines and waste may also limit microbial activity.

The experimental program reviewed by Molecke (1979) yielded valuable data on microbial activity under various conditions. During 1988, a group of experts reviewed this program and relevant microbiological studies conducted for other applications (Brush and Anderson, 1988a; 1988b; 1988c). This group concluded that microbial activity is likely in WIPP disposal

rooms, that it could affect the long-term performance of the repository, and that sterilization of the waste is unfeasible.

It is still unknown whether there will be sufficient nutrients for microbial activity in WIPP disposal rooms, which potentially significant microbial processes (4.2) would occur, at what rates they would produce gas and produce or consume H<sub>2</sub>O, and whether the H<sub>2</sub>O content and pressure of the repository would affect these rates. The extent to which any of these processes would affect the chemical behavior of radionuclides is also unknown. Finally, it is unclear whether microorganisms are likely to survive for periods sufficient to affect the long-term performance of the repository.

The objectives of these laboratory studies are to: (1) determine which potentially significant microbial processes (4.2) occur under overtest conditions (4.4.2); (2) quantify the effects of potentially significant processes on the gas and H<sub>2</sub>O budgets of the repository under realistic conditions, both humid and inundated (4.4.3); (3) quantify the effects of pressure, if necessary, on any significant processes (4.4.4); (4) quantify the effects of potentially significant processes on the chemical behavior of the important radionuclides in TRU waste under realistic conditions (4.4.5); (5) determine whether the microorganisms responsible for any significant processes are likely to survive for long periods (4.4.6).

Bin-scale and alcove tests with CH TRU waste (Molecke, 1990a; 1990b) will also provide results relevant to microbial activity (4.5).

## 1.5 RADIOLYSIS

Most of the data reviewed by Molecke (1979) imply that the radiolytic gas production rate for TRU waste in WIPP disposal rooms will be significantly lower than recent estimates of the gas production rates from anoxic corrosion of metals (3.1) or microbial degradation of cellulose (4.1).

Estimates of the microbial gas production potential, and hence the total gas production potential, are very sensitive to assumptions of the extent to which microorganisms will degrade cellulose, plastics, and rubbers in the WIPP inventory. Lappin et al. (1989) estimated the microbial gas production potential by assuming that microorganisms convert 100% of the cellulose, 50% of the rubbers, but none of the plastics in the WIPP inventory to gas. Their estimate would have been much higher if they had assumed that microorganisms will degrade plastics significantly. Although microorganisms will almost certainly consume cellulose in preference to plastics and rubbers, irradiation of plastics could make them more biodegradable (5.1 and 5.2). A laboratory study of the effects of  $\alpha$  radiolysis on the biodegradability of these materials is necessary to determine the gas production potential of the waste.

Although Molecke (1979) concluded that radiolytic gas production will be relatively insignificant in WIPP disposal rooms, recent developments raise the possibility that radiolysis could be important. Compaction of the waste may increase the radiolytic gas production rate by increasing the density of the waste and the extent to which  $\alpha$  particles interact with it.

Inundation of the waste with brine may also increase the radiolytic gas production rate. Finally, increased pressure caused by gas production and room closure may affect this rate, but whether pressure would increase or decrease it is unknown. A review of the results of other investigations is under way to determine if additional studies are necessary to quantify the effects of waste compaction, inundation, and pressure on the radiolytic gas production rate.

The objectives of these laboratory studies are to: (1) quantify the effects of  $\alpha$  radiolysis on the biodegradability of plastics (5.5.1); (2) determine, if necessary, the effects of waste compaction, inundation, and pressure on the radiolytic gas production rate (5.5.2).

Bin-scale and alcove tests with CH TRU waste (Molecke, 1990a; 1990b) will also provide results pertinent to radiolysis.

## 1.6 BACKFILL ADDITIVES

Brush and Anderson (1988a, 1989) proposed the use of several backfill additives to remove or prevent the production of some of the gases expected in WIPP disposal rooms (6.1).  $\text{CuSO}_4$ , an oxidant, would corrode Fe and Fe-base alloys without producing  $\text{H}_2$ .  $\text{CaCO}_3$ ,  $\text{CaO}$ ,  $\text{Ca(OH)}_2$ ,  $\text{KOH}$ , and  $\text{NaOH}$  would remove  $\text{CO}_2$ , a potentially abundant, microbially produced gas (4.2.2, 4.2.5, and 4.2.6).  $\text{CaO}$ , along with bentonite (a previously proposed backfill additive), would also remove  $\text{H}_2\text{O}$ .  $\text{MnO}_2$ , a potential electron acceptor (4.2.3), might prevent: microbial  $\text{SO}_4^{2-}$  reduction; the concomitant production of  $\text{H}_2\text{S}$ ; the reaction of  $\text{H}_2\text{S}$  with Fe, Fe-base alloys, or their corrosion products to form  $\text{FeS}_2$  (pyrite); the concomitant production of  $\text{H}_2$  (3.2.1.3).

There is no known backfill additive to remove  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{NH}_3$ , or  $\text{H}_2\text{S}$ , or prevent the production of  $\text{CH}_4$ ,  $\text{N}_2$ , or  $\text{NH}_3$  at reasonable cost. Fe, Fe-base alloys, or their corrosion products would remove  $\text{H}_2\text{S}$ , but the concomitant formation of  $\text{FeS}_2$  would release large quantities of  $\text{H}_2$  (3.2.1.3).

How effective these backfill additives would be is also unknown.  $\text{CaCO}_3$  and  $\text{CuSO}_4$  would be effective only if brine were present;  $\text{MnO}_2$  may not be effective under any circumstances (6.1).

It is also unclear whether these backfill additives would affect the long-term performance of the WIPP favorably or unfavorably.  $\text{CaO}$ ,  $\text{Ca(OH)}_2$ ,  $\text{KOH}$ , and  $\text{NaOH}$  could increase the pH of any brine present to very basic values. This could in turn affect the rates of anoxic corrosion of metals and microbial degradation of cellulose, and influence the chemical behavior of radionuclides. Because large quantities of any of these backfill additives could be required (6.1), they could inhibit the closure of WIPP disposal rooms by increasing the strength of the materials in the rooms.

Furthermore, use of these backfill additives could reduce the likelihood of compliance with regulations for the disposal of chemically hazardous waste (1.9).

Whether the advantages of these backfill additives outweigh their disadvantages is still unknown. It is possible, for example, that recent estimates of the gas production potential from anoxic corrosion (3.1) and microbial activity (4.1) are too high. If so, significantly smaller quantities of the backfill additives may be necessary, and their potential disadvantages would be less important.

The objectives of these laboratory and modeling studies (6.2.1 and 6.2.2, respectively) are to: (1) determine whether the backfill additives  $\text{CaCO}_3$ ,  $\text{CaO}$ ,  $\text{CuSO}_4$ ,  $\text{KOH}$ , and  $\text{NaOH}$  remove  $\text{CO}_2$  or prevent the production of  $\text{H}_2$  effectively; (2) quantify their effects on repository chemistry.

Bin-scale and alcove tests with CH TRU waste (Molecke, 1990a; 1990b) will also yield data on the efficacy and effects of backfill additives (6.3).

## 1.7 RADIONUCLIDE CHEMISTRY

Predictions of the chemical behavior of radionuclides in WIPP brines are necessary to define the source term, the quantities of the important radionuclides in the WIPP inventory that would be mobilized by brine for possible transport to the accessible environment, and the scenario-dependent rates at which these radionuclides would be mobilized. Marietta et al. (1989) concluded that from the standpoint of the WIPP PA, the important radionuclides in TRU waste are all isotopes of Pu, Am, Th, and U.

The speciation, solubilities, and sorption of Pu, Am, Th, and U and the extent to which they form colloids will determine their concentrations in any brine present in WIPP disposal rooms. Because there are neither data with which to predict the concentrations of these elements in WIPP brines nor a defensible method for estimating these data (7.2), laboratory studies of these processes are necessary.

The chemical behavior of Pu, Am, Th, and U in aqueous solutions is sensitive to the Eh and pH of any brine present. The Eh and pH in WIPP disposal rooms could, given the heterogeneous nature of design-basis waste, vary significantly with time, and over short distances at any given time (1.10.4). It is necessary to quantify the chemical behavior of these elements under a wide range of conditions.

The objectives of these laboratory studies are to: (1) quantify the speciation of Pu, Am, Th, and U in neutral, mildly acidic, and basic solutions of high ionic strength under a wide range of redox conditions (7.6.1) for calculations of the solubilities of these elements in WIPP brines; (2) determine, if necessary, the solubilities of Pu-, Am-, Th-, and U-bearing solids under similar conditions (7.6.2) to validate the results of the speciation study; (3) quantify the sorption of these elements from WIPP brines under conditions similar to those in the speciation and solubility studies (a description of this study will appear elsewhere); (4) extend the speciation, solubility, and sorption studies to strongly basic WIPP brines (7.6.3), if studies of repository chemistry based on the current or modified designs of the repository imply this is necessary; (5) determine the extent to which Pu, Am, Th, and U form colloids under these conditions (a description of this study will also appear elsewhere).



Bin-scale tests with CH TRU waste (Molecke, 1990a) will also provide information on the chemical behavior of radionuclides in brines (7.7).

## **1.8 MODEL DEVELOPMENT**

Modeling studies (8.0) are necessary to interpret the results of laboratory studies and the bin-scale and alcove tests with CH TRU waste described by Molecke (1990a, 1990b). Modeling studies are also necessary to extend the results of these laboratory, bin-scale, and alcove tests to other possible repository conditions. If successful, modeling studies would reduce the number of experiments required to quantify the effects of variations in chemical conditions on repository gas and H<sub>2</sub>O budgets and the chemical behavior of radionuclides.

Currently available geochemical models such as the EQ3/6 geochemical software package can meet some, but not all, of these objectives (8.2 and 8.3). They can predict chemical reactions between WIPP brines and evaporite minerals, but not reactions between these brines and silicates (clay minerals in the Salado Fm., bentonite and grouts, for example), nor the behavior of radionuclides in brines. Additional development of EQ3/6 is needed.

The objectives of additional development of EQ3/6 are to: (1) extend the Pitzer activity-coefficient model by adding ion-interaction parameters for important aqueous Al(III), Cu(II), Fe(III), Mn(II), Mn(IV), and Si(IV) species to the existing data base (8.4.1); (2) develop an alternative activity-coefficient model based on hydration theory (8.4.2).

## **1.9 HAZARDOUS-WASTE CHEMISTRY**

It is now possible to expand the studies described in this Test Plan to include studies of the chemically hazardous, TRU-waste constituents of regulatory concern pursuant to the Resource Conservation and Recovery Act (RCRA). However, expansion of these studies awaits identification of data required to demonstrate compliance with the regulations promulgated by the Environmental Protection Agency to implement the RCRA.

In some cases, extension of the studies described herein to chemically hazardous constituents of TRU waste would require only modest increases in the existing level of effort. It would be relatively straightforward, for example, to include toxic heavy metals such as Pb in laboratory studies of radionuclide speciation (7.6.1 and 7.6.2) or radionuclide sorption if appropriate experimental data do not exist for these elements in solutions of high ionic strength. However, it would be more difficult to start studies of hazardous waste constituents in the absence of parallel studies of repository or radionuclide chemistry. One example of such a study might be the partitioning of volatile organic compounds between WIPP brine and the gases expected in the repository.

## **1.10 EXPERIMENTAL CONDITIONS FOR LABORATORY STUDIES**

Definition of the conditions expected for WIPP disposal rooms is essential for the design of realistic laboratory studies, to reduce the

number of experiments as much as possible, and to ensure the comparability of the results.

### 1.10.1 Temperature

The WIPP repository horizon is 655 m below the surface. The temperature of the Salado Fm. at this depth, beyond the annular volume affected by ventilation of the mine, is 28°C (Munson et al., 1987).

The CH TRU waste to be emplaced in drums and boxes in WIPP disposal rooms will produce essentially no heat.

The RH TRU waste to be emplaced in canisters in the ribs will produce some heat, but will probably not increase the temperature within WIPP disposal rooms significantly. Beraún and Molecke (1987) modeled the thermal response of backfills consisting of N<sub>2</sub>, crushed salt, or a mixture of bentonite and sand, and the surrounding Salado Fm. to vertically emplaced, simulated defense high-level waste packages with 470-W electric heaters. They compared their results to measured temperature distributions. Torres (1988) modeled the effects of thermal power output (60, 100, and 300 W) and spacing (3.66 and 6.10 m) of horizontally emplaced canisters of RH TRU waste on the thermal response of the Salado Fm. Beraún (1989) modeled the thermal response of the Salado Fm. to horizontally emplaced (2.44-m spacing), simulated RH canisters with 117-W electric heaters. The thermal properties of the materials modeled by these investigators probably encompass those of the contents of WIPP disposal rooms. Extrapolation of their results to the distances of several meters suggests that RH TRU waste will not increase the temperature of CH TRU waste by more than a few degrees Celsius.

Temperature gradients may develop between the CH TRU waste in WIPP disposal rooms and the RH TRU waste in the ribs, or even between large particles containing <sup>238</sup>Pu (an isotope with a high specific activity), <sup>239</sup>Pu, or other radionuclides, and adjacent microenvironments devoid of radionuclides. Although these temperature gradients would be small, they could cause condensation of H<sub>2</sub>O within the rooms. This condensation could dissolve salts from the backfill and form a film of brine on relatively cool surfaces such as drums and boxes (1.10.3).

In lieu of modeling studies of the thermal response of the contents of WIPP disposal rooms to RH TRU waste, Brush specified a temperature of 30°C for the laboratory and modeling studies described herein. Most investigators are carrying out their experiments at this temperature. However, in some cases they conduct experiments at 25°C or at ambient laboratory temperatures.

### 1.10.2 Pressure

The surface elevation of the WIPP Site is 1,039 m above sea level; therefore, the repository horizon is 384 m above sea level. The pressure in WIPP disposal rooms during filling and sealing will be slightly less than 1 atm.

In the absence of gas production by the waste, closure of WIPP disposal rooms would eventually increase the pressure to a value between the hydrostatic pressure at the depth of the repository (about 100 atm) and the lithostatic pressure (about 150 atm).

Weatherby, Arguello, and Stone (1989) concluded that the gas production rates estimated by Lappin et al. (1989) may pressurize the repository slowly enough to maintain a compressive stress field around it. This "hoop stress" would prevent the formation of new fractures, or the extension or widening of preexisting fractures, and would allow the pressure to increase to greater than 150 atm before reversal of room closure would slowly decrease the pressure. Weatherby, Arguello, and Stone calculated a maximum pressure of about 200 atm based on the gas production rates and potentials estimated for anoxic corrosion of Fe and Fe-base alloys (3.1) and microbial degradation of cellulose (4.1) by Lappin et al. Clearly, gas production in excess of the total potential estimated by Lappin et al. would result in a maximum pressure greater than 200 atm; escape of gas through fractures would preclude pressures in excess of 150 atm.

The rates of gas production from anoxic corrosion, microbial activity, and radiolysis may vary inversely with pressure. Experiments at high pressure are difficult and time-consuming. Therefore, most investigators are carrying out their studies of these processes at pressures of about 1 atm, and will extend them to high pressures only if there is reason to suspect that pressure will affect these processes.

### **1.10.3 Water Content**

The humidity in the WIPP underground workings is currently similar to that of the surface air (low and variable) because of ventilation of the mine. However, very soon after the repository is filled and sealed the humidity of mine air trapped in void spaces will rise until it reaches equilibrium with the brine in the surrounding DRZ. Saturation of all of the void spaces in one room will require the evaporation of only a few tens of liters of H<sub>2</sub>O from brine in the DRZ. The thermodynamic activity of H<sub>2</sub>O vapor will then be equal to its activity in the brine, about 0.7 (3.2.1.1), and the relative humidity will be 70%. Brush refers to these conditions as "humid" from this point on.

Brines from the surrounding Salado Fm. will start to accumulate in WIPP disposal rooms after they are filled and sealed and the humidity reaches 73%. These brines are currently seeping into the underground workings, but rarely accumulate because of evaporation caused by ventilation of the mine. Brines could also enter the repository if an exploratory drillhole penetrates both a disposal room and a brine reservoir in the Castile Fm. In the unlikely event of degradation of the shaft and panel seals, fluids from overlying formations could seep down the shafts, along the drifts, and around or through the seals to the rooms.

Even under humid conditions, thermal gradients may cause condensation of H<sub>2</sub>O within WIPP disposal rooms and form small quantities of brine in relatively cool microenvironments (1.10.1).

There are still significant uncertainties in predictions of the rates at which these fluids could accumulate in WIPP disposal rooms and the quantities of fluids that could eventually accumulate. Because of these uncertainties, it is necessary to assume that partial or even complete resaturation of the void spaces could eventually occur. Brush refers to these conditions as "inundated."

The rates of gas production from anoxic corrosion, microbial activity, and radiolysis could be higher under inundated conditions than under humid conditions. Most investigators are carrying out their studies of these processes under both humid and inundated conditions.

#### **1.10.4 Eh and pH**

In general, the concept of a system-wide Eh is invalid in aqueous, geochemical systems at a temperature of 30°C (for example, Lindberg and Runnells, 1984). This is because the kinetics of most oxidation-reduction (redox) reactions are so slow at this temperature that redox reactions rarely reach equilibrium, and the Eh calculated from the activity ratio of one redox couple rarely agrees with the values calculated from other couples or with the value measured with an Eh electrode. However, microbial activity is known to catalyze "inorganic" redox reactions in natural systems (for example, Berner, 1980; Froelich et al., 1979). Significant microbial activity may occur in WIPP disposal rooms, catalyze redox reactions, and make the concept of a system-wide Eh meaningful. Laboratory studies of microbial activity are under way or planned (4.4). The bin-scale and alcove tests with CH TRU waste (Molecke, 1990a; 1990b) will also provide information on microbial activity.

The Eh of any brine accumulating in WIPP disposal rooms immediately after filling and sealing would be similar to that of fluids in equilibrium with atmospheric O<sub>2</sub>. Subsequent reactions between brine and the contents of the repository could decrease its Eh significantly, however. Corrosion of metals and microbial activity will reduce the Eh. Microbial activity, for example, could lower the Eh to values characteristic of denitrification or NO<sub>3</sub><sup>-</sup> reduction, SO<sub>4</sub><sup>2-</sup> reduction, or even fermentation and methanogenesis. It is impossible to specify numerical Eh values for these processes because they depend on pH, which would vary significantly given the current design of the repository.

Reactions between brine and the contents of WIPP disposal rooms could increase or decrease the pH significantly from initial mildly acidic values (2.3.1.3). Microbial production of CO<sub>2</sub> could decrease the pH of the brine to acidic values. Reactions between brine and cements used to remove liquids from sludges, grouts used in seals, or grouts proposed to reduce the permeability of WIPP disposal rooms (Butcher, 1990) could increase the pH to basic values. Reactions between brine and the backfill additives CaO, KOH, or NaOH (6.1) could increase the pH to very basic values.

At any given time, the Eh and pH could vary significantly over short distances, perhaps just a few centimeters, because of the heterogeneous nature of design-basis waste. Oxidizing conditions, for example, could persist for long periods near large, radionuclide-bearing particles because

of continuous radiolytic production of O<sub>2</sub> and other oxidizing species from brine or sludges. Simultaneously, adjacent microenvironments devoid of radionuclides but with large quantities of organic matter and significant anaerobic microbial activity could rapidly become reducing. The pH could vary from acidic values in microenvironments containing microbially produced CO<sub>2</sub> to basic values near cements and grouts.

Because of these expected variations, it is difficult to rule out any possible combinations of Eh and pH at the start of these laboratory studies. Therefore, a major objective of the studies of repository chemistry is to determine whether the processes described above will actually produce such variable conditions.

#### **1.10.5 Nonradioactive Constituents of TRU Waste**

The types and quantities of metals, cellulose, plastics, rubbers, and organic and inorganic ligands in the TRU waste to be emplaced in the WIPP could affect the nature and extent of anoxic corrosion, microbial activity, radiolysis, and the behavior of radionuclides in any brine present in WIPP disposal rooms. An inventory of nonradioactive waste constituents is necessary for the design of realistic laboratory studies and for the interpretation and extrapolation of results from the bin-scale and alcove tests with TRU waste.

Drez and James-Lipponer (1989) developed a preliminary inventory of the nonradioactive constituents of the CH TRU waste to be emplaced in the WIPP. They will revise it if the waste generators modify their use or disposal of materials significantly or supplement it if specific needs for data on additional constituents arise. Descriptions of relevant aspects of this inventory appear throughout this Test Plan.

## 2.0 BRINE CHEMISTRY

### 2.1 JUSTIFICATION FOR LABORATORY AND MODELING STUDIES

Laboratory and modeling studies of repository and radionuclide chemistry, and bin-scale tests with contact-handled (CH) transuranic (TRU) waste (Molecke, 1990a), require the use of brines that simulate the chemical composition of brines that could enter Waste Isolation Pilot Plant (WIPP) disposal rooms after filling and sealing. Because the number of parameters that must be varied in these studies is large, it is necessary to define the composition of a few standard brines to reduce the number of experiments, yet still realistically simulate expected repository conditions. The use of standard brine compositions will also ensure the comparability of experimental results.

Because other studies of repository and radionuclide chemistry are just starting, the extent to which chemical variations in WIPP brines will affect anoxic corrosion of metals, microbial degradation of cellulose, radiolysis, the behavior of proposed backfill additives, or the chemical behavior of radionuclides is still unknown. It is difficult, therefore, to specify the level of understanding of brine chemistry necessary to predict the long-term performance of the repository.

Brush has identified the various sources of fluids that could enter WIPP disposal rooms after filling and sealing (2.2), but laboratory, modeling, and field studies (2.4) are necessary to predict the average compositions and expected variability of these brines as they enter the repository. These studies emphasize the major-element chemistry of WIPP brines. Because it is usually much more difficult to analyze for minor and trace elements in brines, characterization of these constituents is lower priority, unless they could affect repository and radionuclide chemistry significantly. The inorganic C species  $\text{CO}_3^{2-}$ , for example, could increase the solubilities of several of the radionuclides in TRU waste by forming complexes with them.

In lieu of the results of these studies, most investigators are using brines collected from the WIPP underground workings for their initial laboratory studies of repository and radionuclide chemistry. Brush has defined preliminary, standard compositions for synthetic brines for Molecke's (1990a) bin-scale tests with CH TRU waste.

### 2.2 SOURCES OF FLUIDS THAT COULD ENTER THE REPOSITORY

The release events being considered for the long-term performance assessment of the WIPP (Hunter, 1989; Marietta et al., 1989; Guzowski, 1990) imply that brines from the Salado and the Castile Fm. could enter the repository (2.2.1 and 2.2.2, respectively). For the base-case scenario, Brush is also considering fluids from overlying formations (2.2.3).

#### 2.2.1 Salado-Fm. Brines

Intergranular brines from the Salado Fm. at or near the stratigraphic horizon of the repository are seeping into the WIPP underground workings

through the ribs and, to a lesser extent, the back and the floor. These brines rarely accumulate because of evaporation caused by ventilation of the mine. After filling and sealing, however, the air trapped in voids will become saturated with H<sub>2</sub>O vapor, and these brines could accumulate.

The intragranular brines (fluid inclusions) that occur in the Salado Fm., on the other hand, will not migrate in the absence of a significant thermal gradient. Although stress-relief fracturing in the disturbed-rock zone (DRZ) could release minor quantities of these intragranular fluids, which could then mix with intergranular brines, Brush is not considering fluid inclusions in these studies of repository and radionuclide chemistry at this time. "Salado-Fm. brine" refers to intergranular brine from this point on.

### **2.2.2 Castile-Fm. Brines**

Brines also occur in isolated but occasionally large (800,000-m<sup>3</sup>) reservoirs in the underlying Castile Fm. (the volume of an empty, newly excavated WIPP disposal room is 3,640 m<sup>3</sup>). For their calculations, Lappin et al. (1989) assumed that brine reservoirs occur beneath WIPP waste-emplacements panels. These brines could enter the repository if an exploratory drillhole penetrates both a disposal room and a brine reservoir. These brines could in turn react with brines and minerals from the Salado Fm. If so, the composition of these Castile-Fm. brines could change significantly, but would not necessarily resemble that of Salado-Fm. brines.

### **2.2.3 Fluids from Overlying Formations**

In the unlikely event of degradation of the shaft and panel seals, fluids from overlying formations could seep down the shafts, along the drifts, and around or through the seals to the rooms. Because most fluids from overlying formations are undersaturated with respect to the minerals in the Salado Fm., they would dissolve salts from the backfill and the Salado Fm. In the process, they would become saturated brines. The composition of these brines could be significantly different from Salado-Fm. brines.

## **2.3 PRELIMINARY DEFINITION OF STANDARD BRINE COMPOSITIONS**

Most investigators are using brines collected from the WIPP underground workings for their initial laboratory studies of repository and radionuclide chemistry. Brush has defined preliminary, standard compositions for synthetic Salado- and Castile-Fm. brines for Molecke's (1990a) bin-scale tests with CH TRU waste. Brush is evaluating the results of previous studies to define preliminary, standard compositions for fluids from overlying formations.

### **2.3.1 Salado-Fm. Brines**

Two groups are studying the chemistry of brines from the Salado Fm. Stein and Krumhansl (1986, 1988) collected brines from five short (up to 20 cm) floor holes and 24 short (up to 25 cm) horizontal holes in the northern, experimental area of the WIPP underground workings. They

referred to these samples as "brine weeps." Stein and Krumhansl (1986, 1988) also collected brines from 18 downholes in the northern area of the mine; they referred to these holes, which extend to depths of about 1 m, as "floor holes." Stein and Krumhansl (1986, 1988) analyzed their samples at Sandia National Laboratories (SNL). They are collecting and analyzing additional brines from new horizontal holes (2.4.2). Deal et al. (1989) collected brines from several drillholes that penetrate up to 15 m above the back or below the floor of the drifts, as well as from a few short (up to 1 m) horizontal holes and a floor seep. These holes are located mainly in the northern part of the WIPP underground workings. This study is part of the ongoing Brine Sampling and Evaluation Program (BSEP), which is also monitoring the accumulation rates of brines in these holes (Deal and Case, 1987; Deal et al., 1989). Deal et al. (1989) sent their samples to International Technology (IT) Corporation in Export, Pa., and United Nuclear Corporation Geotech (UNC) in Grand Junction, Co., for chemical analysis. In addition to the data reported by Deal et al. (1989), Deal (1989) provided unpublished BSEP results for inclusion in the preliminary, standard Salado-Fm. brines described below (2.3.1.3). This group will continue to collect brines from these and additional holes and will send them to one or both of these laboratories for analysis.

#### 2.3.1.1 CHEMICAL VARIATIONS IN SALADO-FM. BRINES

Chemical variations exist within the BSEP data reported by Deal (1989) and Deal et al. (1989). Because the extent to which these variations will affect repository and radionuclide chemistry is still unknown, it is unclear whether they are significant. The concentrations of  $\text{Br}^-$ ,  $\text{Cl}^-$ , and  $\text{Mg}^{2+}$  in brines collected from three BSEP upholes, for example, generally differ from the respective concentrations of these elements in brines from ten BSEP downholes. The concentrations of  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$ , on the other hand, are generally similar in both BSEP upholes and downholes. The BSEP has obtained data for B (probably present mainly as  $\text{H}_3\text{BO}_3$  and  $\text{HB}_4\text{O}_7^-$  or  $\text{H}_3\text{BO}_3$  and  $\text{B}(\text{OH})_4^-$ , but referred to herein as  $\text{B}^{3+}$ ) and total inorganic carbon (TIC), as well as for pH, specific gravity (SG), and total dissolved solids (TDS), but Brush has not yet compared the concentrations of these elements or the values of these chemical properties in BSEP upholes and downholes. Brush has also not evaluated the results reported by the BSEP for numerous minor and trace elements at this time because these elements will probably not affect repository and radionuclide chemistry significantly. The differences between the concentrations of  $\text{Br}^-$ ,  $\text{Cl}^-$ , and  $\text{Mg}^{2+}$  in BSEP upholes and downholes could result from different sampling artifacts associated with each type of hole. Samples collected from the upholes, for example, accumulate in containers suspended from the collars of the holes. As they trickle down through the DRZ, these brines probably change composition due to evaporation from mine air passing through small fractures caused by excavation of the drifts and subsequent dilation of the rock. As the brines evaporate, they could also change composition due to reactions with minerals in the back. The effects of evaporation are probably more significant in the case of upholes than downholes because all of the fluids collected from the former trickle down through and accumulate in the DRZ, whereas only fluids from the top few meters of the downholes trickle down through the DRZ prior to accumulation. Brines collected from the downholes, on the other hand, could be contaminated during sampling by



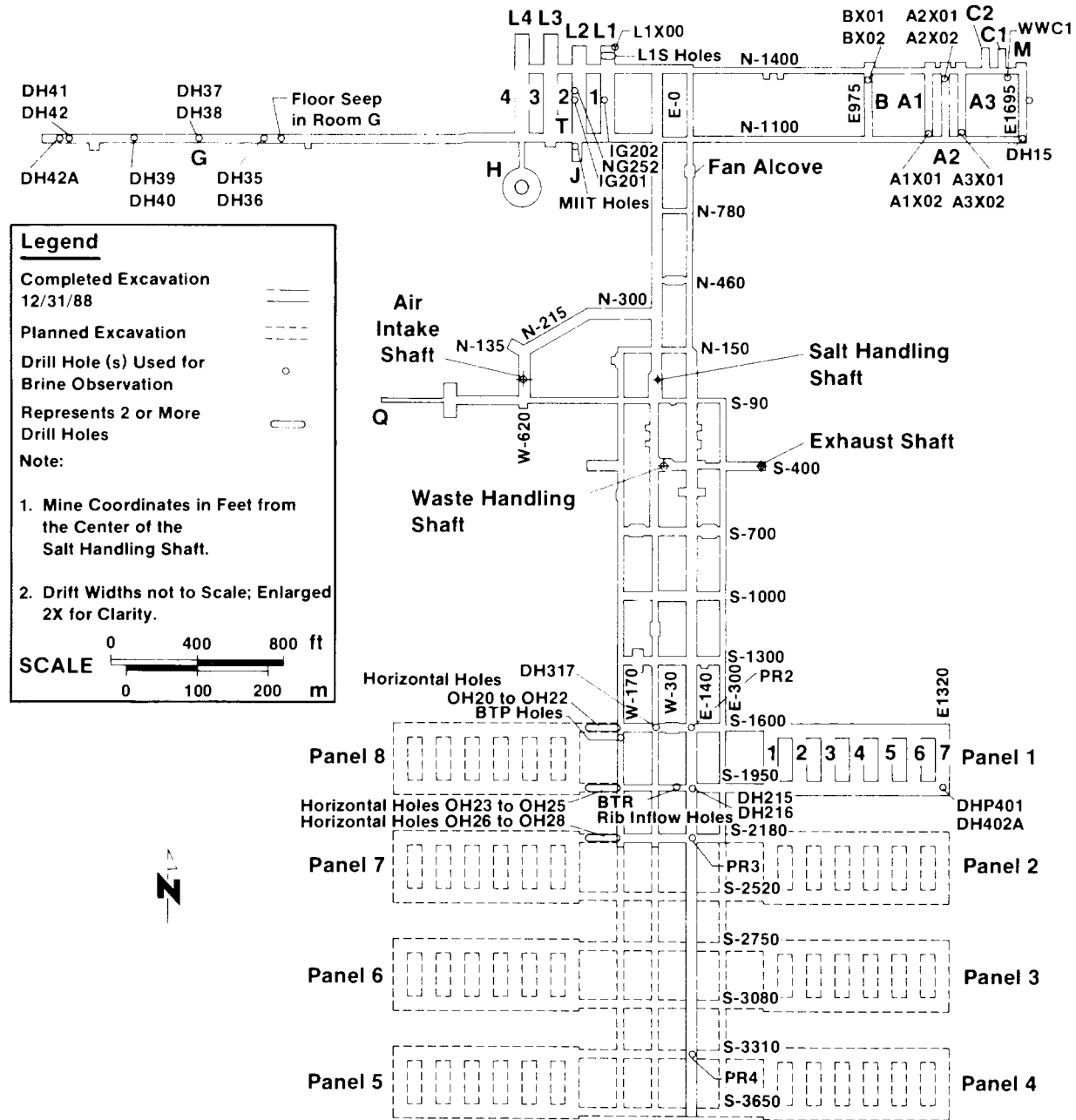
material from the floor of the drifts. The differences between the concentrations of  $\text{Br}^-$ ,  $\text{Cl}^-$ , and  $\text{Mg}^{2+}$  in BSEP upholes and downholes could also result from stratigraphic differences in Salado-Fm. brines.

Potentially significant chemical variations also exist between the data reported by Deal (1989) and Deal et al. (1989), and those obtained by Stein and Krumhansl (1986, 1988). The concentrations of  $\text{Br}^-$  and  $\text{Cl}^-$  in brines from BSEP upholes and downholes, for example, generally differ from the respective concentrations of these elements in samples collected by Stein and Krumhansl (1986, 1988) from 24 horizontal holes. The concentrations of  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{SO}_4^{2-}$ , on the other hand, are generally similar in brines from the BSEP holes and the holes sampled by Stein and Krumhansl (1986, 1988). The differences between the concentrations of  $\text{Br}^-$  and  $\text{Cl}^-$  reported by Deal (1989) and Deal et al. (1989), and those obtained by Stein and Krumhansl (1986, 1988) could result from sampling artifacts such as those discussed above, or stratigraphic differences. They could also result from differences in the sampling techniques, the method of shipping used by the two groups studying these brines, or from differences in the laboratory techniques used at the IT and UNC laboratories, and those used by Stein and Krumhansl (1986, 1988) at SNL.

#### 2.3.1.2 COLLECTION OF SALADO-FM. BRINES AND MINERALS FROM THE WIPP UNDERGROUND WORKINGS

Most investigators are using brines collected from the WIPP underground workings for their initial laboratory studies of repository and radionuclide chemistry. They use these brines instead of synthesizing brines because: (1) the choice of data used to compute the composition of standard brines from the Salado Fm. and how those data are weighted (2.3.1.3) introduce uncertainties as large as the chemical variations observed in brines collected from the WIPP underground workings, at least until Brush quantifies the causes of chemical variations described in 2.3.1.1; (2) it is proving difficult to synthesize a brine with the composition calculated in 2.3.1.3; (3) the concentrations of most minor and trace elements in brines collected from the WIPP underground workings are probably more representative of their concentrations in Salado-Fm. brines than the limited analytical data obtained to date, at least for those elements not sorbed by the walls of the containers, because Brush has not yet included the data for many minor and trace elements in his studies of the causes of chemical variations (2.4.1 through 2.4.4).

Brush has collected brines from three BSEP downholes (DH36, DH42A, and NG252) and a BSEP floor seep (G Seep). Figure 2.1 shows the locations of these holes. He will continue to collect brines from DH36, DH42A, and G Seep as long as these holes continue to produce sufficient quantities of brine. Sampling requirements for the ongoing BSEP chemical analyses receive higher priority than collection of brines for these laboratory studies. Collection of brine from NG252 is no longer possible because Room 2 has been closed due to safety concerns. When sampling brines for laboratory studies, he records the date and the volumes collected and reports them to BSEP personnel for use in their studies of brine influx. A detailed description of the procedures used for the collection of these samples appears elsewhere (Deal and Case, 1987; Deal et al., 1989).



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Figure 2.1. Map of the WIPP Underground Workings with Locations of BSEP Holes (after Deal et al., 1989).

As soon as possible after collection, Brush transports these brines to Albuquerque. He usually transports these samples by automobile, but sometimes hand-carries them aboard commercial aircraft or ships them as checked baggage.

At SNL, Brush stores brines in 25-L polyethylene containers with spigots at room temperature until needed. He combines brines sampled from the same BSEP downhole or floor seep at different times in the same container, but stores brines from different holes in separate containers. As soon as possible after he fills a container, he sends duplicate samples by express air mail to UNC for analysis. He usually ships samples of various sizes to his subcontractors by express air mail, but sometimes hand-carries them aboard commercial aircraft or ships them as checked baggage. He tries to avoid shipping them by surface mail because the prolonged exposure to extreme temperatures and repeated temperature changes that could occur during this form of shipment may induce irreversible dissolution and precipitation of salts and concomitant changes in their composition. To check for compositional changes, each subcontractor analyzes his or her brine as soon as possible after receipt.

Brush maintains records for each 25-L container that include the collection date of all samples added to the container, the name or names of the personnel who collected the samples, the method by which samples were shipped from the WIPP Site to SNL, the distribution date of all samples withdrawn from the container, the subcontractor to whom samples were shipped, the method by which samples were shipped from SNL to the subcontractor, and any chemical analyses of brines from the container, either by SNL or its subcontractors. Table 2.1 gives the average compositions of brines collected to date from DH36 and G Seep.

Brush also collects and stores minerals from the WIPP underground workings for use in some of the studies with brines. He collects these minerals from piles of muck mined from the drifts in which waste will be emplaced.

### 2.3.1.3 PRELIMINARY DEFINITION OF A STANDARD SALADO-FM. BRINE COMPOSITION

Molecke (1990a) is planning bin-scale tests with CH TRU waste. The volume of brine required for these tests is too large to collect from the WIPP underground workings. Brush therefore defined a preliminary, standard composition for brine from the Salado Fm. and is developing a formulation for this brine (a description of this formulation will appear elsewhere). The composition of this or any other "average" Salado-Fm. brine depends on the data used to compute its composition and how those data are weighted. Because he cannot yet explain the chemical variations described in 2.3.1.1, these choices are arbitrary. The composition of this Salado-Fm. brine is subject to revision as he quantifies the causes of these chemical variations.

Brush defined the standard brines presented in Table 2.1, Salado Brines 1, 2, and 3 (SB-1, SB-2, and SB-3), as follows. First, he included data from 29 chemical analyses of brine weeps (brines from five short floor holes and 24 short horizontal holes) from Stein and Krumhansl (1986, 1988), as well as data for brines from 12 holes (ten long downholes, one short

TABLE 2.1

COMPARISON OF THE COMPOSITIONS OF BRINES COLLECTED FROM THE WIPP  
UNDERGROUND WORKINGS AND PRELIMINARY, STANDARD BRINES

| Element or<br>Chemical<br>Property | DH36 <sup>a</sup> | G Seep <sup>b</sup> | SB-1 <sup>c</sup> | SB-2    | SB-3    |
|------------------------------------|-------------------|---------------------|-------------------|---------|---------|
| Alk. (mM) <sup>d</sup>             | 11.9              | 12.0                | 13.7              | 13.8    | -       |
| Alk., ext. (mM) <sup>e</sup>       | -                 | -                   | 14.8              | 15.7    | -       |
| B <sup>3+</sup> (mM) <sup>f</sup>  | 137               | 144                 | 152               | 148     | 127     |
| Br <sup>-</sup> (mM)               | ?                 | 17.1                | 13                | 13      | 14      |
| Ca <sup>2+</sup> (mM)              | 9.60              | 7.68                | 10                | 9       | 9       |
| Cl <sup>-</sup> (M)                | 5.37              | 5.10                | 6.04              | 6.02    | 6.01    |
| Eh (mV) <sup>g</sup>               | -                 | -                   | -                 | -       | -       |
| K <sup>+</sup> (mM)                | 472               | 350                 | 500               | 510     | 510     |
| Mg <sup>2+</sup> (M)               | 0.817             | 0.630               | 1.0               | 1.0     | 1.0     |
| Na <sup>+</sup> (M)                | 3.67              | 4.11                | 3.9               | 3.9     | 3.9     |
| pH (std. units)                    | 6.0               | 6.1                 | 6.0               | 6.1     | 6.0     |
| SG                                 | 1.22              | 1.23                | 1.22              | 1.22    | 1.22    |
| SO <sub>4</sub> <sup>2-</sup> (mM) | 173               | 303                 | 160               | 170     | 170     |
| TDS (mg/l)                         | 346,000           | 355,000             | 385,000           | 378,000 | 372,000 |
| TIC (μM) <sup>h</sup>              | 13.9              | 11.5                | 370               | -       | -       |

- a. Average composition of 25 L of brine collected from the WIPP underground workings and analyzed by UNC (2.3.1.2).
- b. Average composition of 200 L of brine collected from the WIPP underground workings and analyzed by UNC (2.3.1.2).
- c. Defined by Brush and Anderson (1988b).
- d. Alkalinity reported as equivalent HCO<sub>3</sub><sup>-</sup> (solutions titrated to pH = 4.5), but most of the alkalinity probably reflects B(III) species (analyses for TIC average only 370 μM in SB-1).
- e. Extended alkalinity reported as equivalent HCO<sub>3</sub><sup>-</sup> (solutions titrated to pH = 2.5 to 3.0).
- f. Probably present mainly as H<sub>3</sub>BO<sub>3</sub> and HB<sub>4</sub>O<sub>7</sub><sup>-</sup> or H<sub>3</sub>BO<sub>3</sub> and B(OH)<sub>4</sub><sup>-</sup>.
- g. Eh not measured with an Eh electrode or calculated theoretically, but assumed for SB-1, SB-2, SB-3, Brine A, and Brine B to be similar to that of fluids in equilibrium with atmospheric oxygen<sub>2</sub> (for example, Garrels and Christ, 1963, Figure 11.2).
- h. TIC unspecified for SB-2 and SB-3 because it varied by a few orders of magnitude from sample to sample and was undetectable in several samples.

floor hole, and one short horizontal hole) reported by Deal (1989) and Deal et al. (1989). Brush excluded data for fluid inclusions from Stein and Krumhansl (1986, 1988) because intragranular brines will not migrate in the absence of a significant thermal gradient. He also excluded data for the floor holes (downholes) sampled by Stein and Krumhansl (1986, 1988) because they did not evacuate these holes, which were probably contaminated with large quantities of material from the drifts and the sides of the holes (Deal and Case, 1987), prior to collecting their samples. He also excluded the datum for  $\text{SO}_4^{2-}$  from Sample 19 of Stein and Krumhansl (1986, 1988) because the reported value is so high that it is clearly erroneous. He excluded data from all of the BTP holes (a subset of the BSEP holes) because the BTP holes are contaminated with fluids from the Rustler Fm. spread in the mine to control dust and from grout. He excluded data from upholes sampled by Deal (1989) and Deal et al. (1989) because fluids from the upholes probably changed composition to a much greater extent than fluids from the downholes due to evaporation and/or reaction with minerals in the back during accumulation (2.3.1). Second, for those holes that yielded sufficient brine for replicate analyses, Brush averaged the results for each element or chemical property to obtain one value for each sampling date. If two laboratories analyzed samples obtained from a given hole on the same date and either of these laboratories carried out replicate analyses, he averaged all of the replicate results from both laboratories simultaneously to obtain one value for each element or chemical property for that hole on that date. For those holes sampled more than once, he averaged the results for each element or chemical property from each sampling date to obtain one value for each hole. Third, Brush averaged the results for each element or chemical property from the 41 holes considered to obtain an overall average for each element or chemical property in this standard brine. He did not weight the value for each hole for the integrated volume of brine that has accumulated in that hole to date, for the most recently measured accumulation rate, nor for any other such factor. The differences between SB-1, SB-2, and SB-3 (Table 2.1) arise mainly from the fact that Deal (1989) provided additional BSEP data subsequent to the definition of SB-1. Table 2.2 compares the compositions of SB-1, SB-2, and SB-3 to the compositions of the previously defined standard brines, Brines A and B (Molecke, 1976; 1983).

Clearly, Brush could have used different methods to define a standard brine from the Salado Fm. and might do so in the future. It might be preferable, for example, to weight the data obtained for each hole for the volume of brine that has accumulated in that hole to date, for the most recently measured accumulation rate, or for a similar factor. However, this would bias the results in favor of the BSEP data at the expense of the data from Stein and Krumhansl (1986, 1988) because the BSEP requires a relatively large volume of brine for chemical analyses and measures the accumulation rates of these brines on an ongoing basis, whereas Stein and Krumhansl (1986, 1988) analyzed relatively small volumes of brine and sampled their holes only once. Furthermore, the results of the interlaboratory comparison study (2.4.3) might imply that data from one of the analytical laboratories should be excluded. The results of the ongoing investigation of brine chemistry, especially the statistical analysis of the causes of chemical variations, will ultimately determine the best method for the definition of the average composition of Salado-Fm. brines.

TABLE 2.2

COMPARISON OF THE COMPOSITIONS OF G-SEEP, SB-3, AND PREVIOUS STANDARD BRINES

| Element or<br>Chemical<br>Property | G Seep <sup>a</sup> | SB-3    | Brine A <sup>b</sup> | Brine B <sup>c</sup> |
|------------------------------------|---------------------|---------|----------------------|----------------------|
| Alk. (mM) <sup>d</sup>             | 12.0                | -       | -                    | -                    |
| Alk., ext. (mM) <sup>e</sup>       | -                   | -       | -                    | -                    |
| B <sup>3+</sup> (mM) <sup>f</sup>  | 144                 | 127     | 20                   | 20                   |
| Br <sup>-</sup> (mM)               | 17.1                | 14      | 10                   | 10                   |
| Ca <sup>2+</sup> (mM)              | 7.68                | 9       | 20                   | 20                   |
| Cl <sup>-</sup> (M)                | 5.10                | 6.01    | 5.35                 | 4.93                 |
| Eh (mV) <sup>g</sup>               | -                   | -       | -                    | -                    |
| K <sup>+</sup> (mM)                | 350                 | 510     | 770                  | < 5                  |
| Mg <sup>2+</sup> (M)               | 0.630               | 1.0     | 1.44                 | < 0.005              |
| Na <sup>+</sup> (M)                | 4.11                | 3.9     | 1.83                 | 5.00                 |
| pH (std. units)                    | 6.1                 | 6.0     | 6.5                  | 6.5                  |
| SG                                 | 1.23                | 1.22    | 1.2                  | 1.2                  |
| SO <sub>4</sub> <sup>2-</sup> (mM) | 303                 | 170     | 40                   | 40                   |
| TDS (mg/l)                         | 355,000             | 372,000 | 306,000              | 297,000              |
| TIC (mM) <sup>h</sup>              | 0.0115              | -       | 10                   | 10                   |

- a. Average composition of 200 L of brine collected from the WIPP underground workings and analyzed by UNC (2.3.1.2).
- b. Standard brine developed by Molecke (1976, 1983) to simulate fluids equilibrated with K<sup>+</sup>- and Mg<sup>2+</sup>-bearing minerals in overlying potash-bearing zones prior to entering the WIPP.
- c. Standard brine developed by Molecke (1976, 1983) to simulate fluids entering a domal salt repository or relatively pure halite.
- d. Alkalinity reported as equivalent HCO<sub>3</sub><sup>-</sup> (solutions titrated to pH = 4.5), but most of the alkalinity probably reflects B(III) species.
- e. Extended alkalinity reported as equivalent HCO<sub>3</sub><sup>-</sup> (solutions titrated to pH = 2.5 to 3.0).
- f. Probably present mainly as H<sub>3</sub>BO<sub>3</sub> and HB<sub>4</sub>O<sub>7</sub><sup>-</sup> or H<sub>3</sub>BO<sub>3</sub> and B(OH)<sub>4</sub><sup>-</sup>.
- g. Eh not measured with an Eh electrode or calculated theoretically, but assumed for SB-1, SB-2, SB-3, Brine A, and Brine B to be similar to that of fluids in equilibrium with atmospheric O<sub>2</sub> (for example, Garrels and Christ, 1963, Figure 11.2).
- h. TIC unspecified for SB-2 and SB-3 because it varied by a few orders of magnitude from sample to sample, and was undetectable in several samples.

Although SB-3 is still a preliminary estimate of the average composition of brines from the Salado Fm. at or near the stratigraphic horizon of the WIPP underground workings, preliminary modeling carried out by Brush with the geochemical code EQ3NR (Wolery, 1983; Jackson and Wolery, 1985; also 8.2.1) implies that this brine is at or close to equilibrium with most of the major and minor minerals in the Salado Fm. Stein (1985) characterized the mineralogy of the Salado Fm. at and near the stratigraphic horizon of the repository; a brief description of that study appears in 6.2.2. SB-3 is at or close to equilibrium with anhydrite ( $\text{CaSO}_4$ ), basanite ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), and halite ( $\text{NaCl}$ ). Because the concentration of TIC ( $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ) has not been determined reliably (Table 2.1), it is unclear whether SB-3 is in equilibrium with magnesite ( $\text{MgCO}_3$ ). It is also unclear whether SB-3 is in equilibrium with various clay minerals and quartz ( $\text{SiO}_2$ ) because the ion interaction parameters required to compute the activity coefficients for Al(III) and Si(IV) species in brines, and hence the solubilities of clays and quartz, have not yet been determined experimentally and incorporated into the EQ3NR data base (8.2.1, 8.2.3, and 8.3.1.1).

### 2.3.2 Castile-Fm. Brines

Popielak et al. (1983) investigated the occurrence of brine reservoirs in the Castile Fm. in the vicinity of the WIPP Site and analyzed numerous samples of these brines from three drillholes. Because the WIPP Project has not studied the chemistry of these fluids since the investigation of Popielak et al. (1983), Brush will use the results of their chemical analyses to define a standard Castile-Fm. brine for studies of repository and radionuclide chemistry.

Brush and Anderson (1988b) used the average chemical composition of WIPP-12 (Table 2.3) reported by Popielak et al. (1983) for preliminary estimates of the speciation and solubilities of radionuclides in Castile-Fm. brines (7.2). They selected WIPP-12 because, of the three drillholes studied by Popielak et al. (1983), it is the closest to the WIPP Site, about 1.5 km north of the Waste Handling Shaft.

Since these estimates Brush has noticed that the average composition for WIPP-12 reported by Popielak et al. (1983) deviated from electrical neutrality by about 1 M. Because this deviation is so large, Brush decided to use ERDA-6 (Table 2.3) as his standard fluid from a Castile brine reservoir, despite the fact that ERDA-6 is 11 km northeast of the Waste Handling Shaft.

Because the brines from ERDA-6 are not necessarily representative of any Castile-Fm. brines that may occur beneath the repository, Brush may also use data for Union (Table 2.3), the third well studied by Popielak et al. (1983), for his study of reactions between Castile-Fm. brines and Salado-Fm. brines and minerals (2.4.5).

Brush is developing a formulation for ERDA-6 for Molecke's bin-scale tests with CH TRU waste. A description of this formulation will appear elsewhere.

TABLE 2.3

COMPARISON OF THE AVERAGE COMPOSITIONS OF BRINES FROM RESERVOIRS  
IN THE CASTILE FM. <sup>a</sup>

| Element or<br>Chemical<br>Property              | ERDA-6  | WIPP-12 | Union   |
|---|---------|---------|---------|
| Alk. (mM) <sup>b, c</sup>                       | 43      | 47      | 35      |
| B <sup>3+</sup> (mM) <sup>d, e</sup>            | 63      | 92      | 100     |
| Br <sup>-</sup> (mM) <sup>e</sup>               | 11      | 6.4     | 6.0     |
| Ca <sup>2+</sup> (mM) <sup>e</sup>              | 12      | 8.7     | 8.5     |
| Cl <sup>-</sup> (M) <sup>e</sup>                | 4.8     | 5.02    | 4.8     |
| Eh (mV) <sup>f</sup>                            | -152    | -225    | -233    |
| K <sup>+</sup> (mM) <sup>e</sup>                | 97      | 74      | 100     |
| Mg <sup>2+</sup> (mM) <sup>e</sup>              | 19      | 66      | 86      |
| Na <sup>+</sup> (M) <sup>e</sup>                | 4.87    | 6.00    | 4.83    |
| pH (std. units) <sup>f</sup>                    | 6.17    | 7.06    | 7.10    |
| SGS   | 1.216   | 1.215   | 1.216   |
| SO <sub>4</sub> <sup>2-</sup> (mM) <sup>e</sup> | 170     | 190     | 230     |
| TDS (mg/l) <sup>e</sup>                         | 330,000 | 328,000 | 390,000 |
| TIC (mM) <sup>h, i</sup>                        | 16      | 5.6     | -       |

a. From Popielak et al. (1983).

b. Reported as equivalent HCO<sub>3</sub><sup>-</sup>, but probably reflects B(III) species (TIC averages only 16 mM in ERDA 6 and 5.6 mM in WIPP 12).

c. Average of 20 field determinations from ERDA-6, 55 from WIPP-12, and three from Union.

d. Probably present mainly as H<sub>3</sub>BO<sub>3</sub> and HB<sub>4</sub>O<sub>7</sub><sup>-</sup> or H<sub>3</sub>BO<sub>3</sub> and B(OH)<sub>4</sub><sup>-</sup>.

e. Average of ten laboratory determinations from ERDA-6, 13 from WIPP-12, and three from Union.

f. Average of 40 field determinations from ERDA-6, 59 from WIPP-12, and four from Union.

g. Average of 39 field determinations from ERDA-6, 59 from WIPP-12, and four from Union.

h. Reported as equivalent HCO<sub>3</sub><sup>-</sup>.

i. Number and location of determinations unspecified.



### 2.3.3 Fluids from Overlying Formations

Two groups are studying the chemistry of fluids from the Rustler Fm. and the Rustler/Salado contact zone in the vicinity of the WIPP Site. For results from the Water Quality Sampling Program, see: Uhland and Randall, 1986; Uhland, Randall, and Carrasco, 1987; Randall, Crawley, and Lyon, 1988. See Robinson (1988) and Lappin et al. (1989) for results from SNL. These groups participate in an interlaboratory comparison study comparable to that under way for analyses of brines from the Salado Fm. (2.4.3).

Brush is evaluating these previously published results to select chemical analyses of fluids that could seep down the shafts, along the drifts, and around or through the seals to WIPP disposal rooms. Brush is currently using five of these fluids (Table 2.4) for his study of reactions between fluids from overlying formations and Salado-Fm. brines and minerals (2.4.6).

Eventually, Brush might also consider fluids from overlying formations other than the Rustler Fm.

## 2.4 DESCRIPTION OF LABORATORY, MODELING, AND FIELD STUDIES

The objectives of these studies are to: (1) quantify the causes of chemical variations in brines from the Salado Fm. (2.4.1); (2) quantify any spatial or stratigraphic variations in Salado-Fm. brines (2.4.2); (3) quantify the variations caused by differences in the analytical techniques used by the three laboratories analyzing Salado-Fm. brines (2.4.3); (4) quantify the effects of sampling artifacts described in 2.3.1.1 on variations in Salado-Fm. brines (2.4.4); (5) simulate reactions between fluids from the Castile Fm. or overlying formations and Salado-Fm. brines and minerals (2.4.5 and 2.4.6).

B. M. Rutherford of SNL developed a statistical model to quantify the possible causes of chemical variations in brines from the Salado Fm. (2.4.1) and used it to analyze data obtained by Stein and Krumhansl (1986, 1988), Deal (1989), and Deal et al. (1989). This analysis is guiding additional characterization of these brines and an interlaboratory comparison. As Rutherford obtains results from these studies, he will revise the model and use it to define a standard Salado-Fm. brine and its possible compositional variations.

C. L. Stein and J. L. Krumhansl of SNL are quantifying any spatial and stratigraphic chemical variations in Salado-Fm. brines (2.4.2). Rutherford's (1989) statistical analysis of the causes of chemical variations in brines from the Salado Fm. implies that hole type (uphole, horizontal hole, or downhole) is significant. However, it is unclear whether the variations associated with hole type are caused by sampling artifacts peculiar to each type of hole or stratigraphic differences in brine chemistry. His analysis also suggests that brines from the eastern and western ends of the northern, experimental area of the WIPP underground workings are similar chemically; there are insufficient data at present to determine whether the brines from the southern area of the mine, where waste will

TABLE 2.4

COMPARISON OF THE COMPOSITIONS OF SELECTED FLUIDS FROM OVERLYING FORMATIONS<sup>a</sup>

| Element or<br>Chemical<br>Property | Air<br>Intake<br>Shaft <sup>a,b</sup> | H-1 <sup>b,c</sup> | H-1 <sup>c,d</sup> | H-1 <sup>c,e</sup>  | WIPP-19 <sup>b,c</sup> |
|------------------------------------|---------------------------------------|--------------------|--------------------|---------------------|------------------------|
| Alk. (mM) <sup>f</sup>             | 1.1                                   | 1.6                | 1.5                | 11                  | 1.4                    |
| B <sup>3+</sup> (mM) <sup>g</sup>  | 2.8                                   | 0.22               | 0.20               | 10                  | 3.1 <sup>h</sup>       |
| Br <sup>-</sup> (mM)               | 0.37                                  | -                  | -                  | -                   | 1.30 <sup>h</sup>      |
| Ca <sup>2+</sup> (mM)              | 23                                    | 19                 | 22                 | 320                 | 46 <sup>h</sup>        |
| Cl <sup>-</sup> (mM)               | 567                                   | 340                | 230                | 5,900               | 1,700 <sup>h</sup>     |
| K <sup>+</sup> (mM)                | 8.3                                   | 4.9                | 1.8                | 430                 | 21 <sup>h</sup>        |
| Mg <sup>2+</sup> (mM)              | 23                                    | 12                 | 11                 | 1,200               | 88 <sup>h</sup>        |
| Na <sup>+</sup> (mM)               | 600                                   | 410                | 250                | 2,400               | 1,400 <sup>h</sup>     |
| pH (std. units)                    | 7.7 <sup>i</sup>                      | 7.6                | 7.4                | 7.9                 | 7.0                    |
| SG                                 | 1.04                                  | 1.022 <sup>j</sup> | 1.021 <sup>j</sup> | 1.23 <sup>j,k</sup> | 1.07                   |
| SO <sub>4</sub> <sup>2-</sup> (mM) | 77                                    | 77                 | 41                 | 5.4                 | 54 <sup>h</sup>        |
| TDS (mg/l)                         | 42,600 <sup>i</sup>                   | 30,000             | 18,900             | 330,000             | 102,000 <sup>h</sup>   |

a. From Siegel (personal communication).

b. Sampled from the Culebra Dolomite, a member of the Rustler Fm.

c. From a compilation of previous analyses by Lappin et al. (1989).

d. Sampled from the Magenta Dolomite, a member of the Rustler Fm.

e. Sampled from the Rustler/Salado contact zone.

f. Alkalinity reported as equivalent HCO<sub>3</sub><sup>-</sup>.

g. Probably present mainly as H<sub>3</sub>BO<sub>3</sub> and HB<sub>4</sub>O<sub>7</sub><sup>-</sup> or H<sub>3</sub>BO<sub>3</sub> and B(OH)<sub>4</sub><sup>-</sup>.

h. Represents average of range reported by Lappin et al. (1989).

i. Represents average of two values reported by Siegel (personal communication).

j. Represents densities in g/cm<sup>3</sup>.

k. Estimated for use in EQ3/6.

be emplaced, are similar to brines from the northern area. Stein and Krumhansl are therefore carrying out additional characterization (sampling and analysis) of these brines.

Brush is quantifying the variations caused by differences in the analytical techniques used by the laboratories analyzing Salado-Fm. brines (2.4.3). Rutherford's (1989) analysis implies that differences among the

techniques used by the three laboratories analyzing these brines and temporal variations in the techniques used at each laboratory are significant. Brush is carrying out an interlaboratory comparison to quantify these variations.

Brush will also quantify the effects of sampling artifacts on chemical variations in Salado-Fm. brines (2.4.4). Sampling artifacts peculiar to each type of hole could contribute to the chemical differences between brines collected from upholes, horizontal holes, and downholes (2.3.1.1).

Finally, Brush will simulate reactions between brines from the Castile or overlying formations and brines and minerals from the Salado Fm. to predict the most likely compositions and expected variability of these fluids from other formations after they enter the repository and react with its contents (2.4.5 and 2.4.6). Because degradation of the shaft and panel seals and seepage of fluids down the shafts and along the drifts to the waste is unlikely, the study with fluids from overlying formations has low priority.

#### **2.4.1 Quantification of the Causes of Chemical Variations in Salado-Fm. Brines**

Rutherford (1989) developed a statistical model of the causes of chemical variations in brines from the Salado Fm. This model includes terms that represent: (1) variations caused by hole type (this term encompasses variations due to artifacts such as differential evaporation associated with upholes, downholes, floor holes, and horizontal holes, and any stratigraphic variations); (2) large-scale and small-scale spatial variations; (3) interlaboratory and intralaboratory variations caused by differences in personnel or procedures among the three laboratories analyzing Salado-Fm. brines, changes in personnel or procedures at a given laboratory, or the inherent variations in a procedure at a given laboratory at a given time; (4) temporal variations resulting from in situ variations in brine chemistry, variations in collection, storage, and shipping procedures, or seasonal effects on collection, storage, and shipping; (5) random variations. The model includes terms that represent each type of variation separately and terms that represent interactions between separate types of variations.

Based on his analysis of data reported by Stein and Krumhansl (1986, 1988), Deal (1989), and Deal et al. (1989), Rutherford concluded that variations associated with hole type are significant, but it is unclear whether the variations associated with hole type are caused by sampling artifacts or stratigraphic differences. He also concluded that brines from the eastern and western ends of the northern, experimental area of the WIPP underground workings are similar chemically but that data are insufficient at present to determine whether the brines from the southern area of the mine, where waste will be emplaced, are similar to brines from the northern area. Finally, he concluded that interlaboratory and intralaboratory differences are significant.

To guide the design of additional characterization of brines from the Salado Fm. and the interlaboratory comparison, Rutherford (1989) then calculated the probabilities of failing to identify real variations in

the chemical elements or properties of interest, or falsely identifying variations where none exist as a function of the number of samples analyzed. Brush used Rutherford's (1989) results to optimize the number of samples based on the tradeoff between increasing his confidence in the conclusions drawn and the time and expense of carrying out additional sampling and analysis.

#### **2.4.2 Quantification of Spatial and Stratigraphic Variations in Salado-Fm. Brines**

Stein and Krumhansl are carrying out additional sampling and chemical analysis to determine: (1) whether at a given stratigraphic horizon within the drifts, there are significant chemical differences between brines from the northern and southern areas of the WIPP underground workings; (2) whether at a given location within the mine there are significant chemical differences between brines collected from different stratigraphic horizons within the drifts. To reduce possible variations between the previous results and those from this study, they will follow their previous sampling and analytical procedures as closely as possible (Stein and Krumhansl, 1986; 1988).

For the current study, Rutledge and Burford (1989) installed three sampling arrays in the WIPP underground workings. They selected the locations for these arrays to: (1) sample brines from the northern, central, and southern areas of the mine; (2) sample recently excavated drifts to ensure that as many holes as possible produce brine (dehydration of the DRZ with time reduces the likelihood of sufficient sample accumulation with time), and to minimize any reduction of stratigraphic variations by vertical dispersion of brine during flow through the DRZ. Restricting the arrays to recently excavated drifts significantly reduced their choice of locations. Based on these criteria, they installed arrays in the east rib of Room L-4, about 10 m south of the north end; on the south rib of S-90, the access drift to Room Q, about 15 m east of the Room-Q instrument alcove; and in the north rib of S-1600, the north access drift to Panel 1, opposite Room 1 (Figure 2.1).

Rutledge and Burford (1989) used a hand-held drill with a 2.5-cm-diameter bit to drill horizontal holes to a depth of about 20 cm. They removed the cuttings with a bottle brush, followed by blowing with compressed air, which may have caused evaporation and changed the composition of the brines adjacent to the holes. Next, they inserted samplers consisting of sponges wrapped in filter paper to prevent particulate contamination. They then sealed the holes with rubber stoppers and stretched plastic across the openings to minimize evaporation.

The northern array consists of four rows and six columns. The rows are located in the following lithostratigraphic units of Department of Energy (1987b) Map Unit 0 (halite), 3 (halite), 4 (argillaceous halite), and 5 (halite). The central array comprises five rows and six columns; the rows are located in Map Unit 0 (halite), 1 (halite), 2 (argillaceous halite), and 4 (argillaceous halite), and Clay F. The southern array consists of four rows and six columns; the rows are located in Map Unit 0 (halite), 1 (halite), 5 (halite), and 6 (halite). The spacing between holes in each

row varies from 0.2 to 3 m and varies from array to array and even from row to row within the northern and southern arrays.

Clearly, these arrays do not satisfy the objective of sampling fluids from the same strata in the northern, central, and southern areas of the WIPP underground workings; the only stratum sampled by all three arrays is Map Unit 0. Furthermore, personnel mapping S-90 sprayed the central array with asaline H<sub>2</sub>O to expose fresh surface, thus introducing significant uncertainties into any results obtained from this array. Because of the increased permeability of the DRZ, the H<sub>2</sub>O used to spray the drift could have significantly contaminated the brines in and around these shallow holes; there is no way to determine the extent of contamination or the original composition of the brines from this array. Because of the poor stratigraphic control of all three arrays and the loss of the central array, the only strata sampled by two arrays are Map Units 0 and 5.

Despite these problems, Stein and Krumhansl will attempt to obtain as much information as possible from this study.

#### **2.4.3 Quantification of Variations in Analytical Techniques Used for Salado-Fm. Brines**

Brush is carrying out an interlaboratory comparison to quantify chemical variations caused by differences between the techniques used by the three laboratories and temporal differences in the techniques used at each laboratory.

For this study, Brush submits samples of synthetic brines of known composition to each of these laboratories for analysis. The results of Rutherford's (1989) statistical analysis imply that Brush should submit three rounds of samples, with nine samples per round, to each of the three laboratories to reduce the uncertainties in Rutherford's estimates of the interlaboratory and intralaboratory variations as much as possible. Because the BSEP provides most of the data with which he will define the "average" composition of brines from the Salado Fm., Brush submits each round of samples for the interlaboratory comparison study at the same time BSEP samples are sent to the IT and UNC laboratories for analysis. This ensures that the samples of synthetic brines are numbered, handled, prepared, shipped, and analyzed in a manner identical to that of the BSEP samples. SNL personnel attempt to guarantee a "blind" intercomparison by numbering the synthetic brines and interspersing them among the BSEP samples without informing any IT or UNC personnel of the identities of the synthetic samples. Because Stein and Krumhansl sample and analyze brines themselves, it is impossible to intersperse samples of synthetic brines among their samples without their knowledge. Brush nevertheless requests that they treat these samples identically to other samples.

#### **2.4.4 Quantification of the Effects of Sampling Artifacts on Variations in Salado-Fm. Brines**

Brush will carry out a laboratory and modeling study to quantify the effects of different sampling methods (hole type, collection time, etc.) on chemical variations in brines from the Salado Fm.

Brush will conduct laboratory experiments with the apparatus and procedures used for the laboratory study of backfill additives (6.2.1) by bubbling N<sub>2</sub> or other gases through the solution to evaporate H<sub>2</sub>O. Comparison of chemical analyses of the brines before the runs and after various amounts of evaporation are revealing whether this is a plausible explanation for the observed chemical variations between BSEP upholes and downholes. He will evaporate brines collected from the WIPP underground workings (2.3.1.2) to determine if this process causes the differences observed between BSEP upholes and downholes. He may also evaporate a synthetic Salado-Fm. brine once he has defined a standard brine (2.3.1.3) and developed a formulation for it. He will use minerals from the WIPP underground workings (2.3.1.2) in several of these studies.

Brush will also model the evaporation of a variety of brines analyzed by the BSEP, and reactions between these brines and minerals from the repository horizon with the reaction-path code EQ6 (Wolery and Daveler, in preparation; a brief description of this code appears in 8.2.2). He will use the standard mineralogy for the Salado Fm. at or near the stratigraphic horizon of the WIPP specified in 6.2.2.

#### **2.4.5 Simulation of Reactions between Castile-Fm. Brines and Salado-Fm. Brines and Minerals**

Brush will simulate reactions between brines from the Castile Fm. and Salado-Fm. brines and minerals to predict the most likely compositions and expected variability of Castile-Fm. brines after they enter the repository and react with its contents.

Brush will study reactions between brines from the Castile Fm. and brines and minerals from the Salado Fm. with the apparatus and procedures used for the laboratory study of backfill additives (6.2.1). He will use brines and minerals collected from the WIPP underground workings (2.3.1.2) and synthetic Castile-Fm. brines for these experiments. He may also use a synthetic Salado-Fm. brine once he has defined a standard brine (2.3.1.3) and developed a formulation for it.

Brush will also model these reactions with the reaction-path code EQ6 (Wolery and Daveler, in preparation; a brief description of this code appears in 8.2.2). He will use the compositions of brines from the Salado Fm. obtained by the BSEP, his estimates of the average composition of Salado-Fm. brines (2.3.1.3 and Table 2.1), and the average compositions of Castile-Fm. brines reported by Popielak et al. (1983). Table 2.3 gives the compositions of these brines. He will use the standard mineralogy for the Salado Fm. at or near the stratigraphic horizon of the WIPP specified in 6.2.2.

#### **2.4.6 Simulation of Reactions between Fluids from Overlying Formations and Salado-Fm. Brines and Minerals**

Brush will also simulate reactions between fluids from overlying formations and Salado-Fm. brines and minerals to predict the most likely compositions and expected variability of these fluids after they enter the repository and react with its contents.

Brush will study these reactions with the apparatus and procedures used for the laboratory studies of backfill additives (6.2.1). He will sequentially add brines and minerals collected from the WIPP underground workings (2.3.1.2) to synthetic fluids from the Rustler Fm. and the Rustler/Salado contact zone. He may also use a synthetic Salado-Fm. brine once he has defined a standard brine (2.3.1.3) and developed a formulation for it.

Brush will also model this process with the reaction-path code EQ6 (Wolery and Daveler, in preparation; a brief description of this code appears in 8.2.2). He will use the compositions of brines from the Salado Fm. obtained by the BSEP, his estimates of the average composition of Salado-Fm. brines (2.3.1.3 and Table 2.1), and the compositions of brines from the Rustler Fm. and the Rustler/Salado contact zone compiled by Lappin et al. (1989) and Siegel (personal communication). Table 2.4 gives the compositions of these brines. Brush selected the fluids shown in Table 2.4 because: (1) they occur close to the shafts and could seep down the shafts, along the drifts, around or through the seals, and enter WIPP disposal rooms; (2) they exhibit a wide range of salinities and simulate most of the variability expected for the fluids from overlying formations; (3) the analyses of these fluids included enough elements and chemical properties for use in EQ6. Eventually, he may also consider other fluids from the Rustler Fm. and fluids from overlying formations other than the Rustler Fm., such as the Dewey Lake Fm. He will use the standard mineralogy for the Salado Fm. at or near the stratigraphic horizon of the WIPP specified in 6.2.2.

#### **2.4.7 Quality Assurance and Safety**

Rutherford, Stein, and Krumhansl are carrying out their studies of brine chemistry (2.4.1 and 2.4.2, respectively) in accordance with the quality assurance (QA) plan described by SNL (1986). Brush is conducting his studies (2.4.2 through 2.4.6) in compliance with the QA plan discussed by Pickering (1989c). This QA plan meets the requirements of American Society of Mechanical Engineers (1986) and relevant requirements of the Department of Energy (1987a, 1989a, 1989b, 1989c). UNC is analyzing brines from various studies (2.4.4 through 2.4.6) in compliance with a QA plan (UNC, 1989b) approved by Pickering (1990d).

Brush is carrying out his studies in accordance with the safety procedures discussed by Bujewski (1990a, 1990b). UNC is responsible for the development, approval, and implementation of all safety procedures required for its analyses of brines.

### **2.5 RESULTS EXPECTED FROM BIN-SCALE AND ALCOVE TESTS**

Analyses of brines sampled from bin-scale tests with CH TRU waste (Molecke, 1990a) will also provide information on the chemistry of synthetic Salado- and Castile-Fm. brines after reactions with Salado-Fm. minerals used to simulate the crushed-salt backfill. Analyses of brines and gases will also provide results on the chemistry of these brines after reactions with steel containers (3.4), waste constituents such as cellulose and plastics (4.5 and 5.6, respectively), and bentonite and other backfill additives (6.3). Because anoxic corrosion, microbial activity,

radiolysis, and reactions with backfill additives will occur simultaneously in these tests, it may prove difficult to determine the effects of each of these processes on brine chemistry.

## 2.6 SCHEDULES FOR LABORATORY AND MODELING STUDIES

Rutherford (1989) developed a statistical model of chemical variations in brines from the Salado Fm. (2.4.1) at SNL in early FY 1990 and used it to design additional characterization and the interlaboratory comparison of analyses of Salado-Fm. brines. Rutherford will continue to update this model as long as he continues to receive chemical data and will use it to define a standard Salado-Fm. brine.

Stein and Krumhansl started additional characterization of brines from the Salado Fm. (2.4.2) in February 1989. Although Brush expected them to complete this study by the end of September 1989, several problems arose (2.4.2). Rutherford will evaluate the results as soon as he obtains them from Stein and Krumhansl. Based on this evaluation, Brush will decide what additional work is necessary to complete this study. He will provide a schedule later.

Brush started the interlaboratory comparison of analyses of brines from the Salado Fm. in mid-August 1989 and submitted the first round of samples to each of the laboratories that analyze Salado-Fm. brines in early September 1989. He plans to submit three rounds of samples at the same time BSEP samples are sent out for analysis. He will submit the third round of samples in early or mid-March 1990 and will receive the data by the end of April 1990. Statistical analysis of the data and reporting will require about 3 months. Rutherford will complete this study by the end of July 1990.

Brush expected to start studies of the effects of sampling artifacts on chemical variations in brines from the Salado Fm. (2.4.4), and reactions between fluids from other formations and Salado-Fm. brines and minerals (2.4.5 and 2.4.6) at SNL by the beginning of October 1990. He set this date so that he could use the results of additional characterization of Salado-Fm. brines (2.4.2) to reduce the range of possible variations in the compositions of these brines and hence the number of laboratory and modeling experiments in these studies. Because of the problems encountered in the characterization of Salado-Fm. brines during FY 1989 (2.4.2), he may have to delay these studies by 1 year. Rutherford will evaluate the data from Stein and Krumhansl, and Brush will decide whether to reschedule these studies. In either case, he will provide schedules for these studies later.



## 3.0 ANOXIC CORROSION

### 3.1 JUSTIFICATION FOR LABORATORY STUDIES

Lappin et al. (1989) estimated that if brine were present in Waste Isolation Pilot Plant (WIPP) disposal rooms, anoxic corrosion of steel containers (drums and boxes) and Fe and Fe-base alloys in the waste would produce about 2 moles of H<sub>2</sub> per equivalent drum of waste per year for 400 to 500 years, or a total of 900 moles per drum. (See 7.4 for the definition of an equivalent drum.) Anoxic corrosion of steel containers would produce 600 moles of H<sub>2</sub> per drum; anoxic corrosion of Fe and Fe-base alloys in the waste would produce 300 moles of H<sub>2</sub> per drum. Lappin et al. (1989) assumed that brine must be present for anoxic corrosion to occur and that if enough brine were present, anoxic corrosion would consume all of the steel containers and Fe and Fe-base alloys in the waste. These estimates do not include H<sub>2</sub> from anoxic corrosion of Al and Al-base alloys in the waste because there was no estimate of the quantity of these metals in the WIPP inventory at that time. Anoxic corrosion is the process of greatest concern from the standpoint of the gas budget of the repository, despite the fact that these estimates do not include contributions from Al and Al-base alloys, the metals of second greatest concern. Microbial degradation of cellulose, the other significant process, would produce about 1 mole of various gases per drum per year for 600 years, or a total of 600 moles (4.1).

Lappin et al. (1989) also estimated that anoxic corrosion could consume significant quantities of brine. The quantity consumed will depend on the extent to which metals corrode and the H<sub>2</sub>O content of the solid corrosion products, but may be as much as 200 m<sup>3</sup> per room. This estimate does not include the consumption of brine by anoxic corrosion of Al and Al-base alloys.

Because anoxic corrosion would consume brine, the quantity of H<sub>2</sub>O in the disturbed rock zone available for transport to the waste, either by brine inflow or diffusion of H<sub>2</sub>O vapor through the gaseous phase, may prevent the production of 900 moles of H<sub>2</sub> per drum. An integrated model of the effects of gas pressurization, room closure, brine inflow and outflow, and vapor-phase transport of H<sub>2</sub>O is still at an early stage of development. Preliminary calculations suggest that absorption of H<sub>2</sub>O by crushed salt and any bentonite in the backfill and the possible consumption of H<sub>2</sub>O by microbial degradation of cellulose (4.1) may limit the extent of anoxic corrosion of metals.

Although O<sub>2</sub> would prevent anoxic corrosion if present in sufficient quantities (3.2), Brush and Anderson (1988a) estimated that the quantity of O<sub>2</sub> initially present in the air trapped in WIPP disposal rooms at the time they are filled and sealed will oxidize less than 1% of the drums. Radiolysis would produce O<sub>2</sub> if brine were present, but probably not enough to prevent anoxic corrosion. Furthermore, aerobic microorganisms (4.2.1) might consume it faster than anoxic corrosion.

Brush has reviewed the thermodynamic and kinetic evidence for anoxic corrosion of steels in nuclear-waste repositories (3.2). It is still unknown whether anoxic corrosion of Fe and Fe-base alloys would occur if H<sub>2</sub>O vapor or

H<sub>2</sub>O absorbed by backfill materials, but not brine, were present in the repository. The extent to which microbially produced CO<sub>2</sub> will accelerate anoxic corrosion and previously produced H<sub>2</sub> will decelerate anoxic corrosion are also unknown. Finally, the anoxic corrosion rates of Al and Al-base alloys are unclear.

## 3.2 EVIDENCE FOR ANOXIC CORROSION

Thermodynamic calculations and the results of previous laboratory corrosion studies both imply that anoxic corrosion of Fe and Fe-base alloys would produce significant quantities of H<sub>2</sub> in WIPP disposal rooms if sufficient brine were present and O<sub>2</sub> were absent. It is unclear whether anoxic corrosion of Fe and Fe-base alloys by H<sub>2</sub>O vapor would be significant.

### 3.2.1 Thermodynamic Calculations

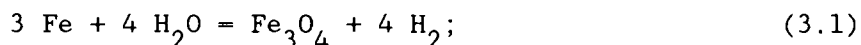
Thermodynamic calculations imply that metallic Fe is unstable in the presence of H<sub>2</sub>O at 25°C and a total pressure of 1 atm (see, for example, the Eh/pH diagrams for Fe in Garrels and Christ, 1965; Pourbaix, 1974; Brookins, 1988). These Eh/pH diagrams and the thermodynamic calculations on which they are based imply: that in the absence of CO<sub>2</sub> and H<sub>2</sub>S, Fe and H<sub>2</sub>O should react to form corrosion products such as Fe<sub>3</sub>O<sub>4</sub> (magnetite), Fe<sub>2</sub>O<sub>3</sub> (hematite), or Fe(OH)<sub>2</sub> (amakinite); that Fe, CO<sub>2</sub>, and H<sub>2</sub>O should react to form FeCO<sub>3</sub> (siderite) if microbially or radiolytically produced CO<sub>2</sub> is present (4.2.1 through 4.2.6); that Fe should react to form FeS<sub>2</sub> (pyrite) if microbially produced H<sub>2</sub>S is present (4.2.5).

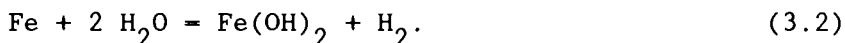
#### 3.2.1.1 CALCULATIONS FOR CARBON-DIOXIDE- AND HYDROGEN-SULFIDE-FREE SYSTEMS

According to the Eh/pH diagrams described in 3.2.1, two possible Fe corrosion products formed in the presence of H<sub>2</sub>O and the absence of CO<sub>2</sub> and H<sub>2</sub>S are Fe<sub>3</sub>O<sub>4</sub> at low values of Eh and Fe<sub>2</sub>O<sub>3</sub> at high values of Eh. Haberman and Frydrych (1988) observed the formation of Fe<sub>3</sub>O<sub>4</sub> in brines with low Mg<sup>2+</sup> concentrations in their study of anoxic corrosion (a description of this study appears in 3.2.2). If conditions were oxidizing enough to stabilize Fe<sub>2</sub>O<sub>3</sub> or other Fe(III)-bearing corrosion products, there could be enough O<sub>2</sub> present to promote oxidic corrosion at the expense of anoxic corrosion. Previously obtained results discussed in 3.2.2 imply that oxidic corrosion is much faster than anoxic corrosion. Fe<sub>3</sub>O<sub>4</sub> is therefore the Fe oxide most likely to be produced by anoxic corrosion in CO<sub>2</sub>-free systems.

In addition to Fe<sub>3</sub>O<sub>4</sub>, Fe(OH)<sub>2</sub> is also a possible anoxic corrosion product in the absence of CO<sub>2</sub>. Haberman and Frydrych (1988) observed this phase, which is actually a solid solution with the formula (Fe,Mg,Mn)(OH)<sub>2</sub>, in brines with high Mg<sup>2+</sup> concentrations (3.2.2).

Anoxic corrosion could increase the gas pressure of WIPP disposal rooms significantly. In CO<sub>2</sub>-free systems, the most likely anoxic corrosion reactions are:





The equation relating the standard free energy of a reaction,  $\Delta G^0$ , and the equilibrium constant for that reaction,  $K$ , is:

$$\Delta G_r^0 = - R T \ln K_r, \quad (3.3)$$

which, with a value of  $0.001987 \text{ kcal mole}^{-1} \text{ }^\circ\text{K}^{-1}$  for the gas constant  $R$  and a temperature of  $25^\circ\text{C}$  ( $298^\circ\text{K}$ ), becomes:

$$\Delta G_r^0 = - 1.364 \log K_r. \quad (3.4)$$

Inserting  $K_r$  for Reactions 3.1 and 3.2 in 3.4 gives:

$$\Delta G_{3.1}^0 = - 1.364 \log \left[ \frac{[\text{Fe}_3\text{O}_4] f_{\text{H}_2}^4}{[\text{Fe}]^3 [\text{H}_2\text{O}]^4} \right]; \quad (3.5)$$

$$\Delta G_{3.2}^0 = - 1.364 \log \left[ \frac{[\text{Fe}(\text{OH})_2] f_{\text{H}_2}}{[\text{Fe}] [\text{H}_2\text{O}]^2} \right]. \quad (3.6)$$

In these equations,  $\Delta G^0$  of the reaction equals  $\Sigma \Delta G^0$  of formation of the products minus  $\Sigma \Delta G^0$  of formation of the reactants in units of kcal; the brackets denote thermodynamic activities of solids or liquids;  $f$  is the fugacity of a gas.

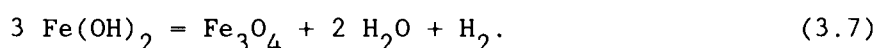
Robie, Hemingway, and Fisher (1978) provided values of  $- 242.0091$  and  $- 56.6781$  kcal per mole for  $\Delta G^0$  of formation for  $\text{Fe}_3\text{O}_4$  and  $\text{H}_2\text{O}$ , respectively. Wagman et al. (1969) gave a value of  $- 116.3$  kcal per mole for  $\Delta G^0$  of formation for  $\text{Fe}(\text{OH})_2$ . These data imply values of  $- 15.2967$  and  $- 2.9$  kcal for  $\Delta G^0$  for Reactions 3.1 and 3.2, respectively. The activity of  $\text{H}_2\text{O}$  in brine from the Salado Fm. at or near the stratigraphic horizon of the WIPP is about 0.7. This value is the average of the activities Brush has calculated to date with the EQ3NR speciation and solubility code (Wolery, 1983; Jackson and Wolery, 1985). Assuming an activity of unity for  $\text{Fe}$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{Fe}(\text{OH})_2$ , Equations 3.5 and 3.6 specify equilibrium  $\text{H}_2$  fugacities of about 400 and 60 atm for Reactions 3.1 and 3.2, respectively.

These calculations imply that if sufficient quantities of  $\text{Fe}$  and  $\text{H}_2\text{O}$  were present and  $\text{O}_2$  were absent from WIPP disposal rooms, anoxic corrosion would produce significant  $\text{H}_2$  pressures. The activity of  $\text{H}_2\text{O}$  vapor in equilibrium with brine from the Salado Fm. at or near the stratigraphic horizon of the WIPP is equal to the activity of  $\text{H}_2\text{O}$  in the brine, about 0.7. The thermodynamic calculations described above apply to  $\text{H}_2\text{O}$  vapor as well as to brine.

Significant anoxic corrosion would thus be possible if there were sufficient H<sub>2</sub>O vapor present.

These calculations also illustrate the sensitivity of the equilibrium H<sub>2</sub> fugacity to the identity of the solid corrosion product. Assuming sufficient Fe and H<sub>2</sub>O, anoxic corrosion would reach equilibrium at an H<sub>2</sub> fugacity of 60 atm if Fe(OH)<sub>2</sub> were the corrosion product, but continue to an H<sub>2</sub> fugacity of 400 atm if Fe<sub>3</sub>O<sub>4</sub> were formed. Because the former value is well below lithostatic pressure at the repository horizon (about 150 atm) and the latter well above it, the identity of the corrosion product formed will affect the extent of pressurization significantly.

Fe(OH)<sub>2</sub>, however, is unstable with respect to Fe<sub>3</sub>O<sub>4</sub>. The reaction for the conversion of Fe(OH)<sub>2</sub> to Fe<sub>3</sub>O<sub>4</sub> is:



Inserting K<sub>r</sub> for Reaction 3.7 in Equation 3.4 gives:

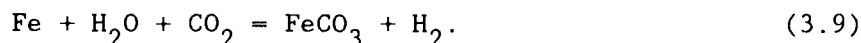
$$\Delta G_{3.7}^0 = - 1.364 \log \left( \frac{[\text{Fe}_3\text{O}_4] [\text{H}_2\text{O}]^2 f_{\text{H}_2}}{[\text{Fe(OH)}_2]^3} \right). \quad (3.8)$$

Values of - 242.0091, - 116.3, and - 56.6781 kcal per mole for Δ G<sup>0</sup> of formation for Fe<sub>3</sub>O<sub>4</sub>, Fe(OH)<sub>2</sub>, and H<sub>2</sub>O, respectively, imply a value of - 6.5 kcal for Δ G<sup>0</sup> for Reaction 3.7. Assuming an activity of 1 for Fe<sub>3</sub>O<sub>4</sub> and Fe(OH)<sub>2</sub>, and an activity of 0.7 for H<sub>2</sub>O in WIPP brine, Equation 3.8 specifies an equilibrium H<sub>2</sub> fugacity of about 1 · 10<sup>5</sup> atm for Reaction 3.7. Clearly, the formation of Fe(OH)<sub>2</sub> would not constrain the H<sub>2</sub> fugacity to 60 atm if Fe<sub>3</sub>O<sub>4</sub> nucleates and replaces Fe(OH)<sub>2</sub>. Both Fe<sub>3</sub>O<sub>4</sub> and Fe(OH)<sub>2</sub> appear as corrosion products in the kinetic studies described in 3.2.2.

All of the calculations described above are sensitive to the quality of the thermodynamic data for both the reactants and products. Because of the complex, highly variable, and often poorly crystalline nature of Fe oxides and hydroxides, it is especially risky to use calculations such as these to predict the extent to which anoxic corrosion would increase the pressure of the repository. Amakinite, for example, is a solid solution of Fe<sup>2+</sup>, Mg<sup>2+</sup>, and Mn<sup>2+</sup>. However, these calculations do show that anoxic corrosion could produce significant H<sub>2</sub> pressures in WIPP disposal rooms.

### 3.2.1.2 CALCULATIONS FOR CARBON-DIOXIDE-BEARING SYSTEMS

In the presence of microbially or radiolytically produced CO<sub>2</sub> (4.2.1 through 4.2.6) and the absence of microbially produced H<sub>2</sub>S (4.2.5), the most likely anoxic corrosion reaction is:



Addition of the equation for the anoxic corrosion of Fe by H<sub>2</sub>O to form Fe<sub>3</sub>O<sub>4</sub> or Fe(OH)<sub>2</sub> and the equation for the reaction of Fe<sub>3</sub>O<sub>4</sub> or Fe(OH)<sub>2</sub> with CO<sub>2</sub> to form FeCO<sub>3</sub> implies that either of these two-step processes is stoichiometrically equivalent to the direct conversion of Fe to FeCO<sub>3</sub> according to the overall reaction depicted by Reaction 3.9.

Inserting K<sub>R</sub> for Reaction 3.9 in Equation 3.4 yields:

$$\Delta G_{3.9}^0 = - 1.364 \log \left[ \frac{[\text{FeCO}_3] f_{\text{H}_2}}{[\text{Fe}] [\text{H}_2\text{O}] f_{\text{CO}_2}} \right]. \quad (3.10)$$

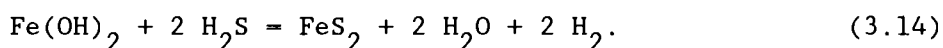
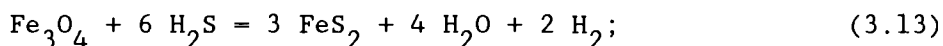
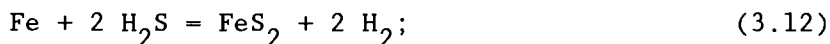
Robie, Hemingway, and Fisher (1978) provided values of - 94.2579, - 159.345, and - 56.6781 kcal per mole for  $\Delta G^0$  of formation for CO<sub>2</sub>, FeCO<sub>3</sub>, and H<sub>2</sub>O, respectively. These data imply a value of - 8.409 kcal for  $\Delta G^0$  for Reaction 3.9. Assuming an activity of 1 for Fe and FeCO<sub>3</sub>, and an activity of 0.7 for H<sub>2</sub>O in WIPP brine (3.2.1.1), the equation relating the equilibrium fugacities of CO<sub>2</sub> and H<sub>2</sub> is:

$$6.01 = \log f_{\text{H}_2} - \log f_{\text{CO}_2}. \quad (3.11)$$

Equation 3.11 implies that the H<sub>2</sub> fugacity would exceed the CO<sub>2</sub> fugacity by a factor of about 1 · 10<sup>6</sup>. If, for example, the H<sub>2</sub> fugacity were 1, 10, or 100 atm, the CO<sub>2</sub> fugacity would be 1 · 10<sup>-6</sup>, 1 · 10<sup>-5</sup>, or 1 · 10<sup>-4</sup> atm, respectively. This in turn implies that Fe, Fe-base alloys, or their corrosion products should consume almost all of the microbially produced CO<sub>2</sub> that could be present in WIPP disposal rooms. Lappin et al. (1989) estimated that there are about 900 moles of Fe and Fe-base alloys per equivalent drum of waste. This includes the steel containers and the Fe and Fe-base alloys in the waste. Because each mole of Fe would consume 1 mole of CO<sub>2</sub> (Reaction 3.9), the conversion of all of these metals to FeCO<sub>3</sub> would consume 900 moles of CO<sub>2</sub>, which is more than the total microbial gas production potential calculated by Lappin et al. (1989), about 600 moles per drum. Not all of this microbially produced gas would be CO<sub>2</sub>; microbial activity would also produce significant quantities of CH<sub>4</sub>, N<sub>2</sub>, and H<sub>2</sub>S.

### 3.2.1.3 CALCULATIONS FOR HYDROGEN-SULFIDE-BEARING SYSTEMS

In the event of microbial SO<sub>4</sub><sup>2-</sup> reduction (4.2.5), H<sub>2</sub>S would react with Fe or its corrosion products to form compounds such as FeS<sub>1-x</sub> (mackinawite), FeS · nH<sub>2</sub>O (hydrotroilite), Fe<sub>3</sub>S<sub>4</sub> (greigite), and, eventually, FeS<sub>2</sub> (pyrite). Because these reactions are complex and involve several intermediate steps, some of which may be mediated by microorganisms, it is easier to describe this process by writing overall equations representative of FeS<sub>2</sub> formation:



Clearly, cessation of this process after formation of a compound with the composition FeS would consume only half as much H<sub>2</sub>S and produce only half as much H<sub>2</sub> per mole of Fe consumed as the formation of FeS<sub>2</sub>.

Inserting K<sub>r</sub> for Reactions 3.12, 3.13, and 3.14 in Equation 3.4 gives:

$$\Delta G_{3.12}^0 = - 1.364 \log \left( \frac{[\text{FeS}_2] f_{\text{H}_2}^2}{[\text{Fe}] f_{\text{H}_2\text{S}}^2} \right); \quad (3.15)$$

$$\Delta G_{3.13}^0 = - 1.364 \log \left( \frac{[\text{FeS}_2]^3 [\text{H}_2\text{O}]^4 f_{\text{H}_2}^2}{[\text{Fe}_3\text{O}_4] f_{\text{H}_2\text{S}}^6} \right); \quad (3.16)$$

$$\Delta G_{3.14}^0 = - 1.364 \log \left( \frac{[\text{FeS}_2] [\text{H}_2\text{O}]^2 f_{\text{H}_2}^2}{[\text{Fe}(\text{OH})_2] f_{\text{H}_2\text{S}}^2} \right). \quad (3.17)$$

Robie, Hemingway, and Fisher (1978) provided values of - 242.0091, - 38.2956, - 56.6781, and - 38.2956 kcal per mole for  $\Delta G^0$  of formation for Fe<sub>3</sub>O<sub>4</sub>, FeS<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>S, respectively. Wagman et al. (1969) gave a value of - 116.3 kcal per mole for  $\Delta G^0$  of formation for Fe(OH)<sub>2</sub>. These data imply values of - 22.2616, - 51.4881, and - 19.3 kcal for  $\Delta G^0$  for Reactions 3.12, 3.13, and 3.14, respectively. Assuming an activity of 1 for Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(OH)<sub>2</sub>, and FeS<sub>2</sub>, and an activity of 0.7 for H<sub>2</sub>O in WIPP brine (3.2.1.1), the equations relating the equilibrium fugacities of H<sub>2</sub> and H<sub>2</sub>S are:

$$8.160 = \log f_{\text{H}_2} - \log f_{\text{H}_2\text{S}}; \quad (3.18)$$

$$19.184 = \log f_{\text{H}_2} - 3 \log f_{\text{H}_2\text{S}}; \quad (3.19)$$

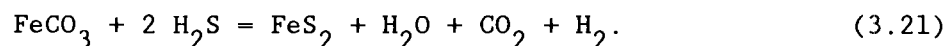
$$14.4 = \log f_{\text{H}_2} - 2 \log f_{\text{H}_2\text{S}}. \quad (3.20)$$

Equations 3.18, 3.19, and 3.20 imply that the H<sub>2</sub> fugacity would exceed the H<sub>2</sub>S fugacity by several orders of magnitude. This in turn implies that Fe, Fe-base alloys, or their corrosion products should consume virtually all of the microbially produced H<sub>2</sub>S that could be present in WIPP disposal rooms. Because there are about 900 moles of Fe and Fe-base alloys per equivalent drum of waste (Lappin et al., 1989) and each mole of Fe would consume at least 1 mole of H<sub>2</sub>S (assuming FeS were formed), and probably 2 moles of H<sub>2</sub>S (assuming FeS<sub>2</sub> were formed), the conversion of all of the Fe and Fe-base alloys to FeCO<sub>3</sub> would consume 900 to 1,800 moles of H<sub>2</sub>S. This is

significantly more than the total microbial gas production potential estimated by Lappin et al. (1989), about 600 moles per drum.

#### 3.2.1.4 CALCULATIONS FOR CARBON-DIOXIDE- AND HYDROGEN-SULFIDE-BEARING SYSTEMS

In the presence of microbially or radiolytically produced CO<sub>2</sub> (4.2.1 through 4.2.6) and microbially produced H<sub>2</sub>S (4.2.5), FeCO<sub>3</sub> will react with H<sub>2</sub>S to form pyrite according to the equation:



Inserting K<sub>r</sub> for Reaction 3.21 in Equation 3.4 yields:

$$\Delta G_{3.21}^0 = -1.364 \log \left[ \frac{[\text{FeS}_2] [\text{H}_2\text{O}] f_{\text{CO}_2} f_{\text{H}_2}}{[\text{FeCO}_3] f_{\text{H}_2\text{S}}^2} \right]. \quad (3.22)$$

Robie, Hemingway, and Fisher (1978) listed values of - 94.2579, - 159.345, - 38.2956, - 56.6781, and - 8.0170 kcal per mole for Δ G<sup>0</sup> of formation for CO<sub>2</sub>, FeCO<sub>3</sub>, FeS<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub>S, respectively. These data imply a value of - 13.8526 kcal for Δ G<sup>0</sup> for Reaction 3.21. Assuming an activity of 1 for FeCO<sub>3</sub> and FeS<sub>2</sub>, and an activity of 0.7 for H<sub>2</sub>O in WIPP brine (3.2.1.1), the equation relating the equilibrium fugacities of CO<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>S is:

$$10.31 = \log f_{\text{H}_2} - \log f_{\text{CO}_2} - 2 \log f_{\text{H}_2\text{S}}. \quad (3.23)$$

Equation 3.23 implies that given reasonable H<sub>2</sub> and H<sub>2</sub>S fugacities, relatively low CO<sub>2</sub> fugacities would be required to stabilize FeCO<sub>3</sub>. If the H<sub>2</sub> fugacity were 1, 10, or 100 atm and the H<sub>2</sub>S fugacity were 1 · 10<sup>-6</sup> atm, the CO<sub>2</sub> fugacity would be 2 · 10<sup>-2</sup>, 2 · 10<sup>-3</sup>, or 2 · 10<sup>-4</sup> atm, respectively. This in turn implies that given these H<sub>2</sub> and H<sub>2</sub>S fugacities, a CO<sub>2</sub> fugacity of only 2 · 10<sup>-2</sup>, 2 · 10<sup>-3</sup>, or 2 · 10<sup>-4</sup> atm would be required to stabilize FeCO<sub>3</sub>. If the CO<sub>2</sub> fugacity were above these values, FeCO<sub>3</sub> would consume microbially or radiolytically produced CO<sub>2</sub> despite the presence of microbially produced H<sub>2</sub>S, at least until all of the Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(OH)<sub>2</sub>, or FeS<sub>2</sub> were consumed.

### 3.2.2 Kinetic Data

Given that Fe is thermodynamically unstable with respect to various Fe oxides and hydroxides, FeCO<sub>3</sub>, and FeS<sub>2</sub>, the next issue is whether anoxic corrosion will occur at significant rates. Molecke (1979) reviewed data obtained by Braithwaite (1978) and Braithwaite and Larson (1978) and concluded that if brine were present in WIPP disposal rooms, anoxic corrosion would produce H<sub>2</sub>.

Braithwaite (1978) studied the oxic and anoxic corrosion of AISI 1018 steel in Brine B (Table 2.2) at room temperature and pressure. In general, the drums to be emplaced in the WIPP are made of an alloy closer in

composition to AISI 1008 steel; however, Brush expects that the corrosion behavior of these two steels, AISI 1008 and 1018, would be very similar. Braithwaite (1978) carried out experiments in a glass tube connected by Swagelok fittings and valves to a pressure gauge and a sampling port. He cleaned the surfaces of the coupons by abrasive blasting. Prior to deaerated runs, he removed all of the air by purging the brine with an inert gas, presumably N<sub>2</sub>, pressurizing the system with N<sub>2</sub>, and venting the system. He repeated this procedure several times prior to every deaerated run to ensure that all residual air was removed.

Braithwaite and Larson (1978) concluded that O<sub>2</sub> was consumed during experiments carried out under aerated conditions and that H<sub>2</sub> was produced during experiments conducted under deaerated conditions. They based these conclusions on pressure decreases measured during aerated runs and pressure increases measured during deaerated runs. Furthermore, they sampled and analyzed the gas above the brine by gas chromatography during and after both types of runs to confirm that O<sub>2</sub> consumption and H<sub>2</sub> production were responsible for these pressure changes. Braithwaite (personal communication) recently pointed out that during at least one aerated run, pressure decreased initially as O<sub>2</sub> was consumed, then increased after the depletion of all the O<sub>2</sub> due to H<sub>2</sub> production. Braithwaite and Larson (1978) measured an O<sub>2</sub> consumption rate of 5.4 moles per m<sup>2</sup> per year under aerated conditions and an H<sub>2</sub> production rate of 0.5 moles per m<sup>2</sup> per year under deaerated conditions.

Because these results imply that oxidic corrosion is about 1 order of magnitude faster than anoxic corrosion, it is reasonable to conclude that given sufficient O<sub>2</sub>, oxidic corrosion will occur at the expense of anoxic corrosion. However, radiolytically produced O<sub>2</sub> will not necessarily preclude anoxic corrosion at other locations because this O<sub>2</sub> could be removed by oxidic corrosion, aerobic microbial activity, radiolytically induced uptake by plastics, or oxidation of dissolved species such as Fe<sup>2+</sup> before it diffuses more than a few centimeters.

Haberman and Frydrych (1988) studied the anoxic corrosion of ASTM A216 Grade WCA steel, another low-C steel, in synthetic Permian Basin brines at temperatures of 90, 150, and 200°C and pressures of 500 and 1,000 psig. The Salt Repository Project (SRP) for commercial spent fuel and high-level waste (HLW) funded this work. They carried out experiments under static and flowing conditions in 4-L Hastelloy C-276 autoclaves. They purged their autoclaves with Ar and maintained an O<sub>2</sub> concentration of less than 50 ppb throughout their experiments, which lasted 1, 3, and 6 months. After each test interval, they identified the corrosion products by x-ray diffraction analysis and determined the corrosion rate by removing the corrosion products and measuring the weight loss (3.3.1).

Haberman and Frydrych (1988) reported significant anoxic corrosion rates for A216 Grade WCA steel at high temperatures, that the anoxic corrosion rate increased with the Mg<sup>2+</sup> concentration of their brines, and that their anoxic corrosion product was Fe<sub>3</sub>O<sub>4</sub> at low Mg<sup>2+</sup> concentrations and Fe(OH)<sub>2</sub> at high Mg<sup>2+</sup> concentrations. Brush and Anderson (1988a) extrapolated these rates to 30°C, the expected temperature of WIPP disposal rooms (1.10.1), and a Mg<sup>2+</sup> concentration of 1 M, its expected concentration in brines from the Salado Fm. (2.3.1.3). They calculated an H<sub>2</sub> production rate of 0.3 moles per m<sup>2</sup> per year.



The rate calculated by Brush and Anderson (1988a) from these extrapolated data is somewhat lower than those obtained by Braithwaite and Larson (1978). It is unclear whether this difference is significant in view of experimental error and the uncertainties in extrapolating the results of Haberman and Frydrych (1988) to expected WIPP conditions. In any case, they averaged these results and calculated an H<sub>2</sub> production rate of 2 moles per drum per year for WIPP disposal rooms.

Finally, Simpson and Schenk (1989) studied the anoxic corrosion of low-C steel in natural and synthetic granitic groundwaters from Switzerland and NaCl solutions at 25, 50, and 80°C and a pressure of 1 atm. They carried out their experiments in glass flasks. They purged their flasks continuously with N<sub>2</sub> and determined the corrosion rate by periodic sampling of the effluent N<sub>2</sub> and analysis for H<sub>2</sub> by gas chromatography. Simpson and Schenk (1989) measured an H<sub>2</sub> production rate of 0.2 moles per m<sup>2</sup> per year at 25°C.

Simpson and Schenk (1989) concluded that Reactions 3.1 and 3.2 (3.2.1) produce H<sub>2</sub> faster than it could diffuse through the compacted bentonite backfill proposed for a Swiss repository for HLW. Their thermodynamic calculations imply an equilibrium H<sub>2</sub> fugacity of about 500 atm for Reaction 3.1 and 100 atm for Reaction 3.2 at 25°C. These pressures exceed or are close to the lithostatic pressure expected for a Swiss repository in granite, 120 atm. Similar experiments carried out with high-purity Cu yielded no H<sub>2</sub>.

These studies imply that anoxic corrosion is a potentially serious issue for any nuclear-waste repository that contains significant quantities of Fe or Fe-base alloys and aqueous solutions, anoxic conditions, and low-permeability backfill or host rock.

It is unknown whether anoxic corrosion will occur in the WIPP, or any other repository, if H<sub>2</sub>O vapor or H<sub>2</sub>O absorbed by backfill materials, but not brine, is present in the repository. The extent to which CO<sub>2</sub> will accelerate or H<sub>2</sub> will decelerate anoxic corrosion, if the partial pressures of these gases is significant, is also unknown. Finally, the rates at which Al and Al-base alloys, the metals of greatest concern after Fe and Fe-base alloys, will corrode under anoxic conditions are unclear.

### 3.3 DESCRIPTION OF LABORATORY STUDIES

The objectives of these studies are to: (1) quantify anoxic corrosion of steels by brine, H<sub>2</sub>O vapor, and H<sub>2</sub>O absorbed by backfill materials in the presence of N<sub>2</sub> or CO<sub>2</sub> at low pressure (3.3.1); (2) quantify anoxic corrosion of steels by brine, H<sub>2</sub>O vapor, and H<sub>2</sub>O absorbed by backfill materials (initially bentonite, but perhaps eventually the proposed backfill additives described in 6.1) in the presence of CO<sub>2</sub> or H<sub>2</sub> at high pressures (3.3.2); (3) determine the effects of other factors, such as basic conditions, O<sub>2</sub> concentration, and the presence of the proposed backfill additive CuSO<sub>4</sub> (6.1) on anoxic corrosion of steels (3.3.3); (4) quantify anoxic corrosion of other metals, especially Al and Al-base alloys (3.3.4).

R. E. Westerman of Pacific Northwest Laboratory (PNL) will quantify anoxic corrosion of steels under humid and inundated conditions, and by H<sub>2</sub>O-bearing backfill materials with N<sub>2</sub> at a pressure of about 1 atm to simulate early, CO<sub>2</sub>-free conditions in WIPP disposal rooms (3.3.1). Steels, which

will be present mainly in drums and boxes, are much more abundant in the WIPP inventory than Fe or any other Fe-base alloy, according to Lappin et al. (1989). CO<sub>2</sub>-free conditions will occur if microbial activity or radiolysis fail to produce significant quantities of CO<sub>2</sub> or if the backfill additives CaO, Ca(OH)<sub>2</sub>, KOH, or NaOH are used (6.1). Although anoxic corrosion would produce significant quantities of H<sub>2</sub> and consume significant quantities of H<sub>2</sub>O under CO<sub>2</sub>-free conditions if brine were present in the repository (3.2.1.1 and 3.2.2), the H<sub>2</sub> production rate for WIPP-specific, inundated conditions is still unknown. It is also unknown whether anoxic corrosion would occur under humid conditions, if various H<sub>2</sub>O-bearing backfill materials contact steels, or to what extent CO<sub>2</sub> would increase the anoxic corrosion rate.

Westerman will also quantify anoxic corrosion of steels under humid and inundated conditions and by H<sub>2</sub>O-bearing backfill materials with CO<sub>2</sub> and H<sub>2</sub> at high pressures (3.3.2). CO<sub>2</sub>, if present in WIPP disposal rooms at pressures of even a few atmospheres, would acidify any brine present, increase the anoxic corrosion rate, and convert Fe and Fe-base alloys to the corrosion product FeCO<sub>3</sub>, which would consume significant quantities of CO<sub>2</sub> (3.2.1.2). This could in turn eliminate the need for backfill additives such as CaCO<sub>3</sub>, CaO, Ca(OH)<sub>2</sub>, KOH, or NaOH (6.1). Previously produced H<sub>2</sub> could slow or even stop additional anoxic corrosion as its fugacity increases.

Westerman will determine the effects of other factors, such as basic conditions, O<sub>2</sub> concentration, and the presence of the proposed backfill additive CuSO<sub>4</sub> on anoxic corrosion of steels (3.3.3). Reactions between brine and cements used to remove liquids from sludges, grouts used in seals, or grouts proposed to reduce the permeability of WIPP disposal rooms (Butcher, 1990) could increase the pH to basic values. Reactions between brine and CaO, Ca(OH)<sub>2</sub>, KOH, and NaOH could increase the pH to very basic values. Basic conditions could, in turn, decrease the anoxic corrosion rates of Fe and Fe-base alloys, but increase the anoxic corrosion rates of Al and Al-base alloys. Because oxic corrosion is much faster than anoxic corrosion (3.2.2), O<sub>2</sub> will cause oxic corrosion at the expense of anoxic corrosion. Therefore, radiolytically produced O<sub>2</sub> will prevent anoxic corrosion, at least to some extent. The proposed backfill additive CuSO<sub>4</sub> would, if brine were present, corrode Fe and Fe-base alloys without producing H<sub>2</sub> (6.1), but it is unclear if this reaction would proceed faster than anoxic corrosion, especially under acidic conditions.

Westerman will quantify anoxic corrosion of other metals (3.3.4). After Fe and Fe-base alloys, Al and Al-base alloys are the metals of greatest concern. Although Al and Al-base alloys will produce more H<sub>2</sub> per unit weight than Fe and Fe-base alloys, they are much less abundant in the WIPP inventory and are hence of less concern. Therefore, quantification of anoxic corrosion of Fe and Fe-base alloys has higher priority.

### **3.3.1 QUANTIFICATION OF ANOXIC CORROSION OF STEELS AT LOW PRESSURES**

Westerman will quantify anoxic corrosion of steels under humid and inundated conditions and by H<sub>2</sub>O-bearing backfill materials at 30°C. In all three cases, he will fill the headspace above the brine or backfill materials with CO<sub>2</sub> or N<sub>2</sub> at pressures of about 1 atm.

For this study and those described in 3.3.2 through 3.3.4, Westerman is adapting the procedures used in previous investigations of anoxic corrosion of various steels for the SRP (Westerman et al., 1987).

The containers for this study will consist of 2.4-L (30-cm-high-by-10-cm-diameter), seal-welded vessels fabricated from Hastelloy C-22. Hastelloy C-22, one of the corrosion-resistant nickel-chromium-molybdenum (Ni-Cr-Mo) alloys, has a nominal composition of: Cr, 22 wt%; Mo, 13%; Ni and various minor and trace elements, balance. All of the tubing and valves will be Hastelloy C-22, Hastelloy C-276, or Inconel 625 (see 3.3.2 for the composition of the Ni-Cr-Mo alloys Hastelloy C-276 and Inconel 625). During previous studies, Westerman et al. (1987) preoxidized these alloys at about 600°C for a few hours. This produced a blue tarnish, which was still visible after experiments carried out with brines at 90, 150, and 250°C. The presence of this tarnish after these runs implied that the containers did not corrode during these experiments. Westerman et al. (1987) also conducted high-temperature experiments without preoxidizing these alloys, and did not observe any corrosion under anoxic conditions. The only corrosion of these Ni-Cr-Mo alloys ever observed occurred during high-temperature experiments in which O<sub>2</sub> was present throughout the run. Each container will be equipped with a pressure gauge to monitor the pressure throughout the experiments.

For this study, Westerman will use two heats of ASTM A366 steel, a low-C alloy, to simulate the material used for the DOT 17C drums, and two heats of ASTM A36 steel, a medium-C alloy, to simulate the material used for the standard waste boxes and tools in the waste. Although the specifications for the standard waste boxes call for ASTM A569 steel, the manufacturer actually uses A36. He will obtain representative sheets of these alloys from the same or equivalent sources that supply the material used to fabricate drums and boxes for the Rocky Flats Plant, the largest waste generator. By carrying out experiments with both ASTM A366 and A36 steels, he will be able to estimate corrosion rates for the materials used to fabricate most of the steel containers to be emplaced in the WIPP. He will conduct experiments with two heats of each alloy to assess this possible cause of variability. If the measured corrosion rates of these alloys or different heats of these alloys differ significantly, he may decide to carry out experiments with additional alloys or more than two heats of each alloy.

After receiving these materials, Westerman will characterize two specimens from each of the two heats of the two alloys. He will carry out chemical analyses to verify the composition certified by the vendor(s), and conduct metallographic analysis to characterize the grain size, texture, grain-boundary contaminants, stringers and other inclusions, the distribution of carbides, and the extent of surface carburization or decarburization.

Pretest preparation typically will consist of cutting specimens, typically 8-by-20-cm, from the sheets provided by the vendor(s), drilling holes for suspension in the experimental apparatus, grinding with 150- to 200-grit abrasive, and cleaning with detergent followed by acetone and high-purity alcohol. After cleaning, Westerman will dry the specimens in a desiccator, weigh them, and return them to the desiccator to minimize oxidation of the surface prior to use.

Westerman will use Salado-Fm. brine collected from G Seep in the WIPP underground workings (2.3.1.2) for this study. He may also use brines collected from other locations in the WIPP underground workings, a synthetic Salado-Fm. brine once Brush has defined a standard brine (2.3.1.3) and developed a formulation for it, or synthetic brines that simulate the composition of Castile-Fm. brines and fluids from overlying formations after equilibration with brines and minerals from the Salado Fm. (2.4.5 and 2.4.6).

The quantity of brine Westerman will add to the containers will depend on the objective of the experiment. To study anoxic corrosion by brine, he will immerse the specimens in brine. In the case of anoxic corrosion by H<sub>2</sub>O vapor, he will pour in only enough brine to fill 3 or 4 cm of the containers. This will leave a "splash space" of 3 or 4 cm between the top of the brine and the bottoms of the specimens.

After adding the brine, Westerman will place at least triplicate specimens of each heat of both metals, or at least 12 specimens, in each container. To ensure electrical isolation, he will suspend the specimens on oxidized Zircaloy wires sheathed in Teflon and place Teflon washers between them. Next, he will seal each container by welding on the preassembled top with a prewelded pressure gauge and valves. He will then evacuate the headspace and refill it with N<sub>2</sub> containing helium (He) for the leak check. After reevacuating and refilling the headspace to a pressure of about 1 atm, he will check each apparatus for leaks by placing it under a bell jar, evacuating the bell jar, and analyzing the residual gas for He by mass spectrometry. If there is any evidence of leakage, he will reseal the apparatus prior to use.

Westerman will specify a purity of  $\geq 99.99\%$  for the N<sub>2</sub> used for this study and analyze each container at PNL after receipt to verify the composition certified by the vendor. The N<sub>2</sub> used for this study will therefore contain  $\leq 100$  ppm of other gases as impurities, and the O<sub>2</sub> concentration in the headspace will be  $\leq 100$  ppm. Oxidic corrosion of a very small mass of the specimens will quickly consume this O<sub>2</sub> after a few hours, and anoxic corrosion will begin immediately thereafter. He would not be able to detect the consumption of even 100 ppm O<sub>2</sub> during these experiments because this would decrease the pressure by only about 0.0001 atm.

After the leak check, Westerman will place each container in a forced-convection incubation chamber at  $30 \pm 5^\circ\text{C}$ . He will monitor the temperature with three thermocouples at different locations. The chamber will have a transparent door to facilitate monitoring of the pressure gauges. He will carry out each type of experiment (anoxic corrosion by brine, H<sub>2</sub>O vapor, and H<sub>2</sub>O absorbed by backfill materials) with four containers, one each for 3, 6, 12, and 24 months.

Posttest analysis will include characterization of the physical appearance, the corrosion product or products, and the microstructural appearance of specimens. Westerman will use visual inspection to characterize the physical appearance of all of the specimens (the color of the corrosion product and whether it is adherent or loose, the extent of attack, and the uniformity of attack). He will use x-ray diffraction analysis to identify the corrosion product. Fe(OH)<sub>2</sub>, a possible corrosion product in brines (3.2.1), must be x-rayed quickly before it oxidizes to an Fe(III) oxide or

hydroxide. During their work for the SRP, PNL personnel observed that  $\text{Fe}(\text{OH})_2$  begins to change from gray to orange after a few hours of exposure to air and oxidizes completely after a few days.  $\text{Fe}_3\text{O}_4$ , a likely corrosion product in  $\text{H}_2\text{O}$  vapor, is stable in air, but rapid analysis would also be required in this case to ensure that oxidation of the specimen after removal from its container does not form corrosion products other than those produced under experimental conditions. He will carry out metallographic analysis of selected specimens with the same objectives as the pretest characterization described above. Additional objectives of the posttest metallographic analysis include determination of the uniformity of attack, which phase or phases in the samples are susceptible to attack, and the physical and mechanical characteristics of the corroded layer, especially its adhesive properties.

Westerman will determine the corrosion rate of each specimen by measuring the amount of material lost to corrosion processes during the test. This gravimetric procedure consists of ultrasonic cleaning in CP-9 solution at room temperature, along with periodic brushing, until the specimen appears free of corrosion product. The CP-9 solution consists of 1 L of concentrated HCl, 1 L of deionized  $\text{H}_2\text{O}$ , and 25 ml of formaldehyde; the HCl removes the corrosion products and the formaldehyde prevents additional corrosion of the specimen. After the specimen appears free of corrosion product, he will rinse it with deionized  $\text{H}_2\text{O}$ , clean it with acetone followed by high-purity alcohol, dry it in a desiccator, and reweigh it. He will calculate the corrosion rate from the weight loss, the surface area of the specimen, and the density of the metal.

Westerman will then calculate the  $\text{H}_2$  production rate for each specimen based on its corrosion rate and the corrosion reaction for the appropriate corrosion product identified by x-ray diffraction analysis.

To check the calculated  $\text{H}_2$ -production rates, Westerman will monitor the pressure increase in each container, analyze the gas before and after each experiment to determine the total quantity of  $\text{H}_2$  produced per container, and divide by the number of specimens per container to obtain an average  $\text{H}_2$  production rate for each specimen. The kinetic data obtained by continuous monitoring of  $\text{H}_2$  build-up will supplement those obtained by periodic determination of weight loss. By relying primarily on the weight-loss method, PNL will be able to place many more specimens in each container and thus carry out experiments much faster than by measuring the  $\text{H}_2$  production rate of each specimen individually.

### **3.3.2 Quantification of Anoxic Corrosion of Steels at High Pressures**

Westerman will quantify anoxic corrosion of steels under humid and inundated conditions, and by  $\text{H}_2\text{O}$ -bearing backfill materials at  $30^\circ\text{C}$ . In all three cases, he will fill the headspace above the brine or backfill materials with  $\text{CO}_2$  or  $\text{H}_2$  at high pressures.

Westerman will carry out this study in 1- to 4-L autoclaves fabricated from the corrosion-resistant, Ni-Cr-Mo alloy Hastelloy C-276 or Inconel 625. Hastelloy C-276 has a nominal composition of: Cr, 15 wt%; Mo, 16%; Ni and various minor and trace elements, balance. Inconel 625 consists of: Cr,

22 wt% Mo, 9% Ni and various minor and trace elements, balance. All of the tubing and valves will be Hastelloy C-22, Hastelloy C-276, or Inconel 625 (see 3.3.1 for the composition of the Ni-Cr-Mo alloy Hastelloy C-22). Each autoclave will be equipped with a pressure gauge to monitor the pressure throughout the experiments and with the same rack for suspending specimens as described in 3.3.1.

Westerman will use specimens from the same two heats of ASTM A366 steel and the same two heats of ASTM A36 steel, and the same pretest preparation procedures described in 3.3.1. He will also use the same brine described above.

After loading the autoclaves with the specimens and brine, Westerman will evacuate and refill the headspace twice with either 99.99% CO<sub>2</sub>, 99.99% H<sub>2</sub>, or a nonflammable mixture of high-purity Ar and H<sub>2</sub>. He will not check for leaks as described in 3.3.1. Instead, he will maintain the autoclaves at the desired pressure throughout the experiments by admitting additional CO<sub>2</sub>, H<sub>2</sub>, or Ar and H<sub>2</sub> as necessary.

Westerman will maintain each autoclave at  $30 \pm 5^\circ\text{C}$ . He has not yet chosen the procedure for temperature control, but the controller for each autoclave will be independent of the other autoclaves. Brush has not yet specified the pressures for these experiments, but Westerman will carry out each type of run (anoxic corrosion by brine, H<sub>2</sub>O vapor, and H<sub>2</sub>O absorbed by backfill materials) with two containers, one for 3 and 6 months and the other for 12 and 24 months.

Westerman will carry out the same posttest characterization procedures as described in 3.3.1, including x-ray-diffraction analysis of the corrosion product, weight-loss measurements to determine the corrosion rate, calculation of the H<sub>2</sub>-production rate, and monitoring the pressure increase and pre- and posttest analysis of the gas to check the calculated H<sub>2</sub>-production rate.

### **3.3.3 Additional Quantification of Anoxic Corrosion of Steels**

Westerman will determine the effects of factors such as basic conditions, O<sub>2</sub> concentration, and the presence of the proposed backfill additive CuSO<sub>4</sub> on anoxic corrosion of low-C steels. Brush will describe this study in detail later.

### **3.3.4 Quantification of Anoxic Corrosion of Other Metals**

Westerman will quantify the anoxic corrosion of other metals, especially Al and Al-base alloys. Brush will describe this study in detail later.

### **3.3.5 Quality Assurance and Safety**

Westerman is carrying out his studies of anoxic corrosion (3.3.1 and 3.3.2) in accordance with applicable sections of the overall quality assurance (QA) plan and implementing procedures described by PNL (1989a, 1989b), and the QA plan developed for WIPP-related studies by PNL (1989c) and approved by Pickering (1990a). These QA plans and procedures meet the requirements of the American Society of Mechanical Engineers (1986) imposed

by Sandia National Laboratories (SNL) (1984b). If necessary, PNL will revise its QA plan for WIPP for future studies of anoxic corrosion (3.3.3 and 3.3.4) before the initiation of these studies.

PNL is responsible for the development, approval, and implementation of all safety procedures required for its studies.

### **3.4 RESULTS EXPECTED FROM BIN-SCALE AND ALCOVE TESTS**

Analyses of gases sampled from bin-scale and alcove tests with contact-handled transuranic waste (Molecke, 1990a; 1990b) will also provide information relevant to anoxic corrosion. Comparison of the H<sub>2</sub> production rates obtained from humid and partially inundated bins may yield results pertinent to the effects of H<sub>2</sub>O content on the rate of anoxic corrosion. Higher O<sub>2</sub> production rates and lower H<sub>2</sub> production rates in partially inundated bins than in humid bins may imply that production of O<sub>2</sub> by radiolysis of brine, and subsequent diffusion of O<sub>2</sub> through brine, backfill, and the waste, inhibit anoxic corrosion of metals. It would be difficult to use laboratory or modeling studies to predict the extent to which competing reactions such as aerobic microbial activity, radiolytically induced uptake by plastics, or oxidation of dissolved species such as Fe<sup>2+</sup> would prevent the diffusion of O<sub>2</sub> through brine. The absence of H<sub>2</sub> from partially inundated bins with the proposed backfill additive CuSO<sub>4</sub> (6.1) may imply that this compound prevents anoxic corrosion effectively under the heterogeneous conditions expected for WIPP disposal rooms.

### **3.5 SCHEDULES FOR LABORATORY STUDIES**

In early December 1989, Westerman started to procure representative samples of low-C steel for all of the studies of anoxic corrosion at PNL from the same or equivalent sources that supply the material used to fabricate drums and boxes for the Rocky Flats Plant. He will start the pretest preparation procedures described in 3.3.1 by the beginning of February 1990.

Westerman will start to quantify anoxic corrosion of steels at low pressure (3.3.1) at PNL as soon as possible. He will start experiments under inundated conditions with N<sub>2</sub> in the headspace by the beginning of April 1990, under inundated conditions with CO<sub>2</sub> in the headspace by the beginning of May 1990, under humid conditions with N<sub>2</sub> by the beginning of June 1990, and under humid conditions with CO<sub>2</sub> by the beginning of July 1990. He will carry out these experiments for periods of 3, 6, and 12 months and will complete these experiments by the end of March, April, May, and June 1991, respectively. Posttest analysis and reporting will require another 3 months. He will thus complete these parts of the study by the end of June, July, August, and September 1991, respectively. He will start experiments with backfill materials and N<sub>2</sub> or CO<sub>2</sub> as soon as Butcher of SNL determines the H<sub>2</sub>O content of these materials in equilibrium with WIPP brine and H<sub>2</sub>O vapor. Brush will provide a schedule for these experiments later.

Westerman will start to quantify anoxic corrosion of steels at high pressures (3.3.2) at PNL after he has started most of the low-pressure experiments. He will start experiments under inundated conditions with H<sub>2</sub> in the headspace by the beginning of August 1990, and under humid conditions

with H<sub>2</sub> by the beginning of September 1990. He will carry out these experiments for periods of 3, 6, and 12 months and will complete these experiments by the end of July and August 1991, respectively. Posttest analysis and reporting will require another 3 months. He will thus complete these parts of the study by the end of October and November 1991, respectively. He will also carry out experiments under humid and inundated conditions with CO<sub>2</sub>, but Brush will provide a schedule for these experiments later.

Westerman will quantify the effects of other factors on anoxic corrosion of steels (3.3.3) at PNL. Whether he starts this study before he quantifies the anoxic corrosion of other metals (3.3.4) at PNL depends on the results of the first two studies described above. If anoxic corrosion of steels were fast under humid conditions or in the presence of H<sub>2</sub>O-bearing backfill materials, he would probably start the study of the effects of other factors on anoxic corrosion of low-C steels before the study of anoxic corrosion of other metals. However, if anoxic corrosion of low-C steels were slow under these conditions, he would probably start the study with other metals first. Brush will provide schedules for these studies later.



## 4.0 MICROBIAL ACTIVITY

### 4.1 JUSTIFICATION FOR LABORATORY STUDIES

Lappin et al. (1989) estimated that if brine or H<sub>2</sub>O vapor were present in Waste Isolation Pilot Plant (WIPP) disposal rooms, microbial degradation of cellulose in the waste would produce about 1 mole of various gases per equivalent drum of waste per year for 600 years, or a total of 600 moles per drum (see 7.4 for the definition of an equivalent drum). These gases could include CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S, N<sub>2</sub>, and NH<sub>3</sub>, but the relative proportions at any given time, and as a function of time, are unknown. Microbial activity is the process of second greatest concern from the standpoint of the gas budget of the repository. Anoxic corrosion of metals, the most important process, would produce about 2 moles of H<sub>2</sub> per drum per year for 450 years, or a total of 900 moles (3.1).

Because microbial activity may consume more H<sub>2</sub>O than it produces (4.2), the quantity of H<sub>2</sub>O in the disturbed rock zone available for transport to the waste, either by brine inflow or diffusion of H<sub>2</sub>O vapor through the gaseous phase, may prevent the production of 600 moles of gas per drum. Development of an integrated model of the effects of gas pressurization, room closure, brine inflow and outflow, and vapor-phase transport of H<sub>2</sub>O is still in progress. Preliminary results suggest that absorption of H<sub>2</sub>O by crushed salt and any bentonite in the backfill and the consumption of H<sub>2</sub>O by anoxic corrosion of metals (3.1) may limit the extent of microbial activity. The quantities of nutrients in WIPP brines and the waste may also limit microbial activity.

The experimental program reviewed by Molecke (1979) yielded valuable data on microbial activity, including the microbial gas production rate used by Lappin et al. (1989). Subsequently, an increased awareness by geochemists of the role of microorganisms in mediating diagenetic oxidation-reduction (redox) reactions has led to the development of a conceptual model of the effects of microbial activity on low-temperature geochemical systems. Froelich et al. (1979) and Berner (1980) have described this model in detail; Brush and Anderson (1988a) applied it to microbial degradation of transuranic (TRU) waste in WIPP disposal rooms (4.2). From the perspective of the long-term performance assessment of the WIPP, the most important results obtained from this model have been: (1) a method for identifying microbial processes (4.2.1 through 4.2.6) that could affect the gas and H<sub>2</sub>O budgets of the repository significantly; (2) the understanding that microbially mediated reactions can determine the Eh and pH of low-temperature geochemical systems, and hence the speciation, solubilities, and sorptive behavior of radionuclides in these systems (Sholkovitz, Cochran, and Carey, 1983).

During 1988, an interdisciplinary group of experts reviewed this model, previous microbiological studies carried out for the WIPP Project, relevant microbiological studies conducted for other applications, and other aspects of repository and radionuclide chemistry (Brush and Anderson, 1988a; 1988b; 1988c). Based on its review, the group concluded that: (1) microbial activity is likely under the conditions expected for WIPP disposal rooms; (2) microbial activity may produce significant quantities of gas, consume or produce significant quantities of H<sub>2</sub>O, affect the Eh and pH of any brine present, and consume or produce ligands that form complexes with the

important radionuclides in the waste; (3) sterilization of the waste to prevent microbial activity is unfeasible.

Despite this progress, it is still unknown whether there will be sufficient nutrients in WIPP disposal rooms for microbial activity, which potentially significant microbial processes (4.2) will occur, at what rates they will produce gas and produce or consume H<sub>2</sub>O under realistic repository conditions, and whether the H<sub>2</sub>O content and pressure of the repository will affect these rates. The extent to which any of these potentially significant processes will affect the chemical behavior of radionuclides under realistic conditions is also unknown. Finally, it is unclear whether the microorganisms responsible for any significant processes are likely to survive for periods sufficient to affect the long-term performance of the repository.

## 4.2 IDENTIFICATION OF POTENTIALLY SIGNIFICANT MICROBIAL PROCESSES

In the natural environment, microorganisms oxidize organic matter (often referred to as the substrate) by using the electron acceptor (oxidant) that yields the most free energy per mole of organic C consumed (for example, Froelich et al., 1979; Berner, 1980). After the depletion of this electron acceptor, many microorganisms use the next most efficient electron acceptor present. If the environment remains conducive to microbial activity, sequential usage of electron acceptors continues until microorganisms have consumed the biodegradable organic matter, the available electron acceptors, or essential nutrients. In natural systems, the order of usage of electron acceptors is O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and CO<sub>2</sub>. Some microorganisms may also be able to use Mn(IV) oxides and hydroxides, and Fe(III) oxides and hydroxides. Microorganisms that use O<sub>2</sub> are referred to as aerobic; microorganisms that use the other electron acceptors listed above are referred to as anaerobic. Facultative anaerobes use O<sub>2</sub> as long as it is available, but can use other electron acceptors such as NO<sub>3</sub><sup>-</sup> after the depletion of O<sub>2</sub>.

For all of these processes, microorganisms will probably use cellulose as the substrate in preference to plastics and rubbers. Estimates of the quantities and proportions of cellulose in WIPP disposal rooms appear in 4.3. Microorganisms might use plastics and rubbers after the depletion of cellulose, especially if radiolysis renders these materials more biodegradable (5.0).

For the sake of simplicity, Brush and Anderson (1988a) described these microbial processes as though they will occur sequentially in WIPP disposal rooms. This is generally the case in natural systems such as lacustrine and marine sediments. The processes described below will probably occur sequentially in many locations in the repository, but will also occur simultaneously in microenvironments separated by short distances, perhaps just a few centimeters, because of the heterogeneous nature of the TRU waste to be emplaced in the WIPP. Aerobic microbial activity, for example, could continue for long periods near large particles containing radionuclides because of continuous radiolytic production of O<sub>2</sub> from brine or sludges. Simultaneously, anaerobic microbial activity could occur in adjacent microenvironments devoid of radionuclides but with large quantities of organic matter.

During any of these microbial processes, the degradation of organic matter is complex and involves several intermediate steps mediated by different microorganisms. Geochemists have described microbial activity by writing overall equations representative of each process (for example, Froelich et al., 1979; Berner, 1980; Brush and Anderson, 1988a). They use various formulas such as CH<sub>2</sub>O (a simplified formula for glucose) or (CH<sub>2</sub>O)<sub>106</sub>·(NH<sub>3</sub>)<sub>16</sub>·(H<sub>3</sub>PO<sub>4</sub>) (the Redfield ratio) to represent the substrate, but do not include the synthesis of cellular material (biomass) by microorganisms. Microbiologists, on the other hand, include synthesis of biomass. To illustrate this difference, both types of equations appear in the discussion below (4.2.1 through 4.2.6).

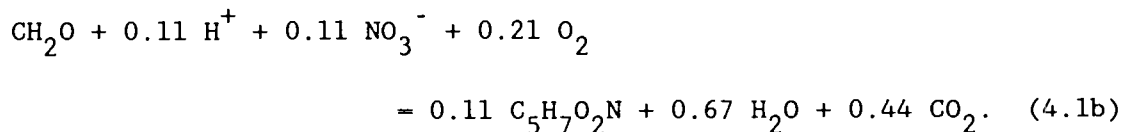
These overall equations imply that all or most of the microbially produced CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S, and N<sub>2</sub> remain in the gaseous phase. It is also possible to write these equations so that all or most of the CO<sub>2</sub> and H<sub>2</sub>S dissolves in the aqueous phase. Significant quantities of CO<sub>2</sub> and H<sub>2</sub>S would dissolve if enough brine were present and the pH of the brine were basic. Because of the heterogeneous nature of the TRU waste to be emplaced in the WIPP, the pH could vary over a wide range (1.10.4). It is therefore difficult to predict the effects of these processes on the CO<sub>2</sub> and H<sub>2</sub>S budgets of the repository.

It is also unknown whether these microbial processes would consume or produce H<sub>2</sub>O in WIPP disposal rooms. The overall reactions described in 4.2.1 through 4.2.6 produce H<sub>2</sub>O, but the hydrolysis of cellulose, the most important potential substrate in the WIPP inventory, consumes H<sub>2</sub>O prior to the start of these reactions. Therefore, the net effect on the H<sub>2</sub>O budget of the repository is unclear.

Despite these uncertainties, it is possible to decide, based on currently available knowledge of the quantities of potential electron acceptors available in WIPP disposal rooms, which of these microbial processes would, if their rates were high enough, be significant in the repository.

#### 4.2.1 Aerobic Respiration

Aerobic microorganisms use O<sub>2</sub> as the electron acceptor and produce CO<sub>2</sub>. The overall equations as written by Berner (1980) and Grbic-Galic (1988), respectively, are:



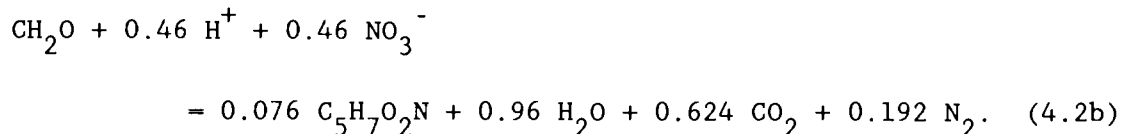
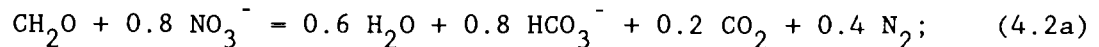
In these equations and the equations for other potentially significant microbial processes (4.2.2 through 4.2.6), CH<sub>2</sub>O represents the substrate. In Equation 4.1b and the second equation for each of the other processes, C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>N represents biomass.

Aerobic respiration will probably not be important in WIPP disposal rooms because the quantity of O<sub>2</sub> is limited. Brush and Anderson (1988a) calculated that the quantity of O<sub>2</sub> present in the air trapped in WIPP disposal rooms at the time they are filled and sealed will only be sufficient to oxidize about 1 or 2% of the cellulosic materials in a room. Radiolytically produced O<sub>2</sub> may promote aerobic microbial activity near large particles containing radionuclides, but oxidic corrosion, radiolytically induced uptake by plastics, and oxidation of dissolved species such as Fe<sup>2+</sup> will compete with microorganisms for radiolytic O<sub>2</sub>.

Whether aerobic respiration and oxidizing conditions are significant in WIPP disposal rooms for an extended period after filling and sealing will depend critically on the H<sub>2</sub>O content of the repository and the production rate of O<sub>2</sub> by radiolysis of brine. Unless ongoing studies of brine inflow and outflow, the planned laboratory study of gas production from the radiolysis of brine (5.4), and observations of the rate and extent of the transformation from oxidic to anoxic conditions in the bin-scale and alcove tests with contact-handled (CH) TRU waste (Molecke, 1989a; 1989b) prove otherwise, the limited quantity of O<sub>2</sub> initially present in the repository implies that aerobic respiration will be insignificant in WIPP disposal rooms.

#### 4.2.2 Denitrification and Nitrate Reduction

After the depletion of O<sub>2</sub>, anaerobic respiration begins. During denitrification, microorganisms use nitrate (NO<sub>3</sub><sup>-</sup>) as the electron acceptor and produce CO<sub>2</sub> and N<sub>2</sub>. The overall equations as written by Berner (1980) and Grbic-Galic (1988), respectively, are:



The equations for NO<sub>3</sub><sup>-</sup> reduction are similar to those for denitrification, but the former process produces NH<sub>3</sub> instead of N<sub>2</sub>.

These processes could be significant in the repository because: (1) sludges in the WIPP inventory contain copious amounts of NO<sub>3</sub><sup>-</sup> which, because of its high solubility, could dissolve in any brine present and diffuse to drums or boxes containing cellulosic materials; (2) N<sub>2</sub> might diffuse into the surrounding Salado Fm. even less readily than other gases because the concentration of N<sub>2</sub> in intergranular brines may already be at or close to its solubility limit; (3) although there is no known backfill additive to remove N<sub>2</sub> or prevent its production at a reasonable cost, emplacement of containers with sludges in different rooms or panels than containers with cellulose might prevent denitrification and NO<sub>3</sub><sup>-</sup> reduction.

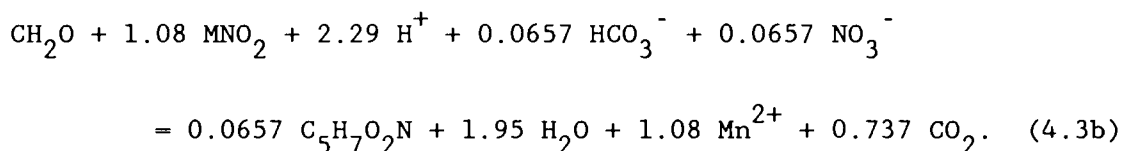
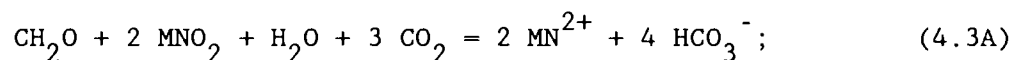
During NO<sub>3</sub><sup>-</sup> reduction, microorganisms also use NO<sub>3</sub><sup>-</sup> as the electron acceptor but produce CO<sub>2</sub>, various oxides of nitrogen (NO<sub>x</sub>), and eventually

ammonia (NH<sub>3</sub>). There is no known backfill additive to remove NH<sub>3</sub> or prevent its production at reasonable cost.

Because cellulose and sludges will be emplaced in separate containers, it is unlikely that cellulose and NO<sub>3</sub><sup>-</sup> will come into contact prior to rupture of drums and boxes, resaturation of the repository with brine, and diffusion of NO<sub>3</sub><sup>-</sup> through the brine. Denitrification and NO<sub>3</sub><sup>-</sup> reduction could, therefore, be significant in WIPP disposal rooms under saline but not asaline conditions.

### 4.2.3 Manganese Reduction

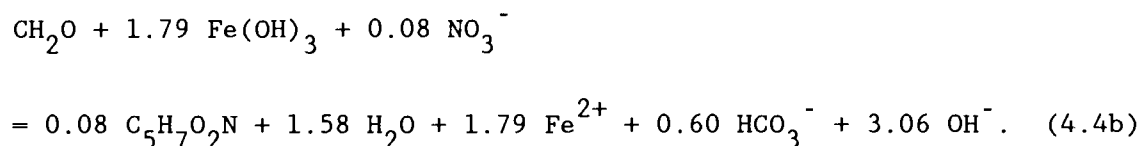
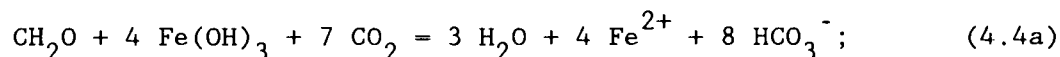
Once denitrification and NO<sub>3</sub><sup>-</sup> reduction deplete all available NO<sub>3</sub><sup>-</sup>, some microorganisms may use Mn(IV) oxides and hydroxides as electron acceptors, thereby reducing them to soluble Mn(II) phases (Lovley and Phillips, 1988). According to Berner (1980) and Grbic-Galic (1989c), the overall equations are:



Although this mode of microbial respiration has received only limited study to date, Mn(IV) reduction would probably be insignificant in the repository because of the absence of significant quantities of this element from the WIPP inventory and brines. Brush and Anderson (1988a) proposed the addition of MnO<sub>2</sub> to the backfill to prevent: SO<sub>4</sub><sup>2-</sup> reduction (4.2.5); the concomitant production of H<sub>2</sub>S; the reaction of H<sub>2</sub>S with Fe, Fe-base alloys, or their corrosion products to form FeS<sub>2</sub>; the concomitant production of H<sub>2</sub>. However, MnO<sub>2</sub> would probably not prevent SO<sub>4</sub><sup>2-</sup> reduction effectively (6.1). Mn(IV) reduction will therefore be insignificant in the repository.

### 4.2.4 Iron Reduction

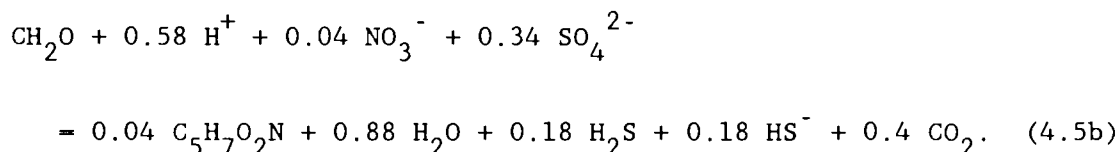
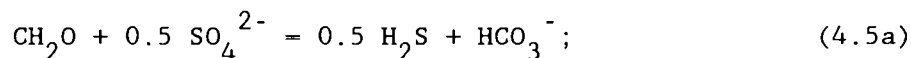
Subsequent to the depletion of NO<sub>3</sub><sup>-</sup>, some microorganisms may also use Fe(III) oxides and hydroxides as electron acceptors, reducing them to soluble Fe(II) phases in the process (Lovley and Phillips, 1986; 1988). The overall equations as written by Berner (1980) and Grbic-Galic (1989b), respectively, are:



Brush and Anderson (1988a) calculated that the quantity of O<sub>2</sub> present in the air trapped in WIPP disposal rooms at the time they are filled and sealed will only be sufficient to oxidize about 1% or less of the drums in a room to magnetite, an Fe(II, III) oxide and the most likely oxitic corrosion product. (Sorensen, personal communication). Haberman and Frydrych (1988) identified Fe(OH)<sub>2</sub> (amakinite), an Fe(II) hydroxide, as their anoxic corrosion product, but Fe<sub>3</sub>O<sub>4</sub> (magnetite) is also a possible anoxic corrosion product under expected WIPP conditions (3.2.1.1). Reaction of Fe, Fe-base alloys, Fe<sub>3</sub>O<sub>4</sub>, or Fe(OH)<sub>2</sub> with CO<sub>2</sub> in the absence of H<sub>2</sub>S, HS<sup>-</sup>, or S<sup>2-</sup> would produce FeCO<sub>3</sub> (siderite), an Fe(III) carbonate. Reaction of H<sub>2</sub>S, HS<sup>-</sup>, or S<sup>2-</sup> with Fe, Fe-base alloys, or their corrosion products would produce FeS<sub>2</sub> (pyrite), an Fe(II) sulfide. Although it is unclear which Fe phase or phases will be formed as a result of these processes, microorganisms would not use the Fe(II) phases Fe(OH)<sub>2</sub>, FeCO<sub>3</sub>, and FeS<sub>2</sub> as electron acceptors, but might use the Fe(II, III) phase Fe<sub>3</sub>O<sub>4</sub>. Fe(III) reduction would only be a potentially significant process in the event of significant formation of Fe<sub>3</sub>O<sub>4</sub>.

#### 4.2.5 Sulfate Reduction

After the depletion of NO<sub>3</sub><sup>-</sup> and, perhaps, any Mn(IV) and Fe(III) oxides and hydroxides, obligately anaerobic microorganisms use SO<sub>4</sub><sup>2-</sup> as the electron acceptor. These microorganisms reduce SO<sub>4</sub><sup>2-</sup> to H<sub>2</sub>S. The overall equations as written by Berner (1980) and Grbic-Galic (1988), respectively, are:



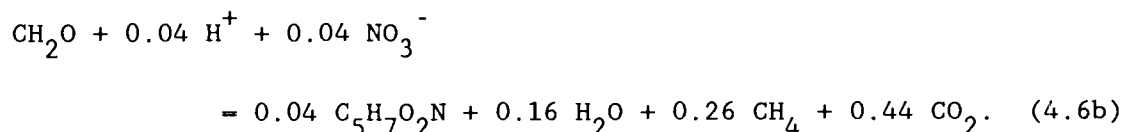
Because the average concentration of SO<sub>4</sub><sup>2-</sup> in SB-3 and ERDA-6 is 170 mM (Tables 2.1 and 2.3), SO<sub>4</sub><sup>2-</sup> reduction could be a significant process if brine were present in WIPP disposal rooms. It is unknown whether microorganisms could use SO<sub>4</sub><sup>2-</sup> from evaporite minerals as an electron acceptor under humid conditions.

The H<sub>2</sub>S produced by SO<sub>4</sub><sup>2-</sup> reduction will probably react with Fe, Fe-base alloys, or their corrosion products to form FeS<sub>2</sub>, H<sub>2</sub>, and (in the case of hydrous corrosion products) H<sub>2</sub>O. These reactions will remove any microbially produced H<sub>2</sub>S effectively as long as the quantity of Fe-bearing phases exceeds either the quantity of SO<sub>4</sub><sup>2-</sup> or substrate available. The release of H<sub>2</sub>O from hydrous corrosion products will facilitate additional oxitic or anoxic corrosion, or microbial activity.

Unless significant quantities of SO<sub>4</sub><sup>2-</sup> occur in sludges, it is difficult to envision the presence of SO<sub>4</sub><sup>2-</sup> in saline solutions in WIPP disposal rooms. SO<sub>4</sub><sup>2-</sup> reduction could therefore be significant in the repository under saline, but not asaline, conditions.

## 4.2.6 Fermentation and Methanogenesis

Fermentative microorganisms convert various substrates to acetic acid, butyric acid, ethyl alcohol, methyl alcohol, propyl alcohol, propionic acid, valeric acid, etc., and CO<sub>2</sub> and H<sub>2</sub>. Next, some microorganisms convert these acids and alcohols, along with H<sup>+</sup>, to acetic acid, CO<sub>2</sub>, and H<sub>2</sub>. This step, H<sup>+</sup>-reducing acetogenesis, only occurs if SO<sub>4</sub><sup>2-</sup>-reducing or methanogenic microorganisms are present to scavenge H<sub>2</sub>. Methanogenic microorganisms then convert CO<sub>2</sub> and H<sub>2</sub> to CH<sub>4</sub> and H<sub>2</sub>O. Methanogens can also convert acetic acid to CH<sub>4</sub> and CO<sub>2</sub>. Although acetic acid could be produced by fermentation and H<sup>+</sup>-reducing acetogenesis, it will also be present in the waste and could dissolve in any brine present in WIPP disposal rooms (7.4). According to Berner (1980) and Grbic-Galic (1988), the overall equations are:



Because fermentation and methanogenesis could occur in unbreached drums or boxes containing cellulose without electron acceptors from sludges or brines, these processes might be significant in WIPP disposal rooms under asaline conditions. Fermentation and methanogenesis will also be potentially significant after the containers rupture and brine enters the repository, especially as the electron acceptors discussed above are depleted.

## 4.3 ESTIMATES OF CELLULOSES IN THE WIPP INVENTORY

Estimates of the quantities of various types of cellulose in the WIPP inventory are necessary to design laboratory studies of microbial activity. Brush and Anderson (1988b) used estimates of cellulose by Drez (personal communication) to calculate the microbial gas production potential (these calculations also appear in Lappin et al., 1989).

Subsequent to these calculations, Drez and James-Lipponer (1989) completed a preliminary inventory of the nonradioactive constituents of the CH TRU waste to be emplaced in the WIPP. This inventory is based on the results of a survey, which included a detailed questionnaire, of the waste generators and storage sites.

To obtain the total quantities of cellulose in the containers and waste to be emplaced in the WIPP, Brush: (1) prorated the quantities for other wood (Table 3-5 in Drez and James-Lipponer, 1989) between treated and untreated lumber (Table 3-5); (2) added other paper (Table 3-5) to paper/Kimwipes (Table 3-5); (3) prorated wood/plywood (Table 3-8 of Drez and James-Lipponer, 1989) among lumber (treated), lumber (untreated), and plywood (all in Table 3-5).

The quantities estimated by Drez and James-Lipponer (1989) are 1,720 kg of cellulose with phenolic binders, 226,000 kg of cloth, 21,000 kg of fiberboard, 327,000 kg of lumber (treated), 652,000 kg of lumber (untreated),

3,890,000 kg of paper, and 723,000 kg of plywood. They did not specify what treated lumber is.

Based on these estimates, Brush calculated that the cellulose in the WIPP inventory will consist of about 0.03% cellulose with phenolic binders, 4% cloth, 0.4% fiberboard, 6% lumber (treated), 10% lumber (untreated), 70% paper, and 10% plywood. These percentages do not add up to 100% because Brush rounded them off to one significant figure.

Brush divided the total quantity of cellulose in the CH TRU waste to be emplaced in the WIPP (Drez and James-Lipponer, 1989), 4,350,000 kg, by the total number of equivalent drums for which data are available, 421,763, to obtain a value of about 10 kg of cellulose per drum. (See 7.4 for the definition of an equivalent drum.) This estimate is similar to the value of 8 kg of cellulose per drum used by Lappin et al. (1989) to calculate the microbial gas production potential. To estimate the total quantity of cellulose per WIPP disposal room, Brush multiplied 10 kg of cellulose per drum by 6,800 drums per room and obtained a value of about 70,000 kg of cellulose per room.

#### 4.4 DESCRIPTION OF LABORATORY STUDIES

The objectives of these studies are to: (1) determine which potentially significant microbial processes (4.2) occur under overtest conditions (4.4.2); (2) quantify the effects of potentially significant processes on the gas and H<sub>2</sub>O budgets of WIPP disposal rooms under realistic conditions, both humid and inundated (4.4.3); (3) quantify the effects of pressure, if necessary, on any significant processes (4.4.4); (4) quantify the effects of potentially significant processes on the chemical behavior of the important radionuclides in TRU waste under realistic conditions (4.4.5); (5) determine whether the microorganisms responsible for any significant processes are likely to survive for periods sufficient to affect the long-term performance of the repository (4.4.6).

D. Grbic-Galic of Stanford University is determining which potentially significant microbial processes (currently denitrification, NO<sub>3</sub><sup>-</sup> reduction, SO<sub>4</sub><sup>2-</sup> reduction, fermentation, and methanogenesis) occur under overtest conditions (4.4.2). These conditions are required to determine which processes occur under saline conditions in relatively short (up to 6-month) experiments. The inocula for these experiments consist of both nonhalophilic microorganisms to simulate the microbes present in TRU waste (some of them may be halotolerant or develop halotolerance when exposed to saline conditions), and halophilic microorganisms from the WIPP Site and vicinity. Observation of microbial activity under overtest conditions would not necessarily imply that a process will be significant in the WIPP; the objective of these studies is to identify microbial processes for studies under realistic conditions.

After determining which potentially significant microbial processes occur under overtest conditions, Grbic-Galic will quantify their effects on the gas and H<sub>2</sub>O budgets of WIPP disposal rooms under various realistic conditions (4.4.3). This study will simulate as closely as possible: (1) fermentation and methanogenesis under humid, asaline conditions in containers emplaced in sealed WIPP disposal rooms before closure-induced rupture of the containers



(because any drums or boxes that contain free liquids have been or will be grouted prior to shipment to the WIPP, the waste could be moist, but will not contain free liquids prior to rupture of containers and resaturation of the repository with brine); (2) any denitrification,  $\text{NO}_3^-$  reduction,  $\text{SO}_4^{2-}$  reduction, fermentation, and methanogenesis under humid, saline conditions expected after rupture of the containers, but before resaturation with brine; (3) any of these potentially significant processes under long-term, humid, saline conditions caused by consumption of all of the brine that flows into the repository by bentonite or chemical reactions such as microbial hydrolysis of cellulose and corrosion of metals, or expulsion of brine by gas; (4) any of these potentially significant processes under inundated, saline conditions. Microbial degradation of cellulose under saline conditions, either humid or inundated, but without any nutrients in addition to those already present in brine and the waste, could be very slow and hence difficult to measure. The inocula for these experiments will consist, therefore, only of microorganisms for which activity was observed under overtest conditions. This study will identify which microbial processes that occur under overtest conditions are actually significant from the standpoint of their effects on the gas and  $\text{H}_2\text{O}$  budgets of the repository.

If microbial gas production is significant under realistic conditions, a study may be necessary to quantify the effects of pressure on the gas production rate. Although techniques currently exist for maintaining deep-sea microorganisms at high pressures in the laboratory, adaptation of existing bioassay procedures to high pressures could be difficult and time-consuming.

A. J. Francis of Brookhaven National Laboratory (BNL) will quantify the effects of potentially significant microbial processes on the speciation, solubilities, and sorption of radionuclides under realistic conditions (4.4.5). Microbial activity could affect the chemical behavior of radionuclides even more than inorganic processes (for example, Sholkovitz, Cochran, and Carey, 1983), and could increase or decrease the concentrations of radionuclides from those expected based on inorganic speciation, solubility, or sorption studies (7.0). Microbial processes could therefore affect the long-term performance of the WIPP significantly even if they do not affect its gas or  $\text{H}_2\text{O}$  budget.

Finally, Grbic-Galic will determine whether the microorganisms responsible for any significant processes are likely to survive for periods sufficient to affect the long-term performance of the WIPP (4.4.6). This study will begin after the identification of those potentially significant processes that affect the repository gas and  $\text{H}_2\text{O}$  budgets or the chemical behavior of radionuclides.

#### **4.4.1 Stanford Batch Bioassay Procedure**

Grbic-Galic is using or will use the batch bioassay procedure developed by Owen et al. (1979) and modified by Tong et al. (in preparation) for most of these laboratory studies (4.4.2, 4.4.3, and 4.4.6). Although investigators at Stanford University developed and modified this technique for methanogenic fermentation studies, it is also suitable for studies of denitrification,  $\text{NO}_3^-$  reduction, and  $\text{SO}_4^{2-}$  reduction.

Owen et al. (1979) used 250-ml glass serum bottles for their study (the actual volume was  $264 \pm 1$  ml when sealed). Grbic-Galic's studies may require larger bottles, possibly as large as 1 or 10 L, especially for conditions under which microbial gas production rates are low. Very low rates are likely in the studies of the effects of microbial activity on the gas and H<sub>2</sub>O contents of WIPP disposal rooms, for example, because these studies must be carried out under expected repository conditions, not overtest conditions (4.4.3). Smaller bottles may be necessary for the experiments to determine whether  $\alpha$  radiolysis increases the biodegradability of plastics and rubbers (3.2.1).

After flushing their bottles for 15 minutes at 0.5 L per minute with an O<sub>2</sub>-free mixture of 30% CO<sub>2</sub> and 70% N<sub>2</sub>, Owen et al. sealed them with plastic serum caps and equilibrated them at incubation temperature before adding a defined medium with nutrients and vitamins for mixed anaerobic cultures, substrate, and inocula. They transferred the substrates, nutrient medium (preequilibrated to incubation temperature), and inocula to the serum bottles under carefully maintained, anaerobic conditions.

Owen et al. (1979) periodically measured the microbial gas production rate by flushing 5- to 50-ml glass syringes equipped with 20-gauge needles with the CO<sub>2</sub>-N<sub>2</sub> gas mixture used above, inserting the needles through the stoppers of the serum bottles, and noting the volume displaced by the plungers after pressure equilibration between each bottle and syringe. They checked these readings by pulling the plungers past the equilibration point and releasing, thus approaching equilibrium from higher and lower pressures. They either analyzed or discarded these gas samples as necessary. Discarding gas prevents excessive pressure build-up within the bottles which, when stoppered, can accommodate differentials of about  $\pm 0.5$  atm.

To maximize the precision and accuracy of their results, ensure that nutrients were not limiting, and avoid possible substrate toxicity, Owen et al. (1979) chose a sample size and liquid-to-volume ratio to produce about 20 to 120 ml of total gas (CH<sub>4</sub> and CO<sub>2</sub>). For readily degradable substrates such as pure cellulose, they generally used a 2- to 20-ml liquid sample (or a dry sample) with 150 mg chemical O<sub>2</sub> demand, with a total liquid volume of 160 ml. Because their 250-ml serum bottles actually had a volume of  $264 \pm 1$  ml, their void volume was 104 ml. Their precision for total gas was typically  $\pm 2\%$ .

For each set of conditions, Owen et al. (1979) carried out triplicate experiments at an incubation temperature of 35°C for a period that usually lasted 30 days.

Owen et al. (1979) corrected their measured gas production rates by subtracting background values obtained from seed blanks, which they prepared according to the procedure described above except for the addition of the substrate.

Tong et al. (1989) modified the medium formulation by adding 20 mg/l of NiCl<sub>2</sub>·6H<sub>2</sub>O to the nutrient solution, increasing the concentration of N and vitamins, increasing the buffer capacity, and reducing the concentrations of other components by about 1 order of magnitude.

#### 4.4.2 Determination of Whether Potentially Significant Microbial Processes Occur

Grbic-Galic is using the batch bioassay procedure developed at Stanford University for methanogenic fermentation studies (4.4.1) with the modifications described below to determine whether the potentially significant microbial processes denitrification,  $\text{NO}_3^-$  reduction,  $\text{SO}_4^{2-}$  reduction, fermentation, and methanogenesis are possible under overtest conditions (inundated with WIPP brine and amended with nutrients).

For this study, Grbic-Galic is using solutions consisting of brine and/or the nutrient medium of Owen et al. (1979), with additional modifications for this study. These solutions contain 0, 30, 60, and 100% Salado-Fm. brine collected from G Seep in the WIPP underground workings (2.3.1.2). She may also use brines collected from other locations in the WIPP underground workings, a synthetic Salado-Fm. brine once Brush has defined a standard brine (2.3.1.3) and developed a formulation for it, or synthetic brines that simulate the composition of Castile-Fm. brines and fluids from overlying formations after equilibration with brines and minerals from the Salado Fm. (2.4.5 and 2.4.6). The use of other brines would be important if the studies with brine from G-Seep fail to yield evidence for microbial activity, but much less important if the initial studies do yield microbial activity. The former result could be caused by atypically high or low concentrations of an element or complex species in brine from G-Seep. For the studies of denitrification,  $\text{NO}_3^-$  reduction, and  $\text{SO}_4^{2-}$  reduction, Grbic-Galic adds  $\text{NO}_3^-$  or  $\text{SO}_4^{2-}$  to the solutions to serve as electron acceptors. She carries out these experiments with and without a carbonic acid-bicarbonate ( $\text{H}_2\text{CO}_3\text{-HCO}_3^-$ ) buffer to maintain the solutions at a pH of about 6.8 to 7.2.

The substrates for this study are: Solka Floc BW200 (a widely used, commercially available, powdered standard cellulose purified from mixed hardwoods) for all of the microbial processes; pure D-glucose (the major product of the hydrolysis of cellulose) for denitrification,  $\text{NO}_3^-$  reduction, and methanogenic fermentation; acetate (a product of the fermentation of glucose) for  $\text{SO}_4^{2-}$  reduction and methanogenesis; lactate for  $\text{SO}_4^{2-}$  reduction.

These substrates are the sole source of organic C and energy in these experiments. Because the objective of these studies is to determine whether potentially significant microbial processes (4.2) are possible under saline conditions, the substrates are readily biodegradable in most cases to facilitate detection of any microbial activity in relatively short experiments (up to 6 months). Microbial hydrolysis of cellulose, the most important substrate in TRU waste, will be very slow; the overall rates of microbial processes in WIPP disposal rooms will therefore be lower than in this study, which cannot be used to obtain realistic microbial gas production rates. A description of the study to obtain realistic, not overtest, gas production rates appears in 4.4.3.

Because a variety of microorganisms could be present in the TRU waste to be emplaced in the WIPP, Grbic-Galic uses several inocula for this study. In all cases, these inocula constitute 5 to 20 vol% of the culture.

The microorganisms in TRU waste could include numerous species capable of fermentation and methanogenesis once anaerobic conditions develop in the unbreached containers. A variety of facultative anaerobes in the waste could carry out denitrification or  $\text{NO}_3^-$  reduction when the containers rupture, brine enters WIPP disposal rooms, and  $\text{NO}_3^-$  diffuses from containers with sludges to those with cellulose or other potential substrates. Although these microorganisms prefer asaline conditions, some of them may be halotolerant or develop halotolerance when exposed to saline conditions. Fermentation and methanogenesis could continue if brine were present. Grbic-Galic carries out experiments to determine whether microbial communities known to conduct denitrification,  $\text{NO}_3^-$  reduction,  $\text{SO}_4^{2-}$  reduction, fermentation, and methanogenesis in asaline solutions can operate in WIPP brines.

To simulate the microorganisms in the waste, Grbic-Galic uses samples of microflora from laboratory air, swipes of laboratory surfaces such as bench tops and floors, laboratory waste, and human skin to inoculate some of these experiments. Although the microbiological laboratories at Stanford University do not produce TRU waste, they probably contain a variety of microorganisms similar to those contained in the facilities that actually do produce TRU waste.

Grbic-Galic may also use an aerobic, activated sewage-sludge inoculum to determine whether denitrification or  $\text{NO}_3^-$  reduction is possible under saline conditions, and anaerobic sludge communities to determine if  $\text{SO}_4^{2-}$  reduction, fermentation, and methanogenesis are possible.

Strictly halophilic microorganisms capable of carrying out denitrification,  $\text{NO}_3^-$  reduction,  $\text{SO}_4^{2-}$  reduction, fermentation, or methanogenesis could also enter the repository on dust particles transported from nearby salt lakes, soils, and the WIPP tailings pile by wind and the mine ventilation system. Because they have evolved under saline conditions, these microorganisms could be better adapted to expected repository conditions than potentially halotolerant microorganisms in TRU waste, and could therefore affect repository chemistry more than halotolerant species. Grbic-Galic will therefore inoculate some experiments with microbial communities from the WIPP Site and vicinity. Vreeland of West Chester University is enriching cultures of halophilic and halotolerant microorganisms from brines and sediments from the salt lakes in Nash Draw, soils adjacent to the WIPP Site, the tailings pile, and the WIPP underground workings. He is attempting to obtain microbial communities from surficial environments in which aerobic organisms are active (these communities could contain facultative anaerobes capable of carrying out denitrification,  $\text{NO}_3^-$  reduction, or fermentation), and (in the case of the lacustrine sediments, the soils, and the tailings pile) from deeper environments which contain anaerobic microorganisms conducting  $\text{SO}_4^{2-}$  reduction, fermentation, and methanogenesis. The enrichment of microbial communities responsible for each of these potentially significant processes could prove difficult and time-consuming; he is especially concerned about  $\text{SO}_4^{2-}$ -reducing microorganisms.

The sterilization procedure for containers, nutrient media, and nonthermolabile substrates consists of heating in a steam autoclave at  $121^\circ\text{C}$  and a pressure of 18 psi for 20 to 30 minutes. The cold sterilization procedure for thermolabile materials such as acetate, glucose, lactate, and vitamin

solutions is filtration through a bacteriological filter with a pore size of 0.20  $\mu\text{m}$ .

Grbic-Galic carries out media preparation, inoculations, and culture transfers with strictly observed aseptic methods under a stream of  $\text{O}_2$ -free  $\text{N}_2$  or in anaerobic chambers under an atmosphere of  $\text{O}_2$ -free  $\text{N}_2$  and  $\text{H}_2$ . She is recording the weight and composition of all materials added to the cultures to construct a mass balance for each experiment.

Grbic-Galic conducts most of these experiments in hermetically sealed glass serum bottles, previously flushed with  $\text{N}_2$ , under an  $\text{O}_2$ -free atmosphere of 30%  $\text{CO}_2$  and 70%  $\text{N}_2$ . The seals consist of black butyl rubber stoppers held in place with Al crimps.

For each set of conditions, Grbic-Galic carries out triplicate experiments in the dark at an incubation temperature of  $30^\circ\text{C}$  for periods up to 6 months.

Grbic-Galic uses three types of controls for this study: (1) abiotic controls prepared according to the procedure described above, except for the addition of the inocula; (2) sterilized (autoclaved) controls with the same constituents as the active cultures, except that inocula have been deactivated; (3) controls with nutrients and active inocula, but without substrate.

Grbic-Galic monitors microbial activity by analyzing for several intermediate and final products of the substrates used for these studies in the solutions of brine and nutrient medium or the gaseous phase. The intermediate products consist of organic acids, volatile acids, and  $\text{H}_2$ ; the final products include  $\text{CH}_4$  (methanogenesis),  $\text{CO}_2$  (denitrification,  $\text{NO}_3^-$  reduction,  $\text{SO}_4^{2-}$  reduction, and methanogenesis),  $\text{H}_2\text{S}$  ( $\text{SO}_4^{2-}$  reduction), and  $\text{N}_2$  (denitrification and  $\text{NO}_3^-$  reduction). She also measures the dissolved concentrations of the potential electron acceptors  $\text{CO}_2$  (methanogenesis),  $\text{NO}_3^-$  (denitrification and  $\text{NO}_3^-$  reduction), and  $\text{SO}_4^{2-}$  ( $\text{SO}_4^{2-}$  reduction) in the solutions, as well as the dissolved concentrations of the nutrients N and P, and the pH.

Grbic-Galic analyzes for organic and volatile fatty acids by chromatographic separation as described by the American Public Health Association (1985). To determine  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{O}_2$  (to ensure that conditions remain anoxic), she uses gas partitioning as discussed by Tong et al. (1989). For  $\text{H}_2$ , she uses gas reduction detection. This method consists of separating  $\text{H}_2$  from other gases, passing it over a heated bed of  $\text{HgO}$ , and analyzing for Hg vapor by ultraviolet photometry (Smith, 1987). The colorimetric procedure for dissolved N is based on American Public Health Association (1976) and Sawyer and McCarty (1978); that for P is based on Environmental Protection Agency (1971) and the references cited for N. She is developing analytical procedures for  $\text{H}_2\text{S}$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  and will develop other analytical procedures as necessary during the course of these studies.

Grbic-Galic will not carry out any taxonomic analyses of the microorganisms responsible for any substrate degradation observed in this study at the present time, but might do so later.

Any procedures not described herein are identical to those discussed previously (4.4.1).

#### **4.4.3 Quantification of the Effects of Potentially Significant Microbial Processes on Repository Gas and Water Budgets**

Grbic-Galic will use the batch bioassay procedure developed at Stanford University for methanogenic fermentation studies (4.4.1) with the modifications described below to measure the rates at which any potentially significant microbial processes observed under overtest conditions (4.4.2) consume or produce gas and H<sub>2</sub>O. She will simulate as closely as possible the conditions expected for WIPP disposal rooms (humid and asaline, humid and saline, or inundated and saline) and avoid as much as possible overtest conditions that might accelerate these processes.

Grbic-Galic will carry out this study with different brines to quantify the effects of chemical variations (2.3 and 2.4) on the rates of these processes. Initially, she will use Salado-Fm. brines collected from the WIPP underground workings (2.3.1.2). She may also use a synthetic Salado-Fm. brine once Brush has defined a standard brine (2.3.1.3) and developed a formulation for it, as well as synthetic brines that simulate the composition of Castile-Fm. brines and fluids from overlying formations after equilibration with brines and minerals from the Salado Fm. (2.4.5 and 2.4.6).

Brush cannot estimate the quantities of nutrients in the TRU waste to be emplaced in the WIPP and, hence, their concentrations in any brine present in the repository. Therefore, Grbic-Galic will amend some, but not all, of these brines with nutrients to encompass possible conditions in WIPP disposal rooms. Bin-scale and alcove tests with CH TRU waste (Molecke, 1990a; 1990b) may reveal whether the availability of nutrients will limit microbial activity (4.5).

In addition, Grbic-Galic will measure the rates of these microbial processes under humid conditions by placing the substrate, electron acceptors, and inocula in an atmosphere saturated with H<sub>2</sub>O vapor in equilibrium with brine, but without placing them directly in the brine. Although the thermodynamic activity of H<sub>2</sub>O in these experiments will be equal to its activity in brine, the former experiments could yield lower rates for these processes because microorganisms must extract H<sub>2</sub>O from the gaseous phase instead of from brine. It may be necessary to reduce the rates measured in these experiments even further to account for the time required for diffusive transport of H<sub>2</sub>O vapor from the Salado Fm. through the repository atmosphere to locations at which microbial activity occurs.

Grbic-Galic will use cellulosics as the substrate for these experiments. Initially, she will use Solka Floc BW200 (4.4.2). She expects that the rates of gas production from denitrification, NO<sub>3</sub><sup>-</sup> reduction, SO<sub>4</sub><sup>2-</sup> reduction, fermentation, and methanogenesis will be very low, perhaps too low to measure (she will add the electron acceptors described in 4.4.2 to these experiments, but will not amend them with any nutrients). If so, she will report upper limits for these rates.

However, if the studies with Solka Floc BW200 yield measurable gas-production rates, Grbic-Galic will probably use paper (laboratory tissues,

paper towels, etc.) to simulate the cellulose in the WIPP inventory (4.3). She will use only paper because: (1) it is the largest constituent, about 70%, of the cellulose in TRU waste; (2) microbial degradation of the other cellulose will probably be too slow to yield measurable rates. She will use scissors to cut the paper to a size larger than that of Solka Floc BW200 (99% < 150  $\mu\text{m}$ ). If these experiments yield measurable rates, she will use paper in larger sizes and possibly other cellulose as well.

Grbic-Galic will use as inocula any microorganisms capable of carrying out denitrification,  $\text{NO}_3^-$  reduction,  $\text{SO}_4^{2-}$  reduction, fermentation, or methanogenesis in the study described in 4.4.2. She may use inocula denser than expected in WIPP disposal rooms to shorten the time period required for the build-up of a small microbial population at the beginning of these experiments.

For each set of conditions, Grbic-Galic will carry out triplicate experiments in the dark at an incubation temperature of 30°C for periods of up to 1 year.

Grbic-Galic will monitor microbial activity as described in 4.4.2. In addition, she will develop a procedure to determine the net consumption or production of  $\text{H}_2\text{O}$  during the microbial degradation of cellulosic materials. Environmental microbiologists have not quantified this parameter in any studies to date.

Any procedures not described herein are identical to those discussed previously (4.4.1 and 4.4.2).

#### **4.4.4 Quantification of the Effects of Pressure on Microbial Processes That Affect the Repository Gas and Water Budgets Significantly**

A study may be necessary to quantify the effects of pressure on any microbial processes that affect the repository gas and  $\text{H}_2\text{O}$  budgets significantly. If so, Brush will describe this study in detail later.

#### **4.4.5 Quantification of the Effects of Potentially Significant Microbial Processes on Radionuclide Chemistry**

Francis will carry out a study of the effects of microbial processes on radionuclide chemistry. Brush will describe this study in detail later.

#### **4.4.6 Determination of Whether Microorganisms Are Likely to Survive for Long Periods**

Grbic-Galic will use the batch bioassay procedure developed at Stanford University for methanogenic fermentation studies (4.4.1) with the modifications described below to determine whether the microorganisms responsible for any significant processes (4.4.3) are likely to survive for periods sufficient to affect the long-term performance of the WIPP. She will carry out both short-term (a few months) and long-term (a few years, if possible) survival experiments.

As inocula, Grbic-Galic will use any microorganisms capable of conducting denitrification,  $\text{NO}_3^-$  reduction,  $\text{SO}_4^{2-}$  reduction, fermentation, or

methanogenesis under realistic conditions at rates sufficient to affect the gas and H<sub>2</sub>O budgets of the repository significantly.

Grbic-Galic will store these microorganisms under humid and, perhaps, inundated conditions without a substrate and with any electron acceptors (4.4.2) with which microbial activity proceeds at significant rates.

After monthly intervals, Grbic-Galic will test for survival of microorganisms by inoculating them into favorable aqueous media. After yearly intervals, she will test for survival by adding substrates such as acetate, cellulosic materials, glucose, or lactate. Detection of microbial activity after inoculation or the addition of these substrates would imply that these microorganisms are still viable.

Any procedures not described herein are identical to those discussed previously (4.4.1 through 4.4.3).

#### **4.4.7 Quality Assurance and Safety**

Grbic-Galic is carrying out her studies of microbial activity (4.4.2, 4.4.3, and 4.4.6) in compliance with a quality assurance (QA) plan developed for WIPP-related studies (Grbic-Galic, 1989a) and approved by Pickering (1989b). This QA plan meets the requirements of American Society of Mechanical Engineers (1986) imposed by Sandia National Laboratories (1984a). The investigators responsible for future studies of microbial activity (4.4.4 and 4.4.5) will develop QA plans prior to the initiation of these studies.

Stanford University is responsible for the development, approval, and implementation of all safety procedures required for its studies. The subcontractors selected for future studies of microbial activity (4.4.4 and 4.4.5) will be responsible for the safety of these studies.

### **4.5 RESULTS EXPECTED FROM BIN-SCALE AND ALCOVE TESTS**

Analyses of gases sampled from bin-scale and alcove tests with CH TRU waste (Molecke, 1990a; 1990b) will also provide results relevant to microbial activity. Because it is difficult to estimate the quantities of nutrients in waste and, hence, their concentrations in any brine present in WIPP disposal rooms, the bin-scale tests provide an opportunity to determine whether the availability of nutrients will limit microbial activity. Comparison of CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>S, N<sub>2</sub>, and NH<sub>3</sub> production rates in bins with different types of waste may provide information on the relative importance of potentially significant microbial processes (4.2). Comparison of these gas production rates obtained from humid and partially inundated bins may provide data on the effects of H<sub>2</sub>O content on the rates of microbial activity. Lower CH<sub>4</sub>, H<sub>2</sub>S, or N<sub>2</sub> production rates in partially inundated bins with the proposed backfill additives CaO, Ca(OH)<sub>2</sub>, KOH, and NaOH than in similar bins without these compounds may imply that basic conditions inhibit microbial activity.

### **4.6 SCHEDULES FOR LABORATORY STUDIES**

Grbic-Galic started to determine which potentially significant microbial processes occur under overtest conditions (4.4.2) at Stanford University in



early October 1989, with nonhalophilic inocula. Vreeland sampled halophilic and halotolerant microorganisms from the WIPP Site and vicinity for the first time in mid-November 1989, but he does not know yet whether he successfully enriched microbial communities responsible for each of the potentially significant processes. He is especially concerned about  $\text{SO}_4^{2-}$ -reducing microorganisms. If Vreeland's first field trip was even partially successful, Grbic-Galic will start bioassays with halophilic and halotolerant inocula at Stanford by the beginning of January 1990. However, if additional field trips are necessary, she may not be able to start all of these experiments at Stanford until the beginning of April 1990 or later. She will carry out these experiments for periods of up to 6 months. She will complete the bioassays by the end of September 1990, if Vreeland enriches microbial communities responsible for all three potentially significant processes by the end of April 1990. Posttest analysis and reporting will require another 3 months. Grbic-Galic will thus complete this study by the end of December 1990.

Grbic-Galic will start to quantify the effects of those potentially significant processes that actually occur on the gas and  $\text{H}_2\text{O}$  budgets of WIPP disposal rooms under realistic conditions (4.4.3) at Stanford University as soon as she identifies which processes occur under overtest conditions. If any of the nonhalophilic microorganisms used to inoculate the first bioassays under overtest conditions prove to be halotolerant, she will start bioassays under realistic conditions by the beginning of April 1990. In any case, she will start experiments under realistic conditions with enrichments of halophilic and halotolerant microorganisms from the WIPP Site and vicinity by the beginning of October 1990. Microbial gas production under realistic conditions could be very slow and hence difficult to measure. She will carry out these experiments for at least 1 year, and perhaps longer if she does not observe any gas production, to ensure that these microorganisms do not affect the long-term performance of the repository significantly. She hopes to complete the bioassays by the end of September 1991. Posttest analysis and reporting will require another 3 months. She will thus complete this study by the end of December 1991.

A study may be necessary to quantify the effects of pressure on the microbial gas production rate (4.4.4). Brush will start this study as soon as possible, but has not selected a subcontractor yet. He will provide a schedule later.

Francis will quantify the effects of microbial processes that occur under overtest conditions on the speciation, solubilities, and sorption of radionuclides under realistic conditions at BNL (4.4.5). He will start this study as soon as possible. Brush will provide a schedule later.

Grbic-Galic will determine whether the microorganisms responsible for any significant processes are likely to survive for long periods (4.4.6) once she or Francis has identified which microbial processes could affect the repository gas and  $\text{H}_2\text{O}$  budgets or the chemical behavior of radionuclides significantly. She will start this study at Stanford University by the beginning of October 1990 and will carry out these experiments for as long as possible.

## 5.0 RADIOLYSIS

### 5.1 JUSTIFICATION FOR LABORATORY STUDIES

Most of the data reviewed by Molecke (1979) imply that the radiolytic gas production rate for transuranic (TRU) waste in Waste Isolation Pilot Plant (WIPP) disposal rooms will be significantly lower than recent estimates of the gas production rates from anoxic corrosion of metals (3.1) or microbial degradation of cellulose (4.1).

Estimates of the microbial gas production potential, and hence the total gas production potential, are very sensitive to assumptions of the extent to which microorganisms will degrade cellulose and plastics in the TRU waste to be emplaced in the WIPP. Lappin et al. (1989) estimated a microbial gas production potential of 600 moles per drum by assuming that microorganisms convert 100% of the cellulose, 50% of the rubbers, but none of the plastics in the WIPP inventory to gas. Their estimate would have been much higher if they had assumed that microorganisms will degrade plastics significantly. The microbial gas production potential is much less sensitive to the conversion of rubbers because there is much less rubber than plastic in the inventory (5.2).

Microorganisms will almost certainly consume cellulose in preference to plastics and rubbers. Irradiation of plastics could, however, cause scission, decreased saturation, and changes in the chemical composition of these materials such as uptake of N<sub>2</sub>, O<sub>2</sub>, and S (5.3), which could make them more biodegradable (Grbic-Galic, personal communication). A laboratory study of the effects of  $\alpha$  radiolysis on the biodegradability of these materials under various repository conditions is necessary to determine the gas production potential of the waste.

### 5.2 ESTIMATES OF PLASTICS AND RUBBERS IN THE WIPP INVENTORY

Estimates of the quantities and proportions of plastics and rubbers in the WIPP inventory are necessary to design laboratory studies of the effects of radiolysis on the biodegradability of these materials, as well as for estimates of their microbial gas production potential.

These estimates are based on the preliminary inventory by Drez and James-Lipponer (1989) of the nonradioactive constituents of the contact-handled (CH) TRU waste to be emplaced in the WIPP. For their inventory, they compiled the results of a survey, which included a detailed questionnaire, of the waste generators and storage sites.

To obtain the total quantities of plastics and rubbers in containers and the waste, Brush: (1) assumed that 50% of the quantity of leaded rubber gloves (Table 3-5 of Drez and James-Lipponer, 1989) consists of Hypalon and neoprene, and prorated the resulting value of 298,000 kg between Hypalon and neoprene (Table 3-5); (2) assumed that the plastic prefilters (Table 3-5) are polypropylene, as suggested by Drez and James-Lipponer (1989); (3) prorated the polyvinyl chloride (PVC)/polyethylene drum liner bags (Table 3-8 of Drez and James-Lipponer, 1989) between polyethylene and PVC (these plastics appear in both Tables 3-5 and 3-8).

The quantities estimated by Drez and James-Lipponer (1989) are: 2,030 kg of Conwed pads (plastic fibers), 254,000 kg of Hypalon, < 1 kg of Kalrez, 582,000 kg of latex, 287,000 kg of neoprene, 18,900 kg of Plexiglas (including Lucite), 3,270,000 kg of polyethylene, 33,600 kg of polypropylene, 2,560 kg of polystyrene, 1,170,000 kg of PVC, 330 kg of Styrofoam, 41,000 kg of Teflon, 133 kg of Viton, 75,500 kg of miscellaneous plastics, and 7,530 kg of miscellaneous rubbers.

Based on these estimates, Brush calculated that the plastics and rubbers in the WIPP inventory will consist of about: 0.04% Conwed pads (plastic fibers), 4% Hypalon, 10% latex, 5% neoprene, 0.3% Plexiglas (including Lucite), 60% polyethylene, 0.6% polypropylene, 0.04% polystyrene, 20% PVC, 0.006% Styrofoam, 0.7% Teflon, 0.002% Viton, 1% miscellaneous plastics, and 0.1% miscellaneous rubbers. These percentages do not add up to 100% because Brush rounded them off to one significant figure.

Clearly, the plastics and rubbers in the WIPP inventory will consist mainly of polyethylene and PVC. The laboratory study of the effects of a radiolysis on the biodegradability of plastics and rubbers will therefore emphasize polyethylene and PVC, at least initially. If revisions of the inventory imply that other plastics and rubbers are major constituents of the waste, experiments with these materials may also be necessary.

### 5.3 REVIEW OF THE EFFECTS OF IRRADIATION OF PLASTICS

Reed (1989a) summarized reviews by Chapiro (1962), Dole and Bodily (1967), and Charlesby (1987) of the effects of ionizing radiation on plastics; his summary appears below. The studies reviewed by these authors mainly considered the effects of  $\beta$  and  $\gamma$  radiation, not  $\alpha$  radiation. These are both low linear-energy-transfer (low LET) forms of ionizing radiation. Low LET radiation is useful for processing plastics, such as initiation of polymerization of monomeric materials or alteration of the physical properties of polymeric materials, because it is highly penetrating and hence more useful for bulk processing. The  $\alpha$  radiation characteristic of TRU waste, however, has a much higher LET than that of  $\beta$  and  $\gamma$  radiation. It will therefore penetrate much less deeply than  $\beta$  or  $\gamma$  radiation and produce more localized damage than observed in previous studies.

The three most important effects of ionizing radiation on plastics are: (1) scission (fragmentation) of the main polymer chains, which lowers the average molecular weight of the polymer; (2) cross-linking and network formation, which forms C-C bonds between adjacent polymer molecules; (3) changes in the chemical composition of the polymer, caused by either formation of C double bonds (decreased saturation), accompanied by the evolution of H<sub>2</sub> and other gases, or the incorporation of components present in the environment into the matrix of the polymer.

Main-chain scission can, by lowering the molecular weight of the polymer, significantly affect its physical properties even at absorbed doses as low as 1 Mrad. Scission breaks the C-C bonds, thus decreasing molecular weight. The removal of H atoms increases saturation and potential uptake of other components by the polymer.

Cross-linking is an important phenomenon in the irradiation processing of some plastics. The formation of C-C bonds may decrease saturation and release H<sub>2</sub> and other gases. Although an absorbed dose of only a few Mrad can produce detectable changes in the physical properties of plastics at room temperature, relatively high doses (1,000 Mrad or higher) are required to produce macroscopic effects. The amount of cross-linking produced by a given dose is very temperature-dependent and increases rapidly above the melting point of the plastic, typically 80 to 120°C for polyethylene and PVC.

Based on his review, Reed (1989a) concluded that the uptake of other components by plastic is poorly understood. Increased unsaturation is apparently an important result of radiolysis. Unsaturation releases H<sub>2</sub> and other gases with yields comparable to that of cross-linking. Unsaturation promotes the uptake of components such as O<sub>2</sub> and S by providing reaction sites for relatively short-lived free radicals at the surface of the plastic or relatively long-lived free radicals diffusing into the plastic.

Reed (1989a) also concluded that low-LET irradiation in aqueous and gaseous environments affects the chemical composition and physical properties of plastics differently, and that irradiation to the same total absorbed dose, but at different dose rates, causes different results attributable to variable periods of environmental interaction. Neither Bibler (1978) nor Kosiewicz (1981) observed a dose-rate dependency for  $\alpha$  radiolysis.

Chapiro (1962), Dole and Bodily (1967), Spinks and Woods (1976), and Charlesby (1987) reviewed several studies of low-LET irradiation of polyethylene (a saturated hydrocarbon), the most frequently studied plastic. The gas produced was mainly H<sub>2</sub> (typically > 65%), with smaller amounts of C<sub>1</sub> to C<sub>3</sub> alkanes present. The G values reported for H<sub>2</sub>, cross-linking, and unsaturation varied from 3 to 5, 1 to 4, and 1 to 2, respectively. The units for G values are molecules per 100 eV of absorbed energy or, in the case of unsaturation, bonds per 100 eV, and are usually omitted. These yields depend on the irradiation environment and the nature of the polyethylene (chemical composition, type of plasticizer, production procedures, etc.). Irradiation of polyethylene without plasticizer in a vacuum gave reproducible results; H<sub>2</sub> evolution and weight loss were the main radiolytic effects. In experiments carried out with O<sub>2</sub> in the gaseous phase, the polyethylene incorporated O<sub>2</sub> at radiolytically produced reaction sites, resulting in weight gain and the formation of carbonyl groups in the polymer. Experiments conducted with CO<sub>2</sub> yielded similar results.

Kosiewicz (1981) observed that the gas produced from the  $\alpha$  radiolysis of polyethylene comprised 98% H<sub>2</sub> and reported G values of 2.6 to 3.2 for H<sub>2</sub>.

Chapiro (1962), Dole and Bodily (1967), Spinks and Woods (1976), and Charlesby (1987) also reviewed a few studies of low-LET irradiation of PVC (a halogenated hydrocarbon), and concluded that irradiation of this plastic produces mainly HCl. The G values reported for HCl varied from 0.25 to 13 and were very sensitive to the plasticizer and the extent of Cl<sup>-</sup> substitution. Large absorbed doses made PVC very hard and brittle. The dominant process during vacuum irradiation was cross-linking accompanied by strong discoloration. In the presence of O<sub>2</sub> the dominant process was main-chain scission, with much less discoloration. Although Reed (1989a) found no

studies of irradiation of PVC in the presence of CO<sub>2</sub>, he expects results similar to those obtained with O<sub>2</sub>.

Neither Zerwekh (1979) nor Kosiewicz (1981) observed HCl in gases released from Pu-contaminated PVC.

Studies reviewed by Spinks and Woods (1976) imply that the range of  $\alpha$  particles in plastics is generally a few tens of microns. This is less than their range in air (a few centimeters) and similar to their range in aqueous solutions. These estimates all assume energies of a few MeV for  $\alpha$  particles. The altered zone will actually extend beyond 10  $\mu$ m due to secondary electrons and  $\gamma$  rays generated by interactions between the  $\alpha$  particles and the polymer matrix. The thickness of the plastics used in the studies described in 5.5.1 is probably greater than the range of  $\alpha$  particles in these materials. Irradiation damage will fall off sharply as a function of depth; therefore, the plastics will be inhomogeneously irradiated. Because a relatively small volume of the samples may be affected, it may be difficult to detect microbial activity even if irradiation actually increases the biodegradability of these plastics. The limited range of  $\alpha$  particles in plastics might also limit the extent to which radiolysis increases their biodegradability in WIPP disposal rooms.

#### 5.4 ADDITIONAL STUDIES OF RADIOLYSIS

Although Molecke (1979) concluded that radiolytic gas production will be relatively insignificant in WIPP disposal rooms, recent developments raise the possibility that radiolysis could be important.

Subsequent to most of the previous studies of radiolysis carried out for the WIPP Project, personnel at the Rocky Flats Plant (RFP) decided to compact their newly generated waste. Compaction of previously generated waste is also under consideration as a possible engineering modification of the WIPP (Butcher, 1990). Even without compaction prior to emplacement, closure of WIPP disposal rooms would compact the waste. Compaction may increase the radiolytic gas production rate by increasing the density of the waste and the extent to which  $\alpha$  particles interact with it. Data exist for super compaction of low-level waste (see Kroth, 1988), but not for TRU waste.

Inundation of the waste with brine may also increase the radiolytic gas production rate. The highest radiolytic gas production rates reviewed by Molecke (1979) occurred in sludges and resulted from the high H<sub>2</sub>O contents of the sludges. Gray and Simonson (1984) carried out a study of  $\alpha$  and  $\gamma$  radiolysis of brines at very high dose rates of 0.3 to 5 Mrad per hour. They used their experimental results, which showed much higher H<sub>2</sub> production rates for  $\alpha$  radiolysis than for  $\gamma$  radiolysis, and a computer code developed by Carver, Hanely, and Chapin (1979) to estimate an equilibrium H<sub>2</sub> pressure of about 300 atm at an absorbed dose of 2,000 Mrad. Because their dose rates were so much higher than those expected for brine in WIPP disposal rooms, the relevance of these results to the WIPP is unknown.

Finally, increased pressure caused by gas production from anoxic corrosion of metals (3.1), microbial degradation of cellulose (4.1), and closure of WIPP disposal rooms may affect the radiolytic gas production rate.

Kosiewicz, Barraclough, and Zerwekh (1979) studied the effects of pressure on  $\alpha$  radiolysis of TRU waste, but reported ambiguous results varying from a decrease to 10% to an increase to 300% of the radiolytic gas production rate at atmospheric pressure.

A review of the results of other investigations is under way to determine whether additional studies are necessary to quantify the effects of waste compaction, inundation, and pressure on the radiolytic gas production rate.

## **5.5 DESCRIPTION OF LABORATORY STUDIES**

The objectives of these studies are to: (1) quantify the effects of  $\alpha$  radiolysis on the biodegradability of plastics (5.5.1); (2) determine, if the review implies it is necessary, the effects of waste compaction and inundation on the radiolytic gas production rate (5.5.2).

D. T. Reed of Argonne National Laboratory (ANL) and D. Grbic-Galic of Stanford University are quantifying the effects of  $\alpha$  radiolysis on the biodegradability of plastics (5.5.1).

S. T. Kosiewicz of Los Alamos National Laboratory and Reed are reviewing other work to determine if additional studies of radiolysis are necessary (5.4). If so, Reed will carry out these studies (5.5.2).

### **5.5.1 Quantification of the Effects of $\alpha$ Radiolysis on the Biodegradability of Plastics**

Reed is irradiating samples of plastics with  $\alpha$  particles for this study (5.5.1.1). After irradiation, Grbic-Galic will use the bioassay procedure described in 4.4.1 and 5.5.1.2 to determine whether  $\alpha$  radiolysis increases the biodegradability of these materials.

#### **5.5.1.1 IRRADIATION OF PLASTICS**

Reed is irradiating samples of polyethylene and PVC under humid and inundated conditions at 30°C and pressures of about 1 atm for periods of 12 weeks. These irradiations and subsequent bioassays (5.5.1.2) are short-term or scoping experiments. The objective of these short-term experiments is to evaluate the procedures for the irradiations and bioassays as quickly as possible. The duration of these experiments places severe constraints on the maximum absorbed dose attainable. After completion of these initial irradiations and bioassays, Reed may carry out longer irradiations with samples of the same materials. If so, Brush will describe these studies in detail later.

Reed (1989b) completed initial development of equipment and procedures for short-term irradiations of polyethylene and PVC. The objectives of this work were to: (1) construct environmental control boxes and sample and source holders; (2) adapt the gaseous-phase dosimetry used at ANL for other applications to conditions relevant to these experiments; (3) determine the extent of  $\alpha$  contamination of plastics during irradiation (Stanford University specifies very low levels of  $\alpha$ -contamination for these samples.)

The containers for the short-term irradiations are 8-L (20-by-20-by-20-cm) polypropylene boxes with clear plastic lids attached with screws and sealed with O-rings placed in grooves in the boxes. The lids have two ports, one fitted with a valve for gas inlet and outlet tubes, the other with a septum for sampling gas with a 10-ml syringe during the experiments.

The effects of  $\alpha$  irradiation on plastics depend on factors such as the chemical composition of the sample, quantity and type of plasticizer, and production procedures (5.3). To ensure that the samples used for this study are representative of the plastics to be emplaced in the WIPP (5.2), Brush requested samples of polyethylene and PVC from Bearly and Detamore at the RFP in Golden, Co. (RFP is the largest generator of TRU waste.) Bearly and Detamore provided the following uncontaminated samples of plastics used by RFP for packaging TRU waste: (1) three lids from 90-mil, polyethylene drum liners (the liners themselves were larger and more difficult to ship than the lids); (2) one folded sheet of the material used to fabricate round-bottom, 10-mil polyethylene drum liners; (3) one folded sheet of the material used to fabricate 5-mil, polyethylene drum liners; (4) one folded sheet of the material used to fabricate 10-mil, PVC O-ring bags. After inspection of these materials at ANL, Reed concluded that the lids from the drum liners were unsuitable for his experiments because the rough surfaces of these materials (variations of  $\pm 1$  cm over distances of several centimeters) precludes an even spacing between the samples and the  $\alpha$  sources in the foil-sample assemblies with a gap (see below). To reduce the number of irradiations, he selected one type of polyethylene (the 10-mil polyethylene sheet), and is irradiating samples of this material along with samples of the 10-mil PVC sheet.

Prior to irradiation, Reed prepares the samples of polyethylene and PVC by cutting them into squares with a surface area slightly in excess of 25 cm<sup>2</sup>. Based on the expected range of  $\alpha$  particles in these plastics (5.3), Reed (personal communication) estimated that a sample size of 25 cm<sup>2</sup> is necessary to ensure that  $\alpha$  particles penetrate about 10 mg of these plastics. This would provide enough substrate for triplicate bioassays and one blank with 2.5 mg of substrate per sample, the minimum required for the detection of microbially produced gas during the bioassays described in 5.5.1.2 (Grbic-Galic, personal communication). The masses of these polyethylene and PVC samples are 1 to 1.5 g and 3 to 3.5 g, respectively. Reed cleans them by rinsing in acetone, methanol, then high-purity H<sub>2</sub>O, weighs them to five significant figures, and marks them with the experiment number. After cleaning, he handles them with tongs to avoid possible contamination with finger grease, which might serve as substrate for microorganisms during the bioassays.

The  $\alpha$  sources for the short-term irradiations are commercially produced foils with various levels of  $\alpha$  activity from either <sup>241</sup>Am or <sup>210</sup>Po. The dimensions of these foils are 6.1 by 6.1 by 0.02 cm; the active area is 5.1 by 5.1 cm. They are surrounded by seals with a width of 0.5 cm. The maximum activities of <sup>241</sup>Am and <sup>210</sup>Po are 1,500 and 9,000  $\mu$ Ci per in<sup>2</sup>, respectively. Additional foils contain 75, 50, and 25% of these maximum activities.

The foils consist of a five-layer composite bonded to a layer of plastic with a thickness of 0.125 in. The layers consist of a thin backing of

metallic Ag, a layer of metallic Au, the radionuclide (incorporated using a proprietary powder metallurgy process), and two additional layers of Au. For durability, the manufacturer bonds the foils to a layer of Lucite with dimensions of 9.5 by 7.6 by 0.3 cm. Despite the Lucite backing, the foils are very fragile and susceptible to damage by abrasion, bending, shearing, etc. The manufacturer seals, surveys, and certifies the foils for leakage of radionuclides.

Reed uses two types of foil-sample assemblies for the short-term irradiations. In one type of assembly, the foil is in direct contact with the sample of polyethylene or PVC to be irradiated. In the other type, there is either a 3-mm or a 2-cm gap between the foil and the plastic.

Reed prepares the foil-sample assemblies without a gap by placing a sample of polyethylene or PVC on the foil, covering the sample with a piece of Lucite with the same areal dimensions, and clamping the assembly together with plastic clamps on two of its edges. The use of this additional layer of Lucite further increases the durability of the assembly. For irradiations under inundated conditions, he wets the surface of the foil with brine prior to placing the polyethylene or PVC on it.

To prepare the foil-sample assemblies with a gap, Reed places the sample of polyethylene or PVC on a piece of Lucite. In these assemblies, the sample extends beyond two of the edges of the Lucite. Next, he places plastic spacers with a width of 6 mm and a thickness of 3 mm or 2 cm on the overhanging edges of the sample to maintain a gap between the foil and the sample. These spacers span the entire length of the edges, but do not touch the active area of the foils. He then aligns the foil on the spacers and clamps one of the edges with a spacer. Finally, he draws the sample as tightly as possible to ensure a constant gap and clamps the other edge.

After preparation of the foil-sample assemblies, Reed places them in a plastic holder, puts the holder into the containers, seals the containers, flushes them with one of the two gases described below, and samples the gas for analysis of its initial composition by gas chromatography.

Because environmental conditions could affect the nature and extent of the effects of  $\alpha$  irradiation (5.3), Reed irradiates samples of polyethylene and PVC under both humid and inundated conditions. To establish humid conditions, he pours about 50 ml of brine into the containers to saturate the gas with H<sub>2</sub>O vapor, but does not immerse the foil-sample assemblies. He uses Salado-Fm. brine collected from G Seep in the WIPP underground workings (2.3.1.2) for all of the short-term irradiations, and gases with two different compositions for the humid experiments. Because quantitative prediction of the proportions of the gases in WIPP disposal rooms is still unfeasible, Brush arbitrarily specified two gas compositions for these experiments. One of these gases consists of 10% CO<sub>2</sub> and 90% N<sub>2</sub>, and simulates a microenvironment free of H<sub>2</sub> and O<sub>2</sub>. The other consists of 6.25% CO<sub>2</sub>, 2.50% H<sub>2</sub>, 1.25% O<sub>2</sub>, and 90% N<sub>2</sub>, and simulates a microenvironment in which radiolytic decomposition of H<sub>2</sub>O has produced stoichiometric proportions of H<sub>2</sub> and O<sub>2</sub>. Because safety regulations at ANL limit the concentration of H<sub>2</sub> to 2.5%, the stoichiometrically related proportion of O<sub>2</sub> is 1.25%, and the concentration of CO<sub>2</sub> required to maintain a 90%-N<sub>2</sub>-10%-other-gases mixture is



6.25%. Reed uses commercially available, certified mixtures for both of these gases and verifies their composition prior to use. To simulate inundated conditions, he adds enough brine to immerse the foil-sample assemblies and bubbles the gas consisting of 6.25% CO<sub>2</sub>, 2.50% H<sub>2</sub>, 1.25% O<sub>2</sub>, and 90% N<sub>2</sub> through the brine for 20 minutes prior to sealing the containers.

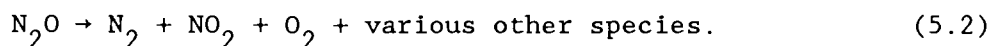
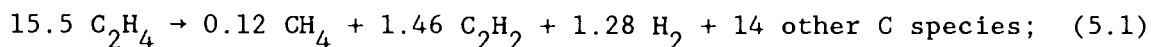
Reed irradiates seven samples of polyethylene and seven samples of PVC in each of the two gases described above under humid conditions, or a total of 28 samples under humid conditions. For these irradiations, he uses <sup>210</sup>Po-bearing foils because they have a higher maximum activity than the <sup>241</sup>Am-bearing foils, and because the contamination observed with <sup>210</sup>Po-bearing foils under inundated conditions is not a problem in these humid experiments. One sample of each material is in direct contact with a foil with the maximum activity in each of the two gases to provide information on the effects of irradiation with minimal interactions with the gas and its radiolysis products. Four samples of each material are separated by a gap of 3 mm from foils with 100, 75, 50, and 25% of the maximum activity in each of the two gases to study the simultaneous effects of irradiation and interactions with the gas and its radiolysis products. After attenuation by two surficial layers of Au on the foils, the average energy of  $\alpha$  particles from <sup>210</sup>Po-bearing foils is about 3.9 MeV; their range in these gases is about  $2.4 \pm 0.2$  cm. One sample of each material is separated by a gap of 2 cm from a foil with the maximum activity in each of the two gases to study the effects of interactions with the gas and its radiolysis products with minimal irradiation of the plastics ( $\leq 5\%$  of the dose absorbed by samples in direct contact with the <sup>210</sup>Po-bearing foils). Finally, one sample of each material without a foil is well out of range of  $\alpha$  particles in each of the two gases to study the effects of interactions with gas and its radiolysis products in the absence of any irradiation of the plastics. Although any effects of gaseous radiolysis products on the last two samples will probably be small, these conditions also simulate those expected for WIPP disposal rooms, in which radionuclides will probably not be in direct contact with plastics in most cases.

Reed irradiates six samples of polyethylene and six samples of PVC in brine, or a total of 12 samples under inundated conditions. For these irradiations, he uses <sup>241</sup>Am-bearing foils because the  $\alpha$  particles they emit have a longer range than those emitted by <sup>210</sup>Po-bearing foils. The average energy of  $\alpha$  particles from <sup>210</sup>Po-bearing foils, after attenuation, is about 4.8 MeV. Furthermore, the contamination from <sup>241</sup>Am-bearing foils under inundated conditions is less of a problem than that from <sup>210</sup>Po-bearing foils. Four samples of each material are in direct contact with foils with 100, 75, 50, and 25% of the maximum activity to provide information on the effects of irradiation with minimal interactions with the brine and its radiolysis products. Actually, there is a thin film of brine between the samples and the foils. One sample of each material is separated by a gap of 3 mm from a foil with the maximum activity to study the effects of interactions with the brine and its radiolysis products in the absence of any irradiation of the plastics. The effects of aqueous radiolysis products on this sample may be small, but this experiment is necessary to simulate cases in which radionuclides are not in direct contact with plastics. Finally, one sample of each material without a foil is well out of the range of  $\alpha$  particles and radiolysis products from the brine to study the effects of interactions with unirradiated brine.

Reed irradiates these samples for periods of 12 weeks. He does not control the temperature during these irradiations, but does monitor it occasionally. Self-heating generally maintains the temperature within the containers at about 26 or 27°C. After periods of 2, 4, 8, and 12 weeks, he samples about 5 to 10 ml of gas for analysis.

Reed (1989b) extended the gaseous-phase dosimetry used at ANL for other studies to conditions expected for these experiments by: (1) establishing that existing dosimeters for  $\beta$  and  $\gamma$  radiation are also applicable to  $\alpha$  radiation; (2) developing a procedure to measure the dose rates of the  $^{241}\text{Am}$ - and  $^{210}\text{Po}$ -bearing foils used for the short-term irradiations; (3) establishing a method to determine the doses absorbed by the dosimeter gases and, after correction for molecular weight, those absorbed by the test gases. Subtraction of the doses absorbed by the test gases from those emitted by the  $\alpha$  sources yields the doses absorbed by the plastics. Because he assumes that all of the energy will be deposited in the plastics in those assemblies with no gap between the foils and the samples, and none of it will be deposited in the inundated experiments with assemblies with a gap, the third objective applies to humid experiments with a gap.

Most investigators use pure ethylene or  $\text{N}_2\text{O}$  at measured pressures of about 1 atm for gaseous-phase dosimetry. Ionizing radiation decomposes ethylene and  $\text{N}_2\text{O}$  by the reactions:



For both  $\beta$  and  $\gamma$  radiation, the production of  $\text{H}_2$  from Reaction 5.1 is linear with absorbed dose in the range 0.5 to 20 Mrad with a G value of 1.35. The  $\text{N}_2$  yield from Reaction 5.2 is linear with dose in the range 0.05 to 20 Mrad with a G value of 10. ANL personnel have used  $\text{N}_2\text{O}$  as a dosimeter for other studies.

Reed (1989b) carried out experiments with both of these dosimeters to estimate the doses absorbed from the  $\alpha$  sources and to determine whether the yields for these dosimeters are linear with dose. The  $\text{H}_2$  yield was linear up to an effective dose of 6 Mrad. This was within the recommended range of the dosimeter gas. Reed uses the term "effective" because irradiation is inhomogeneous. The effective dose is the dose absorbed by the entire volume of the dosimeter gas. The dose absorbed by gas near the foils is significantly higher. The  $\text{N}_2$  yield was linear up to an effective dose of 6.4 Mrad. This exceeds the recommended limit for this dosimeter by about a factor of 3. The yield for the  $\text{N}_2\text{O}$  dosimeter is higher than that of ethylene, but the intercept of the linear plot of the irradiation time versus its yield can be displaced significantly from 0 by the presence of residual air in the container. This error leads to overestimates of the dose. The ethylene dosimeter is less sensitive to contamination than  $\text{N}_2\text{O}$ , has a lower yield than  $\text{N}_2\text{O}$  (requiring longer exposure times), and is susceptible to errors caused by the presence of  $\text{H}_2$ , which may be produced by the radiolytic decomposition of the samples. Therefore, he will rely mainly on the ethylene dosimeter during the short-term irradiations, but may also use the  $\text{N}_2\text{O}$  dosimeter.

Reed carries out gaseous-phase dosimetry on the foils with and without plastics in place to determine both the doses absorbed by the gas and those absorbed by the plastics. Because deposition of organic radiolysis products from the dosimeter gases on the foils or the plastics could reduce the doses or affect the results of the bioassays, he conducts all of the dosimetry in containers separate from those used to irradiate plastics for the bioassays. He evaluates foils and foil-sample assemblies representative of each activity level. For each activity level, he places foils and foil-sample assemblies into polypropylene containers identical to those described above. Next, he evacuates and refills the containers twice with ethylene or N<sub>2</sub>O. Because the total pressure of these gases affects the dosimetry significantly, he fills the containers to a final pressure of 700 to 900 torr, measured with a pressure gauge traceable to standards calibrated by the National Bureau of Standards. After 8 to 16 hours, depending on the activities of the foils, he analyzes the gas for H<sub>2</sub> or N<sub>2</sub> by gas chromatography. Finally, he uses published yield values to calculate the doses absorbed by the plastics.

Reed (1989b) carried out three 2-week experiments (one each with polyethylene and PVC under humid conditions, and one each under inundated conditions) to determine the extent of  $\alpha$  contamination of these plastics after direct contact with foils. Prior to rinsing with deionized H<sub>2</sub>O, the samples irradiated under humid conditions had activities about 3 orders of magnitude below the limit for unlicensed handling specified by Stanford University (5.5.1.2), and those irradiated under inundated conditions had activities about 2 or 3 orders of magnitude below this limit. Rinsing did not decrease these activities significantly. Nevertheless, he will carry out a radiation survey of the samples after the 12-week irradiations. If the measured activities are acceptable, he will reweigh and store them at 0°C prior to shipment to Stanford. If not, he will rinse them repeatedly in deionized H<sub>2</sub>O to reduce the contamination to acceptable levels. Rinsing may remove any soluble radiolysis products from the plastics irradiated under humid conditions. Any soluble radiolysis products formed under inundated conditions will probably have dissolved in the brine prior to rinsing. He will therefore analyze any H<sub>2</sub>O used to rinse these samples. If he cannot achieve acceptable levels, he will store them at ANL until Brush determines if there are a sufficient number of contaminated samples to justify bioassay at a facility that can accept higher levels of  $\alpha$  contamination.

Reed will reweigh the samples to determine if the weight is affected by irradiation and analyze the gas again.

Reed will ship all samples to Stanford University in a freezer at 0°C, or at slightly lower temperatures to prevent the consumption of any biodegradable materials.

#### 5.5.1.2 BIOASSAY OF IRRADIATED PLASTICS

Grbic-Galic will use the batch bioassay procedure developed at Stanford University for CH<sub>4</sub> fermentation studies (4.4.1) with the modifications described below to determine whether  $\alpha$  radiolysis increases the biodegradability of plastics.

Grbic-Galic will carry out this study with 100 ml of Salado-Fm. brine collected from G Seep in the WIPP underground workings (2.3.1.2) in 150-ml glass serum bottles. She may also use brines collected from other locations in the WIPP underground workings, a synthetic Salado-Fm. brine once Brush has defined a standard brine (2.3.1.3) and developed a formulation for it, or synthetic brines that simulate the composition of Castile-Fm. brines and fluids from overlying formations after equilibration with brines and minerals from the Salado Fm. (2.4.5 and 2.4.6).

The substrates for this study will consist of irradiated samples of polyethylene and PVC (5.5.1.1). Stanford University does not require that Grbic-Galic obtain a license to handle radioactive samples if the activity in each sample is less than 0.1  $\mu\text{Ci}$  per sample, or if the total activity in ten such samples is less than 1  $\mu\text{Ci}$ . For multiple samples with a total activity of 1 to 10  $\mu\text{Ci}$ , 10  $\mu\text{Ci}$  to 1 mCi, and greater than 1 mCi, she must obtain various licenses from Stanford's Engineering Safety Committee. She prefers not to work with multiple samples with a total activity higher than 10  $\mu\text{Ci}$  at one time and will not work with multiple samples with more than 1 mCi at one time. Reed will carry out a radiation survey to determine if the levels of surface  $\alpha$  contamination of the samples are acceptable prior to shipping them to Stanford.

Grbic-Galic will cut the 25-cm<sup>2</sup> samples of polyethylene and PVC into four pieces with approximately equal irradiated areas for triplicate bioassays and one blank. A sample size of 25 cm<sup>2</sup> would provide enough substrate for detection of any microbially produced gas during these bioassays (5.5.1.1).

Because the number of samples of irradiated plastics will be limited, Grbic-Galic will use as inocula those microorganisms described in 4.4.2 that are most active under saline, inundated conditions, and carry out these experiments under conditions appropriate to these microorganisms. This will facilitate the detection of any microbial degradation of small amounts of radiolytically altered plastics.

Grbic-Galic will carry out the bioassays in the dark at an incubation temperature of 30°C for periods of up to 1 year.

Grbic-Galic will use two types of controls for this study: (1) abiotic, irradiated controls prepared identically to the other irradiated materials, except for the addition of the inocula; (2) unirradiated controls prepared identically to the irradiated materials, except for irradiation. For the unirradiated controls, Reed will handle samples of plastics, prepare them for irradiation, store them, and ship them to Stanford University along with the irradiated materials.

Any procedures not described herein are identical to those discussed previously (4.4.1 through 4.4.3).

## **5.5.2 Determination of the Effects of Waste Compaction, Inundation, and Pressure on the Radiolytic Gas Production Rate**

Additional studies of the effects of waste compaction, inundation, and pressure on the radiolytic gas production rate may be necessary (5.4). If so, Brush will describe these studies in detail later.

### 5.5.3 Quality Assurance and Safety

Reed and Grbic-Galic are carrying out their study of the effects of  $\alpha$  radiolysis on the biodegradability of plastics (5.5.1.1 and 5.5.1.2, respectively) in accordance with quality assurance (QA) plans developed for WIPP-related studies (ANL, 1989; Grbic-Galic, 1989a) and approved by Pickering (1989b, 1990b). These QA plans meet requirements of the American Society of Mechanical Engineers (1986) imposed by Sandia National Laboratories (1984a). ANL will revise its QA plan for WIPP, if necessary, for future studies of radiolysis (5.5.2) prior to the initiation of these studies.

ANL and Stanford University are responsible for the development, approval, and implementation of all safety procedures required for their study.

### 5.6 RESULTS EXPECTED FROM BIN-SCALE AND ALCOVE TESTS

Analyses of gases sampled from bin-scale and alcove tests with CH TRU waste (Molecke, 1990a; 1990b) will also provide results pertinent to radiolysis. Significant radiolytic gas production rates in bin-scale or alcove tests with compacted wastes, or in bin-scale tests with partially inundated waste may imply that radiolysis must be included in estimates of the overall gas production rate under these conditions.

### 5.7 SCHEDULES FOR LABORATORY STUDIES

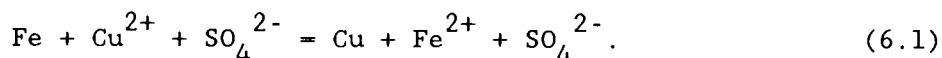
Reed started short-term  $\alpha$  irradiations of samples of polyethylene and PVC (5.5.1.1) at ANL in early December 1989, and will complete them in early March 1990. He will survey the samples for contamination and ship them to Stanford University during March 1990. Grbic-Galic will start the bioassays (5.5.1.2) at Stanford by the beginning of April 1990. Even if irradiation increases the biodegradability of these plastics, microbial gas production could still be very slow. She will carry out these bioassays for at least 6 months, and preferably for up to 1 year if she does not observe any gas production, to ensure that the biodegradability of these materials is not enhanced by  $\alpha$  radiolysis. She will complete the bioassays by the end of September 1990 at the earliest, but perhaps not until the end of March 1991. Posttest analysis and reporting will require another 3 months. She will complete this study by the end of December 1990 at the earliest, but perhaps not until the end of June 1991.

Kosiewicz and Reed are reviewing the results of other investigations to determine if additional studies of the effects of waste compaction, inundation, and pressure on the radiolytic gas production rate are necessary. If so, Reed will start these studies as soon as he completes the short-term irradiations of plastics. Brush will provide schedules for these studies later.

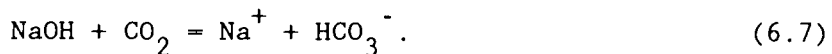
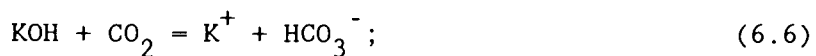
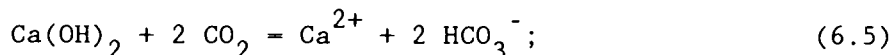
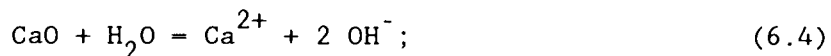
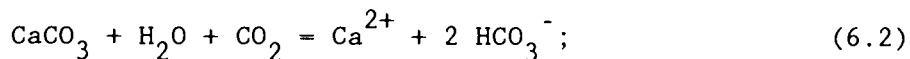
## 6.0 BACKFILL ADDITIVES

### 6.1 JUSTIFICATION FOR LABORATORY AND MODELING STUDIES

Brush and Anderson (1988a, 1989) proposed the use of several backfill additives to remove or prevent the production of some of the gases expected in Waste Isolation Pilot Plant (WIPP) disposal rooms.  $\text{CuSO}_4$ , an oxidant, would corrode Fe and Fe-base alloys without producing  $\text{H}_2$  by the reaction:



Because  $\text{CuSO}_4$  readily hydrates to  $\text{CuSO}_4 \cdot n\text{H}_2\text{O}$  with  $n$  usually equal to 1, 3, 5, or 7, anhydrous  $\text{CuSO}_4$  would also consume brine.  $\text{CaCO}_3$ ,  $\text{CaO}$ ,  $\text{Ca(OH)}_2$ ,  $\text{KOH}$ , and  $\text{NaOH}$  would remove microbially or radiolytically produced  $\text{CO}_2$  (4.2.2, 4.2.5, and 4.2.6) from WIPP disposal rooms by the reactions:



$\text{MnO}_2$ , a potential electron acceptor (4.2.3), might prevent microbial  $\text{SO}_4^{2-}$ -reduction, the concomitant production of  $\text{H}_2\text{S}$ , the reaction of  $\text{H}_2\text{S}$  with metals or their corrosion products to form  $\text{FeS}_2$  (pyrite), and the concomitant production of  $\text{H}_2$  (3.2.1.3). The corresponding equations for  $\text{MnO}_2$  appear in 4.2.3.

There is no known backfill additive to remove  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{NH}_3$ , or  $\text{H}_2\text{S}$ , or prevent the production of  $\text{CH}_4$ ,  $\text{N}_2$ , or  $\text{NH}_3$  at reasonable cost. Fe, Fe-base alloys, or their corrosion products would remove  $\text{H}_2\text{S}$ , but the concomitant formation of  $\text{FeS}_2$  would release large quantities of  $\text{H}_2$  (3.2.1.3).

How effective these backfill additives would be is also unknown.  $\text{CuSO}_4$  would only be effective if brine were present (Reaction 6.1), but anoxic corrosion may not occur in the absence of brine anyway.  $\text{CaCO}_3$  would remove  $\text{CO}_2$  only if brine were present (Reaction 6.2), but  $\text{CaO}$ ,  $\text{Ca(OH)}_2$ ,  $\text{KOH}$ , and  $\text{NaOH}$  would remove  $\text{CO}_2$  in the absence of brine (Reactions 6.3, and 6.5 through 6.7).  $\text{MnO}_2$  may not be effective because: (1) there might not be halophilic or halotolerant microorganisms that can use  $\text{MnO}_2$  as an electron acceptor under expected WIPP conditions; (2) these microorganisms, if they exist,

might not survive in the repository until conditions conducive to  $MnO_2$  reduction occur, and throughout the period during which  $MnO_2$  reduction would be required; (3)  $MnO_2$  is very insoluble and might not migrate through any brine present fast enough to prevent significant  $SO_4^{2-}$  reduction in isolated locations in WIPP disposal rooms. Studies of  $MnO_2$  are therefore low priority at this time.

It is also unclear whether these backfill additives would affect the long-term performance of the WIPP favorably or unfavorably.  $CaO$ ,  $Ca(OH)_2$ ,  $KOH$ , and  $NaOH$  would increase significantly the pH of any brine present. Because calculations of the required quantities of these backfill additives are unfeasible at this time, predictions of the pH of brine after it reacts with these compounds or their  $CO_2$ -bearing reaction products are also unfeasible. The pH could increase to very basic values, which could affect the rates of anoxic corrosion of metals and microbial degradation of cellulose, and influence the chemical behavior of radionuclides.

Because large quantities of these backfill additives could be required, they could inhibit the closure of WIPP disposal rooms by increasing the strength of the materials in the rooms. Brush and Anderson (1989) calculated that about 900,000 kg of  $CuSO_4$  per room would be required to corrode all of the Fe and Fe-base alloys in the waste without producing  $H_2$ . The quantity of  $CaCO_3$ ,  $CaO$ ,  $Ca(OH)_2$ ,  $KOH$ , or  $NaOH$  required for the removal of  $CO_2$  depends critically on how much of the microbially produced gas is in fact  $CO_2$ , which is unknown at present. Although the required quantities of any of these backfill additives are still unclear, they would probably be large.

Finally, use of some or all of these backfill additives could reduce the likelihood of compliance with regulations for the disposal of chemically hazardous waste (1.9).

Whether the advantages of these backfill additives outweigh their disadvantages is still unknown. It is possible, for example, that recent estimates of the gas production potential from anoxic corrosion (3.1) and microbial activity (4.1) are too high. If so, significantly smaller quantities of the backfill additives may be necessary, and their potential disadvantages would be less important.

## **6.2 DESCRIPTION OF LABORATORY AND MODELING STUDIES**

The objectives of these studies (6.2.1 and 6.2.2) are to: (1) determine whether the backfill additives  $CaCO_3$ ,  $CaO$ ,  $CuSO_4$ ,  $KOH$ , and  $NaOH$  remove  $CO_2$  or prevent the production of  $H_2$  effectively; (2) quantify their effects on repository chemistry.

L. H. Brush of Sandia National Laboratories (SNL) is carrying out these studies.

### **6.2.1 Laboratory Study of Backfill Additives**

Brush is using glassware to study backfill additives under humid and inundated conditions at  $30^\circ C$  and a pressure of about 1 atm. His apparatus

consists of a 1-L, jacketed glass flask with a removable four-neck glass top. The 24/40 ground-glass taper-joint necks allow him to: (1) bubble gas through the solution to sweep out dissolved gases such as CO<sub>2</sub> and introduce an atmosphere of any desired composition into the 1-L headspace; (2) continuously monitor the temperature, pH, and composition of dissolved species with a thermometer, pH electrode, or other specific-ion electrodes; (3) insert a pipette and sample the solution at various intervals for additional chemical analyses. He clamps the sealed flask onto a magnetic stirrer and maintains contact between the brine and minerals by stirring the mixture continuously with a Teflon-coated stir bar. To control the temperature of the solution and gas within each flask, he connects the inlet and outlet ports of the glass jacket with insulated rubber tubing to a constant-temperature circulator. For runs at or near room temperature, it is possible to connect up to three flasks in series to one circulator and maintain them at the desired temperature.

For the experiments under inundated conditions, Brush adds about 1 L of solution to the flasks. He uses solutions with  $I \leq 1$  M to evaluate the performance of the apparatus and Salado-Fm. brines collected from the WIPP underground workings (2.3.1.2) for the actual experiments. He may also use a synthetic Salado-Fm. brine once he has defined a standard brine (2.3.1.3) and developed a formulation for it, as well as synthetic brines that simulate the composition of Castile-Fm. brines and fluids from overlying formations after equilibration with brines and minerals from the Salado Fm. (2.4.5 and 2.4.6). He analyzes all of these brines prior to use as described below.

For the inundated experiments, Brush adds minerals collected from the WIPP underground workings (2.3.1.2), minerals and bentonite, or steel coupons to the solutions described above to simulate a backfill consisting of crushed salt or crushed salt and bentonite, and steel drums and boxes. He uses these materials to simulate repository conditions more closely and determine the effects of backfill additives on these materials. For experiments under humid conditions, he uses these solids without the solutions.

Although Brush has not yet determined the optimum solution:solid ratio for the experiments simulating inundated conditions, it will probably be higher than that likely to occur in WIPP disposal rooms. A relatively high solution:solid ratio is necessary to facilitate repeated sampling of the solution during these experiments, demonstrate that equilibrium has been attained, and quantify the kinetics of these reactions. Brush also carries out some experiments without any solids to isolate reactions between the gas and the solution from solution-solid reactions.

For CaCO<sub>3</sub>, CaO, KOH, and NaOH, Brush measures the consumption of CO<sub>2</sub> both directly and indirectly. In the former experiments, he uses manometers (4-L graduated dispensing burettes) to measure the volume of CO<sub>2</sub> consumed by predetermined quantities of these backfill additives. Before these experiments, he bubbles 99.995% N<sub>2</sub> through the test solution, head-space, and all other glass vessels and rubber tubing for various periods to remove atmospheric CO<sub>2</sub> that could contaminate the backfill additives or solutions. He first adds preacidified (to remove CO<sub>2</sub>), deionized H<sub>2</sub>O to the manometers, then solutions or solids containing the backfill additive of interest to 1 L of solution in the flask. To add solutions, he pours them into a burette (a 125-ml



cylindrical separatory funnel) clamped into one of the necks of the flask. As he adds solutions to the graduated cylinder of this burette, the flow of N<sub>2</sub> through the auxiliary tube and out the top minimizes contamination of the solutions by CO<sub>2</sub> prior to sealing the 24/40 ground-glass taper-joint top of the burette. Just prior to adding the backfill additives, he bubbles pure CO<sub>2</sub> through the solution and head-space of the flask for a few minutes to replace the previously added N<sub>2</sub>. After shutting off the flow of CO<sub>2</sub>, he dispenses solutions from the burette or adds solid backfill additives directly to the solutions. Because he does not bubble gas through the system after addition of the backfill additives, these are closed-system experiments, and the CO<sub>2</sub> fugacity decreases with time. Throughout the run, he adjusts the height of the manometer open to the atmosphere to maintain the levels of H<sub>2</sub>O in the two manometers at the same height; the cumulative change in the level of the manometer connected to the flask is equal to the volume of CO<sub>2</sub> consumed. He uses the ideal gas law to calculate the number of moles of CO<sub>2</sub> consumed.

To measure CO<sub>2</sub> uptake indirectly, Brush bubbles N<sub>2</sub> through the test solution, head space, and burette. Next, he determines the pH and siphons duplicate samples of about 40 ml each (a 30-ml bottle filled to the rim to reduce the quantity of head-space air containing CO<sub>2</sub>) for analysis for total inorganic C (TIC). Before the first sample and after the second, he discards about 20 ml of solution to reduce the possibility of contamination. He then adds solutions or solids containing the backfill additives and bubbles pure CO<sub>2</sub> through the solution and head space for the duration of the experiment. Because he bubbles CO<sub>2</sub> through the system continuously, these are open-system experiments, and the CO<sub>2</sub> fugacity is constant, about 1 atm. After various periods, he samples the solution for TIC as described above. Because each pair of samples and the discarded solution consume a total of 120 ml of solution, he samples the apparatus no more than five times during each experiment, including the sample taken after bubbling N<sub>2</sub> but prior to bubbling CO<sub>2</sub> through the solution.

Brush will also place CuSO<sub>4</sub>, mild-steel coupons, and 1 L of the solutions described above in the flasks under atmospheres of pure CO<sub>2</sub> and N<sub>2</sub>.

Brush determines the pH of brines as described in 7.6.1. As he measures the pH, he bubbles gas through the solution and out the neck of the flask to prevent contamination of the head-space gas with air. Next, he removes and filters 105 ml of solution through 0.45 μm filters. He acidifies a 25-ml sample with a few drops of 10% HNO<sub>3</sub> to adjust the pH to a value below 2, and stores it for analysis for B<sup>3+</sup> (probably present mainly as H<sub>3</sub>BO<sub>3</sub> and HB<sub>4</sub>O<sub>7</sub><sup>-</sup> or H<sub>3</sub>BO<sub>3</sub> and B(OH)<sub>4</sub><sup>-</sup>, but referred to herein as B<sup>3+</sup>), Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup>. After experiments with CuSO<sub>4</sub>, he also analyzes the acidified sample for Cu<sup>2+</sup> and Fe<sup>2+</sup>. He stores a 50-ml, unacidified sample for analysis for alkalinity, Br<sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, specific gravity (SG), total dissolved solids (TDS), and TIC.

About once a month, Brush sends samples to United Nuclear Corporation Geotech (UNC) in Grand Junction, Co., for chemical analysis. UNC personnel use the acidified samples to analyze for B<sup>3+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Na<sup>+</sup> by inductively coupled plasma emission spectroscopy or, in the case of high concentrations of K<sup>+</sup> and Na<sup>+</sup>, atomic absorption spectroscopy. They use the unacidified samples to: (1) titrate for alkalinity (this analysis requires

the most solution, about 50 ml); (2) analyze for  $\text{Br}^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  by ion chromatography; (3) determine SG by weighing the solution and an equivalent volume of deionized  $\text{H}_2\text{O}$ ; (4) determine TDS by drying to constant weight at 103 to 105°C; (5) analyze for TIC by coulometric analysis. A detailed description of these procedures appears in UNC (1989a).

Brush will characterize the minerals and other solids before and after these experiments with x-ray diffraction analysis.

## 6.2.2 Modeling Study of Backfill Additives

Brush will also model the behavior of backfill additives with the EQ3/6 geochemical software package (Wolery, 1983; Jackson and Wolery, 1985; Wolery and Daveler, in preparation; a brief description of EQ3/6 appears in 8.2). Successful prediction of the results of experiments such as these would also provide additional validation of EQ6 for systems consisting of brines and evaporite minerals (see Jackson, 1988, for the results of previous validation studies).

Brush will use the speciation and solubility code EQ3NR (8.2.1) to model the distribution of  $\text{CO}_2$  among possible aqueous species in these experiments. Because the Pitzer activity-coefficient model (8.2.1) which EQ3NR uses for solutions with ionic strengths  $> 1$  M explicitly recognizes few complexes, he uses the B-Dot model (8.2.1) to predict the speciation of dissolved  $\text{CO}_2$  in the dilute solutions used to evaluate the performance of the apparatus described in 6.2.1. Although he cannot use these results to interpret experiments carried out with brines, they do help define the reactions responsible for the consumption of  $\text{CO}_2$ .

Brush will also use the reaction-path code EQ6 (8.2.2) to model the consumption of  $\text{CO}_2$  by dilute solutions and brines during open- and closed-system experiments (6.2.1). To model open-system runs, he will use the fixed-fugacity option of Delany and Wolery (1984).

Brush specified a standard mineralogy for the Salado Fm. at or near the stratigraphic horizon of the WIPP for this and other modeling studies (2.4.4 through 2.4.6). He based this composition on Stein's (1985) characterization of 46 core samples from a 15-m-long uphole and a 15-m-long downhole from the northern end of Room 4 (Figure 2.1).

Stein (1985) placed crushed samples of these cores in beakers of distilled  $\text{H}_2\text{O}$  to dissolve halite ( $\text{NaCl}$ ) and reported that the mean concentration of the  $\text{H}_2\text{O}$ -insoluble residues was 5.56 wt% of the whole-rock samples. Brush calculated a mean concentration of 6.77% from Stein's (1985) Table 1 and specified the concentration of halite at 93.2 wt%.

Based on x-ray diffraction analysis, Stein (1985) reported that anhydrite ( $\text{CaSO}_4$ ), bassanite ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), magnesite ( $\text{MgCO}_3$ ), polyhalite ( $\text{K}_2\text{MgCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ ), and quartz ( $\text{SiO}_2$ ) were present in the  $\text{H}_2\text{O}$ -insoluble residues. She did not determine the concentrations of these minerals quantitatively because standard x-ray diffraction techniques are only semiquantitative.

Stein (1985) also treated portions of the H<sub>2</sub>O-insoluble residues in solutions containing 0.25 M ethylenediaminetetraacetic acid (EDTA) to remove the Mg<sup>2+</sup>-bearing mineral MgCO<sub>3</sub> and the Ca<sup>2+</sup>-bearing minerals anhydrite, bassanite, gypsum, and polyhalite. The EDTA-insoluble residues consisted of quartz and various unidentified clay minerals. Stein (1985) reported that the mean concentration of the EDTA-insoluble residues was 0.64 wt% of the whole-rock samples. Brush obtained the same result by averaging the results presented in Stein's (1985) Table 3.

Because Stein (1985) did not quantitatively determine the concentrations of any of the minerals except halite, Brush assumed equal values for the concentrations of anhydrite, gypsum, magnesite, and polyhalite. He omitted bassanite because it only appeared in the diffractogram for one of the samples studied. He omitted all of the silicates because EQ3/6 cannot yet model the behavior of Al- and Si-bearing compounds in high-ionic-strength solutions. Omission of silicates, especially clay minerals in the Salado Fm., bentonite, and grouts, could affect the results of these and other modeling studies significantly; therefore, the additional development of EQ3/6 described in 8.2.3 is necessary. Brush set the concentrations of anhydrite, gypsum, magnesite, and polyhalite equal to 1.7 wt%. Although this estimate is probably not accurate to more than 1 significant figure, Brush used 1.7 wt% to retain the same ratio of halite to other minerals reported by Stein (1985). These values, along with the value of 93.2 wt% specified above for halite, bring the total for these five minerals to 100 wt%. Preliminary results obtained with EQ3NR imply that these minerals are at or close to equilibrium with most Salado-Fm. brines collected from the WIPP underground workings (2.3.1.3).

### **6.2.3 Quality Assurance and Safety**

Brush is carrying out studies of backfill additives (6.2.1 and 6.2.2) in accordance with applicable sections of the overall quality assurance (QA) plan described by Pickering (1989c). This QA plan meets requirements of the American Society of Mechanical Engineers (1986) and the relevant requirements of the Department of Energy (1987a, 1989a, 1989b, 1989c). UNC is analyzing solutions from the study discussed in 6.2.1 in compliance with a QA plan (UNC, 1989b) approved by Pickering (1990d).

Brush is also conducting these studies in accordance with the safe operating procedures described by Bujewski (1990a, 1990b). UNC is responsible for the development, approval, and implementation of all safety procedures required for its analyses of solutions.

### **6.3 RESULTS EXPECTED FROM BIN-SCALE AND ALCOVE TESTS**

Analyses of brines and gases sampled from bin-scale and alcove tests with contact-handled transuranic waste (Molecke, 1990a; 1990b) will also yield data on the efficacy and effects of backfill additives. The absence of H<sub>2</sub> from partially inundated bins with CuSO<sub>4</sub> and the absence of CO<sub>2</sub> from bins or alcoves with CaO, Ca(OH)<sub>2</sub>, KOH, or NaOH may imply that these compounds are effective under the heterogeneous conditions expected for WIPP disposal rooms. CH<sub>4</sub>, H<sub>2</sub>S, N<sub>2</sub>, or NH<sub>3</sub> production rates in partially inundated bins with CaO, Ca(OH)<sub>2</sub>, KOH, and NaOH that are lower than in similar tests without these compounds may imply that basic conditions inhibit microbial activity.

#### 6.4 SCHEDULES FOR LABORATORY AND MODELING STUDIES

Brush started laboratory studies of backfill additives (6.2.1) at SNL in late July 1989 and will start modeling studies (6.2.2) at SNL in January 1990. The objective of these studies is to determine whether these compounds remove gas or prevent its production effectively. He will complete the laboratory and modeling studies with this objective by the end of September 1990. Posttest analysis and reporting will require another 3 months. He will complete the first part of these studies by the end of December 1990. Thereafter, the objective will be to quantify the effects of backfill additives on repository chemistry. He will complete the laboratory and modeling studies with this objective by the end of September 1991. Posttest analysis and reporting will require another 3 months. He will thus complete the second part of these studies by the end of December 1991.

## 7.0 RADIONUCLIDE CHEMISTRY

### 7.1 JUSTIFICATION FOR LABORATORY STUDIES

Predictions of the chemical behavior of radionuclides in Waste Isolation Pilot Plant (WIPP) brines are necessary to define the source term, the quantities of the important radionuclides in the WIPP inventory that would be mobilized for possible transport to the accessible environment, and the scenario-dependent rates at which these radionuclides would be mobilized. Because most plausible release scenarios involve mobilization of radionuclides by dissolution or suspension in brines, the source term comprises: (1) the product of the concentrations of radionuclides in any brine that could enter WIPP disposal rooms after they are filled and sealed and the volumes of this brine; (2) the rates at which brine accumulates and these concentrations are attained.

The long-term performance of the WIPP is sensitive to the mobilization and transport of isotopes of Am, Pu, Th, and U. It is more sensitive to Pu than to Am, Th, and U, and it is relatively insensitive to the mobilization and transport of isotopes of other elements. For these heavy elements, it is reasonable to assume that the chemical behavior of isotopes of the same element are identical.

The speciation and solubilities of Pu, Am, Th, and U, the sorption of these elements by bentonite (a possible component of the backfill) and Fe oxides and hydroxides (possible products of anoxic corrosion of steel containers and Fe and Fe-base alloys in the waste), and the extent to which Pu, Am, Th, and U form colloids will determine their concentrations in any brine present in WIPP disposal rooms. Because there are neither data with which to predict the concentrations of Pu, Am, Th, and U in WIPP brines nor a defensible method for estimating these data (7.2), laboratory studies of the chemical behavior of these elements are necessary. However, it would be extremely difficult to determine the rates at which Pu, Am, Th, and U dissolve. These rates depend critically on the chemical and physical nature of the solid phases with which the various isotopes of these elements are associated. Because transuranic (TRU) waste is heterogeneous and difficult to characterize, it would probably be impossible to specify the nature of these phases accurately enough for a meaningful laboratory study of dissolution kinetics. Furthermore, the equilibrium concentrations of Pu, Am, Th, and U in WIPP brines could be so low that the rates at which these concentrations are attained would not affect the long-term performance of the repository even if they could be predicted. Therefore, a laboratory study of the dissolution kinetics of Pu, Am, Th, and U in WIPP brines is probably unnecessary. Instead, the assumption that the expected concentrations of these elements are attained instantaneously will suffice until Molecke (1990a) obtains kinetic data by analyzing brines from his bin-scale tests with contact-handled (CH) TRU waste. These results will simultaneously reflect the effects of dissolution and reprecipitation, sorption and desorption, transport processes, and perhaps colloid formation.

The chemical behavior of Pu and U is sensitive to the Eh of any brine present. Pu can occur in four oxidation states (III, IV, V, or VI) under natural conditions; U can occur in two (IV or VI). The behavior of these

elements differs significantly from one oxidation state to another. Corrosion of metals and microbial activity will decrease the average Eh of the repository and the oxidation state of Pu and U with time, but at any given time the Eh could vary significantly over short distances, perhaps just a few centimeters, because of the heterogeneous nature of the TRU waste to be emplaced in the WIPP. Oxidizing conditions, for example, could persist for long periods near large, radionuclide-bearing particles because of continuous radiolytic production of O<sub>2</sub> from brine or sludges. Simultaneously, adjacent microenvironments devoid of radionuclides but with large quantities of organic matter and significant anaerobic microbial activity could rapidly become reducing.

The chemical behavior of Pu, Am, Th, and U is sensitive to the pH of any brine present. Microbial production of CO<sub>2</sub> could decrease the pH to acidic values. Reactions between brine and cements used to remove liquids from sludges, grouts used in seals, or grouts proposed to reduce the permeability of WIPP disposal rooms (Butcher, 1990) could increase the pH to basic values. Reactions between brine and CaO, Ca(OH)<sub>2</sub>, KOH, and NaOH, backfill additives proposed for the removal of CO<sub>2</sub> (6.1), could increase the pH to very basic values. As with Eh, the average pH of the repository could, given the heterogeneous nature of design-basis waste, vary significantly with time and over short distances at any given time. Therefore, it is necessary to quantify the chemical behavior of these elements under a wide range of conditions.

## 7.2 ESTIMATES OF RADIONUCLIDE SPECIATION AND SOLUBILITIES

Choppin (1988a) recently attempted to estimate the speciation and solubilities of Am, Np, Pu, U, and Th in WIPP brines under expected repository conditions. Marietta et al. (1989) had not yet concluded that the long-term performance of the WIPP is relatively insensitive to the behavior of Np. He attempted these estimates to provide input for the methodology demonstration by Marietta et al. (1989).

For this exercise, Drez (1988) estimated the total quantities of the following organic compounds in the WIPP inventory: citrate, dihexyl N,N-diethylcarbanoyl-methylenephosphonate (CMPO), ethylenediaminetetraacetic acid (EDTA), 8-hydroxyquinoline (oxine), 1-thenoyl-3,3,3-trifluoroacetone (TTA), tributyl phosphate (TBP), and trioctylphosphinic oxide (TOPO). He based his estimates on the annual rates at which these compounds are used at the Rocky Flats Plant, which he obtained from discussions with Rocky Flats personnel, and multiplied the annual rates by 44 years to obtain the total quantity of each of these compounds in the WIPP inventory. The WIPP will accept waste produced from the beginning of 1970 through the end of 2013. The estimated quantities were: citrate, 1,950 moles; CMPO, 431 moles; oxine, 683 moles; TTA, 167 moles; TBP, 612 moles; TOPO, 200 moles. He did not estimate the quantity of EDTA because Rocky Flats stopped using it in the early 1970s, and he could not determine the rate at which it was used.

Although there is probably very little EDTA in the WIPP inventory, Brush and Anderson (1988b) estimated the total quantity as follows. They assumed that Rocky Flats used EDTA through the end of 1974 and that Rocky Flats used EDTA at one third the annual rate of TTA. They multiplied the annual rate

for TTA by one third and 5 years to obtain the total quantity of EDTA in the WIPP inventory (6.35 moles), assumed that Rocky Flats substituted TTA for EDTA, and reduced the total quantity of TTA from 167 to 148 moles to take account of the 5 years during which they used EDTA.

Choppin (1988a) omitted CMPO, TBP, and TOPO from further consideration; these organic compounds do not dissolve in aqueous solutions such as WIPP brines and therefore could not affect the speciation and solubilities of radionuclides in these brines.

Next, Brush and Anderson (1988b) defined two standard brines: PAB-1, an average brine from the Salado Fm. now referred to as SB-1, and WIPP-12, a representative fluid from a brine reservoir in the Castile Fm. (see Tables 2.1 and 2.2, respectively, for the composition of these brines.) They also estimated how much brine could eventually enter WIPP disposal rooms by assuming that the residual void volume of each room will be 2, 5, or 10% of the initial volume of a 13-by-33-by-300-ft room (42,900 ft<sup>3</sup> or 3,640 m<sup>3</sup>), and that brine would eventually saturate these volumes. They estimated that there could eventually be 72.8, 182, or 364 m<sup>3</sup> of brine per room.

Brush and Anderson (1988b) used the estimates described above to calculate the maximum, intermediate, and minimum concentrations of citrate, EDTA, oxine, and TTA in Salado- and Castile-Fm. brines in WIPP disposal rooms (Table 7.1). Drez (1988) suggested that these organic ligands will probably occur only in sludges, which will not be stored in boxes. Brush and Anderson (1988b) divided the total quantity of each of these ligands by 399,000 (the estimate at that time of the total number of drums to be emplaced in the WIPP), but did not include the 24,100 boxes in the denominator. This yielded the quantity of each ligand per drum. They multiplied these values by 7,180 drums per room to calculate the quantities of these ligands per WIPP disposal room, and divided these quantities by 72.9, 182, and 364 m<sup>3</sup> to obtain the maximum, intermediate, and minimum concentrations of each ligand.

Because WIPP disposal rooms will include boxes as well as drums, there will be less than 7,180 drums per room. The values shown in Table 7.1 were probably overestimates of the maximum, intermediate, and minimum concentrations.

Choppin (1988a) then attempted to estimate the speciation and solubilities of Am, Np, Pu, U, and Th in both the Salado- and Castile-Fm. brines with the estimated concentrations of four organic ligands. He concluded that there are no thermodynamic data (stability constants for complexes between these elements and organic or inorganic ligands, or solubility products for solids containing these elements) for these Am, Pu, Np, Th, and U in solutions with ionic strengths (I) equal to those of the Salado- and Castile-Fm. brines defined by Brush and Anderson (1988b), 7.66 and 6.14 M, respectively. Most existing data apply to solutions with I less than or equal to 1 M, and only a few pertain to values of I as high as 2 or 3 M. Furthermore, most of the data are for 1:1 (metal:ligand) or 1:2 complexes; very few data exist for 1:3 or 1:4 complexes, which could be important species in these brines.

Choppin (1988a) attempted to estimate stability constants and solubility products for Pu, Am, Np, and Th by: (1) extrapolating existing data to the

TABLE 7.1

PREVIOUS ESTIMATES OF THE CONCENTRATIONS OF FOUR ORGANIC LIGANDS  
IN ANY BRINE PRESENT IN WIPP DISPOSAL ROOMS

| Ligand                    | Total Quantity<br>of Ligand in<br>WIPP Inventory<br>(Moles) <sup>a</sup> | Concentration of Ligand in Brine<br>(see each ligand for units) |                           |                      |
|---------------------------|--|---|---------------------------|----------------------|
|                           |  | Maximum <sup>b</sup>  | Intermediate <sup>c</sup> | Minimum <sup>d</sup> |
| Citrate ( $\mu\text{M}$ ) | 1,952  | 500   | 200                       | 100                  |
| EDTA (nM)                 | 6.53   | 2,000   | 600                       | 300                  |
| Oxine (nM)                | 683  | 200   | 70                        | 30                   |
| TTA (nM)                  | 148  | 40  | 10                        | 7                    |

a. Citrate, oxine, and TTA from Drez (1988); EDTA calculated by Brush and Anderson (1988b).

b. Based on 72.9 m<sup>3</sup> of brine (2% of initial room volume resaturated).

c. Based on 182 m<sup>3</sup> of brine (5% of initial room volume resaturated).

d. Based on 364 m<sup>3</sup> of brine (10% of initial room volume resaturated).

ionic strengths of WIPP brines; (2) using these data directly for the WIPP brines or arbitrarily adding 1 log unit to them in those cases in which the availability of data at lower values of I is so limited that extrapolation is impossible; (3) extrapolating data for chemically analogous organoactinide or organolanthanide complexes in those cases in which there are no data at all for the appropriate complex.

Because there is no accepted method for extrapolating stability constants or solubility products to such high ionic strengths, it is impossible to defend estimates of these data in WIPP brines, or the uncertainties in these estimates. A laboratory study is necessary to quantify the speciation and solubilities of Pu, Am, Th, and U in these brines.

In lieu of these data or defensible estimates of these data, Brush and Anderson (1989) proposed a best estimate of 10<sup>-6</sup> M for the solubilities of Pu, Am, Th, and U in any brine present in WIPP disposal rooms as the source term for the transport calculations described by Lappin et al. (1989) and Marietta et al. (1989). This is the intermediate value (on a logarithmic scale) of the range of radionuclide solubilities (10<sup>-3</sup> to 10<sup>-9</sup> M) used for various sensitivity studies (for example, Marietta et al., 1989). Neither the intermediate value nor the range can be justified at this time on the basis of experimental data or modeling studies. It is unlikely that the solubilities of these radionuclides in WIPP brines will significantly exceed this intermediate value.



### 7.3 EFFECTS OF OTHER PROCESSES ON THE SOURCE TERM

In addition to the solubilities of radionuclide-bearing solids, sorption of Pu, Am, Th, and U by bentonite or Fe oxides and hydroxides could affect the source term significantly. Unfortunately, there are no data on the sorption of these elements from saturated brines under the highly variable conditions expected for WIPP disposal rooms. R. D. Klett of Sandia National Laboratories (SNL) is carrying out a sensitivity study of the relative importance of solubility and sorption in determining the concentration of radionuclides in any brine present.

Finally, mobilization of Pu, Am, Th, and U by colloids could be significant. Brush will assemble a group of experts to identify the conditions under which colloids could affect the source term significantly and to estimate the extent of colloid formation under these conditions.

### 7.4 ESTIMATES OF LIGAND CONCENTRATIONS IN WIPP BRINES

Estimates of the likely concentrations of organic and inorganic ligands in any brine present in WIPP disposal rooms are necessary to design realistic laboratory speciation and solubility studies, as well as other laboratory studies of radionuclide chemistry. Brush and Anderson (1988b) estimated the concentrations of the organic ligands citrate, EDTA, oxine, and TTA in three quantities of brine that could eventually resaturate WIPP disposal rooms for Choppin's (1988a) estimates of radionuclide solubilities (7.1 and Table 7.1).

Subsequently, Drez and James-Lipponer (1989) revised previous estimates of the quantities of citrate and oxine in the WIPP inventory and made new estimates for eight additional organic and inorganic ligands not considered previously. The estimates of the quantities of EDTA and TTA in the WIPP inventory that Brush and Anderson (1988b) used (7.1) are still the best estimates available. Furthermore, Brush revised his estimates of the quantities of brine that could eventually resaturate WIPP disposal rooms.

During the preparation of their preliminary inventory of the nonradioactive constituents of the CH TRU waste to be emplaced in the WIPP, Drez and James-Lipponer (1989) identified numerous, additional organic compounds (Table 7.2) that might form complexes with Pu, Am, Th, and U in any brine present in WIPP disposal rooms and increase their solubilities. Based on his review of this list, Choppin (1988b) concluded that if present at high enough concentrations, ten of the 60 compounds listed in Table 7.2 could increase radionuclide solubilities. These ten compounds are soluble in aqueous solutions, at least under some conditions. They are acetamide, acetic acid, ammonium thiocyanate, ascorbic acid, citric acid, di(2-ethylhexyl)-phosphoric acid (DHP),  $\alpha$ -hydroxy isobutyric acid, lactic acid, oxalic acid, and 1,10-phenanthroline. Choppin (1988b) also concluded that dihexyl-n,n-diethylcarbamoyl methyl phosphonate (DHDECMP), TBP, and TOPO could also increase radionuclide solubilities, but only in organic solvents. Unlike the ten compounds listed above, DHDECMP, TBP and TOPO are insoluble in aqueous solutions under any conditions.

Drez and James-Lipponer (1989) used the results of a detailed survey of the waste generators and storage sites to compile most of their preliminary

TABLE 7.2

ORGANIC COMPOUNDS IDENTIFIED IN THE PRELIMINARY INVENTORY OF NONRADIOACTIVE  
CONSTITUENTS OF THE TRU WASTE TO BE EMPLACED IN THE WIPPA<sup>a</sup>

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Acids, Organic

Acetic acid  
Ascorbic acid  
Citric acid  
DHP  
 $\alpha$ -hydroxyisobutyric acid  
Lactic acid  
Oxalic acid

Alcohols and Glycols

Butanol  
Ethanol  
2-ethyl-1-hexanol  
Glycerin  
Isopropanol  
Methanol  
Polyethylene glycol

Aldehydes

Formaldehyde

Amides

Acetamide

Amines, Aliphatic and Aromatic

Adogen-364-hp(tri-laurylamine)  
Hydroxylamine

Azo Compounds, Diazo Compounds, and Hydrazines

Hydrazine  
Hydrazine mononitrate

Esters

Amyl acetate

Halogenated Organics

Bromoform  
Carbon tetrachloride

TABLE 7.2

ORGANIC COMPOUNDS IDENTIFIED IN THE PRELIMINARY INVENTORY OF NONRADIOACTIVE  
CONSTITUENTS OF THE TRU WASTE TO BE EMPLACED IN THE WIPPA<sup>a</sup>  
(Continued)

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Chloroform  
Dichloroethane  
Methylene chloride  
Tetrachloroethylene  
Trichloroethane  
1,1,1-trichloroethane  
Trichloroethylene  
1,1,2-trichloro-1,2,2-trifluoroethane

Hydrocarbons, Aliphatic, Saturated

Decane  
N-dodecane  
Hexane  
Kerosene  
Nonane  
Octane  
Oils (C6 to C20)  
Pentane  
Petroleum ether

Hydrocarbons, Aliphatic, Unsaturated

Butadiene  
Styrene

Hydrocarbons, Aromatic

Diethylbenzene  
Diisopropylbenzene  
Ethyl benzene  
Toluene  
Xylene

Isocyanates

Ammonium thiocyanate

Ketones

Acetone  
2-5-di-tert-butyl-hydroquinone  
Methyl acetone  
Methyl ethyl ketone  
Methyl isobutyl ketone  
Thenoylfluoroacetone

TABLE 7.2

ORGANIC COMPOUNDS IDENTIFIED IN THE PRELIMINARY INVENTORY OF NONRADIOACTIVE  
CONSTITUENTS OF THE TRU WASTE TO BE EMPLACED IN THE WIPPA<sup>a</sup>  
(Continued)

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## Nitro Compounds

Nitrocellulose  
Urea nitrate

## Organophosphates, Phosphothioates, Phosphodithioates

TBP  
TOPO

## Phenols, Cresols

Picric acid

## Polymerizable Compounds

Epoxy

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a. From Drez and James-Lipponer (1989); most of these organics present in trace amounts only.

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nonradioactive inventory. Because the ten organic compounds listed above were identified too late for inclusion in the questionnaire, they requested additional information in a separate letter. Drez and James-Lipponer (1989) revised previous estimates of the total quantities of citric acid and oxine and provided preliminary estimates of the quantities of seven organic compounds and the inorganic ligands  $\text{CO}_3^{2-}$  and  $\text{NO}_3^-$  present in the waste. The original questionnaire requested information on  $\text{CO}_3^-$  and  $\text{NO}_3^-$ . An estimate of the quantity of  $\text{CO}_3^{2-}$ , which could (depending on pH) also dissolve in brine to form  $\text{HCO}_3^-$ , is important because these ligands could increase the solubilities of Pu, Am, Th, and U under certain conditions. Furthermore, the quantity of  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$  leached from the waste could greatly exceed that originally present in WIPP brines (Tables 2.1, 2.2, 2.3, and 2.4). An estimate of  $\text{NO}_3^-$  is required for predictions of denitrification and  $\text{NO}_3^-$  reduction, potentially significant microbial processes (4.2.2). The quantities estimated by Drez and James-Lipponer (1989) are: 42,900 moles of acetic acid, 65,000 moles of ascorbic acid, 4,290 moles of citric acid, 6,780,000 moles of  $\text{CO}_3^{2-}$ , 474 moles of DHDECMP, 2.52 moles of  $\alpha$ -hydroxy isobutyric acid, 1,180 moles of lactic acid, 2,770,000 moles of  $\text{NO}_3^-$ , 57,800 moles of oxalic acid, 687 moles of oxine, and 2.91 moles of 1,10-phenanthroline. Drez and James-Lipponer (1989) did not estimate the quantities of acetamide, DHP,

or picric acid in the WIPP inventory, or revise the previous estimates by Drez (1988) of TBP or TOPO. They will estimate the quantities of acetamide, DHP, and picric acid and, if necessary, revise their estimates of all of the H<sub>2</sub>O-soluble organic compounds that could increase the solubilities of Pu and Am.

Next, Brush assumed that brine could eventually resaturate all of the residual void volume of a WIPP disposal room, 2.4, 3.0, or 3.4% of its initial volume of 3,640 m<sup>3</sup>. Lappin et al. (1989) provided these estimates of the residual void volume by assuming that the residual porosity of the room contents will be 15, 18, or 21%. These estimates imply that there could eventually be 89, 106, or 123 m<sup>3</sup> of brine per room. Because the difference between the maximum and minimum estimates is small relative to uncertainties in the total quantity of ligands in the WIPP inventory, Brush used only the intermediate estimate of 106 m<sup>3</sup> of brine per room and arbitrarily defined maximum and minimum estimates of the dissolved ligand concentrations.

Brush then used the estimates discussed above, along with previous estimates of the quantities of EDTA and TTA in the WIPP inventory, to calculate the maximum, intermediate, and minimum concentrations of these 12 organic and inorganic ligands in any brine that resaturates WIPP disposal rooms (Table 7.3). Contrary to his previous assumption (7.2), the organic and inorganic ligands estimated by Drez and James-Lipponer (1989) occur in drums, old boxes, and new boxes (standard waste boxes). Brush cannot, however, estimate the relative proportions of the ligands in each type of container. Drez and James-Lipponer (1989) determined that there are inventory data for 283,298 drums, 5,541 old boxes (each of which contains the equivalent of 14.7 drums of waste), and 9,502 new boxes (each of which contains 6 drums). Brush multiplied 5,541 by 14.7 and 9,502 by 6, and added these products to 283,298 to obtain 421,763, the number of equivalent drums for which data are available. Drez and James-Lipponer (1989) determined that a total of 333,188 drums, 6,772 old boxes, and 9,502 new boxes will be emplaced in the WIPP; this is equivalent to 489,748 drums. Brush divided the total quantity of each ligand by 421,763 to obtain the quantity of each ligand per drum for which there are data. He assumed that there will be 6,800 drums per room and multiplied the quantity of each ligand per drum by 6,800 to obtain the quantities of these ligands per room. He divided these quantities by 106 m<sup>3</sup> of brine per room to obtain his intermediate estimates of the concentrations of these ligands in any brine present in WIPP disposal rooms. He arbitrarily multiplied his intermediate estimates by 0.1 and 10 to obtain his minimum and maximum estimates; this range of  $\pm 1$  order of magnitude should encompass changes in the estimates of the ligand concentrations caused by revisions of the inventory or new estimates of the residual void volume. He did not calculate concentrations for DHDECMP because it is insoluble in aqueous solutions.

Brush will compare the estimates shown in Table 7.3 to the concentrations of ligands measured in brines sampled from the planned bin-scale tests with CH TRU waste (Molecke, 1989a).

TABLE 7.3

CURRENT ESTIMATES OF THE CONCENTRATIONS OF 13 ORGANIC AND INORGANIC LIGANDS IN ANY BRINE PRESENT IN WIPP DISPOSAL ROOMS

| Ligand                             | Total Quantity of Ligand in WIPP Inventory (Moles) <sup>a</sup> | Concentration of Ligand in Brine (see each ligand for units) |                           |                      |
|------------------------------------|---|--|---------------------------|----------------------|
|                                    |   | Minimum <sup>b</sup>   | Intermediate <sup>c</sup> | Maximum <sup>d</sup> |
| Acetate (mM)                       | 42,900  | 0.7  | 7                         | 70                   |
| Ascorbate (mM)                     | 65,000  | 1  | 10                        | 100                  |
| Citrate ( $\mu$ M)                 | 4,290   | 70   | 700                       | 7,000                |
| CO <sub>3</sub> <sup>2-</sup> (M)  | 6,780,000   | 0.1  | 1                         | 10                   |
| EDTA (nM)                          | 6.53  | 100  | 1,000                     | 10,000               |
| $\alpha$ -hydroxy-isobutyrate (nM) | 2.52  | 40   | 400                       | 4,000                |
| Lactate ( $\mu$ M)                 | 1,180   | 20   | 200                       | 2,000                |
| NO <sub>3</sub> <sup>-</sup> (mM)  | 2,770,000   | 40   | 400                       | 4,000                |
| Oxalate (mM)                       | 57,800  | 0.9  | 9                         | 90                   |
| Oxine ( $\mu$ M)                   | 687   | 10   | 100                       | 1,000                |
| 1,10-phenanthroline (nM)           | 2.91  | 40   | 400                       | 4,000                |
| TTA ( $\mu$ M)                     | 148   | 2  | 20                        | 200                  |

- a. All ligands except EDTA and TTA from Drez and James-Lipponer (1989); EDTA calculated by Brush and Anderson (1988b); TTA from Drez (1988).
- b. Arbitrarily set to 0.1 times the intermediate estimate.
- c. Based on 106 m<sup>3</sup> of brine (3.0% of initial room volume resaturated or a residual porosity of 18%).
- d. Arbitrarily set to 10 times the intermediate estimate.

## 7.5 IDENTIFICATION OF POTENTIALLY SIGNIFICANT LIGANDS

For his estimates of radionuclide solubilities in Salado- and Castile-Fm. brines (7.2), Choppin (1988a) also estimated the speciation of several radionuclides in these brines. Because of the uncertainties in extrapolating existing stability constants to the ionic strengths of WIPP brines, he based his estimates of radionuclide speciation mainly on data for dilute solutions and previous estimates of the concentrations of organic ligands in any WIPP brines present (Table 7.1). He concluded that complexes between the ligand

Cl<sup>-</sup> and Am, Np, Pu, Th, and U and hydrolysis of these elements would be much more important than organic complexes because of the low concentrations of organic ligands, and because Mg<sup>2+</sup> and Ca<sup>2+</sup> would compete very effectively with radionuclides for the binding sites on these organic ligands. He decided to emphasize determination of apparent stability constants for Cl<sup>-</sup> and a study of hydrolysis initially, but to extend these studies to the organic ligands citrate, EDTA, oxine, and TTA later.

Based on current estimates of the concentrations of organic and inorganic ligands in WIPP brines (Table 7.3) and stability constants for dilute solutions, Choppin (1988a) concluded that the ligands most likely to increase the solubilities of radioelements are acetate, ascorbate, citrate, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, EDTA, lactate, and oxalate. Hydrolysis could also be significant. Because of the uncertainties in the estimated concentrations of these ligands in WIPP brines and extrapolations of their stability constants to solutions of high ionic strength, it is difficult to predict the relative effects of these ligands on radionuclide solubilities. He will carry out studies with these organic and inorganic ligands in an order dictated as much by experimental expediency as by estimates of their relative effects on radionuclide solubilities. It is also possible that revisions of the inventory of nonradioactive waste constituents might force us to either add ligands to or remove ligands from the list given above.

## 7.6 DESCRIPTION OF LABORATORY STUDIES

The objectives of these studies are to: (1) quantify the speciation of Pu, Am, Th, and U in neutral, acidic, and basic solutions of high ionic strength under a wide range of redox conditions (7.6.1) for calculations of the solubilities of these elements in WIPP brines; (2) determine, if necessary, the solubilities of Pu-, Am-, Th-, and U-bearing solids under similar conditions (7.6.2) to validate the results of the speciation study; (3) quantify the sorption of these elements from WIPP brines under conditions similar to those in the speciation and solubility studies (a description of this study will appear elsewhere); (4) extend the speciation, solubility, and sorption studies to strongly basic WIPP brines (7.6.3), if studies of repository chemistry based on the current or modified designs of the repository imply extension of this work is necessary; (5) determine the extent to which Pu, Am, Th, and U form colloids under these conditions (a description of this study will appear elsewhere).

G. R. Choppin of Florida State University is quantifying the speciation of Pu, Am, Th, and U in WIPP brines by measuring apparent stability constants for complexes between these elements and organic and inorganic ligands in neutral, acidic, and basic solutions of high ionic strengths (7.6.1). The use of Am(III) or Eu(III), Th(IV), Np(V), and U(VI) as oxidation-state analogs of Pu(III), Pu(IV) and U(IV), Pu(V), and Pu(VI), respectively, will provide data for all four elements under a wide range of redox conditions. These results will be applicable to: (1) neutral or nearly neutral conditions expected before reactions between brine and the waste; (2) acidic conditions caused by pressure-induced dissolution of microbially produced CO<sub>2</sub> in brine; (3) basic conditions caused by the reaction of brine with cements or grouts; (4) redox conditions characteristic of oxidizing radiolysis products, corrosion of metals, and microbial activity.

Choppin may determine apparent solubility products for Pu-, Am-, Th-, and U-bearing solids or analogous compounds in neutral, acidic, and basic WIPP brines (7.6.2) to validate solubility predictions based on results of the speciation study. Bin-scale tests with CH TRU waste (Molecke, 1990a) provide the best opportunity to validate the results of laboratory studies of radionuclide chemistry, but the results of these tests could prove difficult to interpret (7.7). A laboratory solubility study may be necessary.

M. D. Siegel of SNL will quantify the sorption of Pu, Am, Th, and U from WIPP brines by bentonite and Fe oxides and hydroxides. Siegel is currently studying radionuclide sorption from solutions of low and intermediate ionic strengths to obtain data for use in modeling radionuclide transport in formations above the repository. He is extending this study to the sorption of radionuclides by bentonite, Fe oxides, and Fe hydroxides from solutions of high ionic strength under conditions similar to those in the speciation study described above. A description of this sorption study will appear elsewhere.

Choppin may extend his studies to strongly basic conditions (7.6.3). These conditions would result from reactions between brine and the proposed backfill additives CaO, Ca(OH)<sub>2</sub>, KOH, and NaOH (6.1). This study would be necessary in the event of serious consideration of the use of these compounds in the repository.

A study of the formation of Pu-, Am-, Th-, and U-bearing colloids would be required if expert judgment implies that they could be important under the conditions expected for WIPP disposal rooms, or colloids in brines sampled from the bin-scale tests with CH TRU waste (Molecke, 1989a). A description of this study will appear elsewhere.

### **7.6.1 Quantification of the Speciation of Pu, Am, Th, and U in Neutral, Acidic, and Basic Solutions of High Ionic Strengths under Various Redox Conditions**

Choppin is using the solvent extraction technique developed by Caceci and Choppin (1983a, 1983c), Rosta (1987), and Khalili, Choppin, and Rizkalla (1988) to measure apparent stability constants of organic and inorganic Pu, Am, Th, and U complexes. Although Choppin has used this technique mainly with solutions of low ionic strength, Rosta (1987) used solvent extraction to study actinide speciation in highly saline solutions.

The extraction vials for these studies consist of 20-ml borosilicate-glass scintillation counting vials with low-density polyethylene screw caps. To minimize sorption of radionuclides, Choppin uses the procedure of Caceci and Choppin (1983b) to silanize all extraction vials, caps, volumetric flasks, pipettes, or other vessels used for neutral or nearly neutral solutions that contain radionuclides. Silanization consists of coating the walls of these vessels with trimethylsilane, thus making them hydrophobic. Before each experiment, he rinses the extraction vials twice with samples of the same aqueous solutions used for the experiments.

The aqueous solutions contain NaClO<sub>4</sub> to set the ionic strength, the ligand or ligands, and the radionuclide of interest in deionized H<sub>2</sub>O buffered at various values of pH. Choppin uses 5, 6, 7, or 8 M NaClO<sub>4</sub>, which does not



form complexes, to bracket the ionic strengths observed for WIPP brines. In those cases in which it is necessary to add significant concentrations of other ions, such as the ligand  $\text{Cl}^-$ , he adjusts the amount of  $\text{NaClO}_4$  to maintain the ionic strength at the desired value. He may also use  $\text{NaCl}$  to set the ionic strength. He will not carry out any of these experiments in WIPP brine because this would unnecessarily complicate the calculation of apparent stability constants. He will use WIPP brine in some of the solubility experiments described in 7.6.2 to check the solubilities calculated using apparent stability constants and solubility products. He will buffer the pH of the solution at values of about 4 for the experiments with the ligands  $\text{Cl}^-$  and  $\text{NO}_3^-$ , and between 6 and 8 for the experiments with the ligand  $\text{HCO}_3^-$  and the study of hydrolysis. For the experiments with the other organic ligands, he will buffer the pH of the solutions at values approximately equal to the pKa of the ligand (see the descriptions of the experiments with various ligands below.) To prevent complexation by  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$ , he will use  $\text{CO}_2$ -free  $\text{H}_2\text{O}$  deionized by passage through mixed-bed resin columns. Above a pH of 6, he will work in a glove box to ensure  $\text{CO}_2$ -free conditions.

The organic solutions consist of 0.002 to 0.02 M dibenzoylmethane (DBM) in benzene. For these solutions, Choppin purifies a 98% DBM solution by vacuum distillation on an oil bath at  $125^\circ\text{C}$ , but does not purify benzene or TBP. If any results suggest contamination of benzene, TBP, or any other reagents, he will use chromatography, crystallization, distillation, or other standard procedures specified for the reagent to purify them. He stores the 0.10 M stock solutions of distilled DBM in benzene in the dark.

Prior to the addition of radionuclides, Choppin filters all solutions through  $0.45\ \mu\text{m}$  cellulose  $\text{NO}_3^-$  filters. He then adds the solutions to the extraction vials with 10-ml, borosilicate-glass syringes fitted with  $0.2\ \mu\text{m}$  cellulose  $\text{NO}_3^-$  filters. He prewashes all filters to remove  $\text{H}_2\text{O}$ -soluble compounds. This also prevents sorption of actinides from neutral or nearly neutral solutions. Caceci and Choppin (1983b) have described these filtration procedures in detail.

After addition of 5 ml each of the aqueous and organic solutions to the extraction vials, Choppin adds small volumes, generally 0.001 ml, of stock solutions containing trace amounts of  $^{241}\text{Am}$ ,  $^{238}\text{Pu}$ ,  $^{239}\text{Pu}$ ,  $^{242}\text{Pu}$ ,  $^{230}\text{Th}$ , and  $^{233}\text{U}$  in 0.2 M hydrochloric acid. This yields a final activity of about 10 to 100 counts per second in both solutions, or depending on the radioisotope used, radionuclide concentrations of about 1 nM to 1  $\mu\text{M}$ . Prior to the addition of these radioisotopes, he checks their purity by  $\alpha$  or  $\gamma$  spectrometry according to the methods of Rydberg and Choppin (1987).

Although previous studies by Caceci and Choppin (1983a, 1983c) have indicated that solutions containing  $\text{CO}_2$ -free deionized  $\text{H}_2\text{O}$  prepared and sampled under a laminar-flow hood are sufficient to prevent complexation by  $\text{CO}_3^{2-}$  or  $\text{HCO}_3^-$ , Choppin is also handling solutions in a glove box from which  $\text{CO}_2$  has been removed with an inert gas bubbled through an alkaline solution. If comparison of the results suggests that preparation and sampling under the laminar-flow hood can result in  $\text{CO}_2$  contamination, he will carry out all of these operations in the  $\text{CO}_2$ -free glove box.

For each set of conditions, Choppin rotates duplicate extraction vials in a  $25 \pm 0.1^\circ\text{C}$   $\text{H}_2\text{O}$  bath. Although the expected temperature of WIPP disposal rooms is about  $30^\circ\text{C}$ , he carries out these studies at  $25^\circ\text{C}$  to ensure comparability of these data with thermodynamic data for dilute solutions, which were obtained mainly at  $25^\circ\text{C}$ . Because preliminary experiments by Caceci and Choppin (1983a, 1983c) with a solution of DBM in benzene and Am(III), Eu(III), and U(VI) indicated that equilibrium is attained in less than 1 hour, he conducts his experiments for periods of 2 to 4 hours.

After equilibration, Choppin separates the aqueous and organic solutions by centrifugation for 10 minutes, and removes two aliquots from each phase for duplicate analyses of the radionuclide of interest, and two aliquots from the aqueous phase for duplicate pH measurements.

Choppin analyzes for radionuclides in the aqueous and organic solutions by liquid scintillation counting according to Caceci and Choppin (1983c) and Kobashi, Choppin, and Morse (1988). He also uses  $\gamma$  counting as described by Caceci and Choppin (1983a). Choppin (1961) and Choppin and Rydberg (1980) have discussed the procedures for calibration, and corrections for background and quenching. To determine the oxidation-state distribution of the radionuclide in the aqueous solution, he uses the methods developed by Saito and Choppin (1983) and Kobashi, Choppin, and Morse (1988) for solutions of high ionic strength (4 to 6 M).

Choppin measures the pCH (the negative logarithm of the concentration, not the activity, of  $\text{H}^+$ ) of the aqueous solutions with combination glass electrodes after spectrophotometric calibration based on the method developed by Robert-Baldo, Morris, and Byrne (1985), Byrne (1987), Byrne et al. (1988), and Byrne and Breland (1989). This spectrophotometric method consists of measuring the absorbance of the test solution at two wavelengths, one characteristic of the partially protonated and the other the completely deprotonated form of the sulfonephthalein indicator cresol red, and calculating pCH from the apparent second dissociation constant for cresol red, the absorbance ratio for the two wavelengths, and the molar absorptivities of the two species. Determination of pCH is appropriate in this case because he is measuring apparent stability constants or apparent solubility products (7.6.2). He has adapted this procedure to WIPP brines by: (1) measuring the second apparent dissociation constant for cresol red in solutions of high ionic strength to determine the pCH-versus-salinity curve; (2) measuring the molar absorptivities of cresol red in solutions of high ionic strengths; (3) calibrating standard buffers in solutions of high ionic strength.

Because KCl is relatively insoluble in solutions with high  $\text{Cl}^-$  concentrations, the use of saturated KCl solution in the salt bridge can produce erratic results. Choppin replaces the saturated KCl solution in the salt bridge of his electrodes with an NaCl solution adjusted to the same ionic strength as the test solutions. He calibrates each electrode prior to its first use, then recalibrates every 2 weeks, or whenever results suggest a problem. Between measurements, he stores the electrodes in  $\text{NaClO}_4$  solutions with ionic strength and pCH similar to those of the test solutions.

The following example illustrates the use of solvent extraction. Caceci and Choppin (1983a) measured the distribution of Am(III) or Eu(II) (the

extractants) between an aqueous solution of 0.7 M NaCl and oxalate buffered at a pH of 6.0 by the hydroxylamine buffer or 8.02 with the hydrazine buffer, and an organic solution (the extractor) of DBM and TBP in benzene. By varying the concentration of oxalate in the aqueous phase and observing the resulting distribution of Am or Eu between the aqueous and organic solutions, Caceci and Choppin (1983a) calculated the apparent stability constants ( $\beta_1$ ) for the Am(III)-oxalate and Eu(III)-oxalate complexes. They then determined the apparent stability constants for the complexes  $\text{Am}(\text{OH})^{2+}$  and  $\text{Eu}(\text{OH})^{2+}$ . The equations used for these calculations appear in Caceci and Choppin (1983a).

One advantage of the solvent extraction technique is that it is possible to determine apparent stability constants, in this case the first hydrolysis constants ( $\beta_1$ ), even though it is impractical to vary the concentration of one of the ligands of interest. Although the pH determines the concentration of  $\text{OH}^-$ , varying the pH also changes the speciation of Am(III) and Eu(III) and hence the relative proportions of  $\text{Am}(\text{OH})_2$  or  $\text{Eu}(\text{OH})_2$  and other hydroxyl complexes. Another advantage is that it is sometimes possible to measure apparent stability constants for two ligands of interest, in this case hydroxyl ion ( $\text{OH}^-$ ) and oxalate, from one set of experiments. However, it is necessary to avoid ligands that form mixed-ligand complexes with the radionuclide in the aqueous phase, or significantly dissolve in the organic phase. Choppin and Caceci (1983a) reported a precision of  $\pm 0.05$  to  $\pm 0.2$  log units for  $\beta_1$ .

Because of the heterogeneous nature of design-basis waste, redox conditions in WIPP disposal rooms could differ significantly between micro-environments separated by short distances, perhaps just a few centimeters. Furthermore, redox conditions in any given microenvironment could change significantly with time. Because of these redox variations, it is possible that Pu will occur in any of its four oxidation states: III, IV, V, or VI. Choppin must attempt to determine stability constants for the four oxidation states of Pu for all of the ligands discussed above.

Pu often occurs in more than one oxidation state simultaneously, and it converts from one oxidation state to another readily. For these reasons, it would be very difficult to control the oxidation state of Pu during these experiments. Choppin will use other elements that are easier to maintain in the III, IV, V, or VI oxidation state and that mimic the chemical behavior of Pu in the same oxidation state. The stability of an oxidation state, as measured by its area on an Eh/pH diagram, may differ significantly from one actinide element to another. Chemical properties such as stability constants or solubility products are generally very similar for different actinide elements in the same oxidation state (for example, Seaborg, 1958).

Am(III) and Eu(III) species are excellent oxidation-state analogs of Pu(III) species. The results obtained with these Am(III) and Eu(III) will be directly applicable to predictions of the behavior of Pu(III). The use of Am(III) will, of course, also provide data for that element, which will probably occur only as Am(III) despite the variety of redox conditions expected for the WIPP.

Direct studies with Pu(IV) species are very difficult because the solubility of Pu in this oxidation state is extremely low, especially in

neutral or nearly neutral solutions, and because its hydrolysis products form colloids, or sorb to colloids and other surfaces very readily. U(IV) poses similar problems. The chemical properties of Th(IV), the commonly used analog, are not as similar to those of Pu(IV) as those of the other analogs are to their Pu counterparts; Th(IV) is somewhat more soluble than Pu(IV) and its hydrolysis is slightly less. Nevertheless, it is possible to use Th(IV) because the required adjustments of the data introduce less uncertainty than the use of Pu(IV). Choppin will base these adjustments on experience with the direction and extent of differences in the relative behavior of various Pu(IV) and Th(IV) species in other systems. The use of Th(IV) will also yield results applicable to U(IV).

Np(V) species are good analogs for Pu(V) species, and the stability field of this oxidation state is much larger than that of Pu(V). It will still be necessary to verify that Np remains in this oxidation state, but this is far more likely than for Pu.

Finally, the chemical behavior of U(VI) species are nearly identical to that of Pu(VI) species, and the long-term performance of the WIPP is also sensitive to isotopes of U (Marietta et al., 1989).

Choppin has started this study with the ligands  $\text{Cl}^-$  and  $\text{NO}_3^-$ . It was important to start experiments with  $\text{Cl}^-$  because this ligand is present at high concentrations in all WIPP brines. Furthermore, he may use NaCl to set the ionic strength of the aqueous solution in at least some of these experiments; therefore, he must determine its effects to separate them from the effects of the other organic and inorganic ligands present. Although the current estimate of the concentration of  $\text{NO}_3^-$  in WIPP brine is not high enough to cause concern, it is so easy to include  $\text{NO}_3^-$  in these experiments that he is studying it in case future estimates of its concentration increase. He uses the methods of Bertrand and Choppin (1982), TTA as the extractor, and carries out these experiments at a pH of about 4. TTA is an excellent extractor for the actinide elements under acidic conditions, which are acceptable for these experiments because  $\text{Cl}^-$  and  $\text{NO}_3^-$  are the conjugate bases of such strong acids that they are completely dissociated even at a pH of 0.

Choppin will start hydrolysis experiments as soon as possible after starting experiments with  $\text{Cl}^-$  and  $\text{NO}_3^-$ . He must start these experiments as quickly as possible because hydrolysis could be important and because it is essential to determine the apparent hydrolysis constants under  $\text{CO}_2$ -free conditions before measuring the apparent stability constants for the ligand  $\text{CO}_3^{2-}$  (hydrolysis and  $\text{CO}_3^{2-}$  complexation occur simultaneously and competitively in the presence of  $\text{CO}_2$ ). He will use the procedures of Caceci and Choppin (1983a) described above for this study at pH values of 6 to 8. Because TTA is too soluble in the aqueous solution if the pH exceeds 4, he is using DBM as the extractor. The extraction kinetics are slower with DBM than with TTA; this necessitates experiments for this study. This technique requires the use of a competitive ligand (for example, Caceci and Choppin, 1983a). He will attempt to use oxalate as the competitive ligand to provide data for one of the organic ligands of concern (7.5). He must therefore study oxalate complexation with TTA at a pH of about 4 prior to the study of hydrolysis. These pH values are high enough to deprotonate oxalic acid, but

still low enough to preclude competition from hydrolysis. Once he has determined the apparent stability constants for the oxalate complexes, he can study hydrolysis with oxalate as the competitive ligand and, from the variation of the apparent stability constants for oxalate, calculate the apparent hydrolysis constants. If precipitation of oxalates precludes the use of oxalate as the competitive ligand, he will determine apparent stability constants for citrate with TTA at a pH of 4 and use it as the competitive ligand in the study of hydrolysis. Citrate is also an organic ligand of concern (7.5).

Next, Choppin will study complexation by  $\text{CO}_3^{2-}$ .  $\text{HCO}_3^-$  does not form significant complexes with the actinide elements. He will carry out this study in a high-quality glove box to control the concentration of  $\text{CO}_2$  in the gaseous phase. By varying the partial pressure of  $\text{CO}_2$  at a constant pH, he will be able to control the concentration of  $\text{H}_2\text{CO}_3$  and  $\text{HCO}_3^-$  in the aqueous solution better than by adding sodium bicarbonate or sodium carbonate. By studying the extraction of radionuclides by DBM as a function of the  $\text{H}_2\text{CO}_3$  or  $\text{HCO}_3^-$  concentration at a constant pH of 6, 7, and 8, he will determine apparent stability constants which include the effects of hydrolysis. From the previously determined apparent hydrolysis constants, he will calculate the apparent stability constants for  $\text{CO}_3^{2-}$ . He recently developed this technique by determining the stability constant for Am(III) at an ionic strength of 0.1 M; the results agree well with previously published values. Furthermore, he foresees no problems in extending it to ionic strengths of 5, 6, 7, and 8 M.

Choppin will then study the ligands EDTA, acetate, ascorbate, and lactate (in that order) with the extractor TTA at a pH of about 4. This assumes that he will have determined stability constants for citrate and oxalate in connection with the study of hydrolysis. Determination of apparent stability constants for EDTA could be difficult because EDTA forms such strong complexes with the actinide elements. He will probably determine the apparent stability constant for another metal, such as  $\text{Mg}^{2+}$ . He will then add  $\text{Mg}^{2+}$  to the experiments with the actinides. The radionuclide will compete with the other cation for the EDTA binding sites; he will use the reduction in the apparent stability constant for each actinide cation to calculate the proper stability constants for the actinides.

Finally, Choppin will repeat selected experiments with all of the ligands discussed above with  $\text{Mg}^{2+}$  in the aqueous solution. These experiments are necessary because  $\text{Mg}^{2+}$  in WIPP brines (Tables 2.1, 2.2, and 2.3) will compete effectively with the actinide elements for binding sites on the ligands.

### **7.6.2 Determination of the Solubilities of Pu-, Am-, Th-, and U-Bearing Solids in Neutral, Acidic, and Basic Solutions of High Ionic Strengths under Various Redox Conditions**

Choppin may determine apparent solubility products for Pu-, Am-, Th-, and U-bearing solids in high-ionic-strength solutions under neutral, acidic, and basic conditions. This study may be necessary to validate solubility predictions based on results of the speciation study (7.6.1), especially if the results of the bin-scale tests with CH TRU waste (see Molecke, 1990a) prove difficult to interpret (7.7).

If Choppin proceeds with this study, he will probably measure the solubilities of solids that contain oxidation-state analogs (7.6.1) in brines collected from the WIPP underground workings (2.3.1.2). Brush will describe this study in detail later.

### **7.6.3 Extension of the Speciation and Solubility Studies to Strongly Basic Conditions**

Choppin may extend the speciation and solubility studies (7.6.1 and 7.6.2) to strongly basic conditions, if use of the proposed backfill additives CaO, Ca(OH)<sub>2</sub>, KOH, and NaOH (6.1) receives serious consideration. Brush will describe this study in detail later, if necessary.

### **7.6.4 Quality Assurance and Safety**

Choppin is carrying out his radionuclide speciation study (7.6.1) in compliance with a quality assurance (QA) plan developed for WIPP-related studies (Choppin, 1989) and approved by Pickering (1989a). This QA plan meets requirements of the American Society of Mechanical Engineers (1986) imposed by SNL (1984a). Choppin will revise this QA plan, if necessary, for future studies of radionuclide solubilities and speciation (7.6.2 and 7.6.3) prior to the initiation of these studies. The investigators responsible for the studies of radionuclide sorption and colloid formation will develop QA plans for these studies (descriptions of these studies will appear elsewhere).

Florida State University is responsible for the development, approval, and implementation of all safety procedures required for its studies. The subcontractors selected for the studies of radionuclides sorption and colloid formation will be responsible for the safety of these studies.

## **7.7 RESULTS EXPECTED FROM BIN-SCALE TESTS**

Analyses for Pu, Am, Th, and U in brines sampled from partially inundated bin-scale tests with CH TRU waste (Molecke, 1990a) will also provide information on the chemical behavior of these elements in brines. The bin-scale tests provide a unique opportunity to examine the behavior of these elements in a system large enough to simulate the heterogeneity expected in WIPP disposal rooms, yet still small enough to investigate the effects of several types of waste and a variety of conditions on their behavior. Comparison of analyses obtained from bins with and without significant anoxic corrosion, microbial activity, and radiolysis may provide information relevant to the effects of Eh on radionuclide chemistry. Comparison of analyses from bins with and without microbial activity and the backfill additives CaO, Ca(OH)<sub>2</sub>, KOH, or NaOH may provide results on the effects of pH. Because the concentrations obtained from these analyses will reflect the simultaneous effects of solubility, sorption, and colloid formation, they may turn out to be difficult to interpret.

## 7.8 SCHEDULES FOR LABORATORY STUDIES

Choppin started the adaptation of a spectrophotometric method for the determination of pCH to concentrated brines (7.6.1) at Florida State University in early August 1989 and completed it in late October 1989.

Choppin started to measure apparent stability constants for organic and inorganic Pu, Am, Th, and U complexes in neutral, acidic, and basic, 5- to 8-M NaClO<sub>4</sub> solutions (7.6.1) at Florida State University in early November 1989. He is using the oxidation-state analogs Am(III), Eu(III), Th(IV), Np(V), and Pu(VI) to provide data for all four elements under the wide range of redox conditions expected for WIPP disposal rooms. He started experiments with the inorganic ligands Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> in early November 1989, and will complete them by the end of March 1990. He will start hydrolysis experiments by the beginning of April 1990. These experiments will be much more time-consuming, and will require about 1-1/2 years to complete. Silanization of all extraction vials, caps, volumetric flasks, pipettes, or other vessels used for neutral or nearly neutral solutions that contain radionuclides will be necessary. He will complete the experiments by the end of September 1991. He could start concurrent experiments to determine the extent of CO<sub>3</sub><sup>2-</sup> complexation by the beginning of July 1990. These experiments will also be very time-consuming and will require about 2 years. Both silanization and careful control of the CO<sub>2</sub> content of the glove box will be necessary. He could therefore complete the experiments by the end of June 1992, if he starts them by the beginning of July 1990. Finally, he will start experiments with the organic ligands EDTA, acetate, ascorbate, and lactate, in that order, assuming that he will have determined stability constants for citrate and oxalate in connection with the hydrolysis experiments. He will start experiments with these organic ligands by the beginning of October 1991, after the completion of the hydrolysis experiments. Because the matrix for these experiments will consist of at least four ligands at four ionic strengths, they will require about 2 years to complete. He will complete them by the end of September 1993. Posttest analysis and reporting will require another 3 months. He will thus complete this study by the end of December 1993. It would be possible to accelerate this schedule and complete this study by the end of December 1992.

Choppin may determine apparent solubility products for Pu-, Am-, Th-, and U-bearing solids (7.6.2) under conditions similar to those of the speciation study (7.6.1) to validate the results of the latter study, especially if the results of the bin-scale tests with CH TRU waste (Molecke, 1990a) prove difficult to interpret (7.7). Brush will provide a schedule for this study later.

Choppin may also extend the speciation and solubility studies to strongly basic conditions (7.6.3). Brush will provide a schedule later.

## 8.0 MODEL DEVELOPMENT

### 8.1 JUSTIFICATION FOR MODEL DEVELOPMENT

Modeling studies are necessary to interpret the results of laboratory studies and the bin-scale and alcove tests with contact-handled transuranic (TRU) waste described by Molecke (1990a, 1990b). Modeling studies are also necessary to extend the results of these laboratory, bin-scale, and alcove tests to other possible repository conditions. If successful, modeling studies would reduce the number of experiments required to quantify the effects of variations in chemical conditions on repository gas and H<sub>2</sub>O budgets and the chemical behavior of radionuclides.

Currently available geochemical models such as the EQ3/6 geochemical software package can meet some, but not all, of these objectives. They can predict chemical reactions between Waste Isolation Pilot Plant (WIPP) brines and evaporite minerals, but not reactions between these brines and silicates (clay minerals in the Salado Fm., bentonite, and grouts, for example), nor the behavior of radionuclides in brines. Additional development of EQ3/6 is therefore necessary.

### 8.2 DESCRIPTION OF EQ3/6

The EQ3/6 software package is a set of computer codes and supporting thermodynamic and kinetic data bases that calculate the speciation of solutes and the solubilities of minerals and other solids in aqueous solutions (EQ3NR), and predict chemical reactions between these solutions and solids, gases, or other aqueous solutions (EQ6). Wolery (1978) first developed EQ3/6 to model basalt/seawater reactions in hydrothermal systems at mid-ocean ridges; he patterned EQ3/6 after the PATHI code developed by Helgeson (1968) and Helgeson et al. (1970). Subsequently, Wolery and his colleagues at Lawrence Livermore National Laboratory (LLNL) have continued the development of EQ3/6 for the commercial radioactive waste repository projects (Wolery, 1979; 1980; 1983; Wolery et al., 1984; 1990; Wolery and Daveler, in preparation).

#### 8.2.1 EQ3NR

The input for EQ3NR (Wolery, 1983) consists of the composition of the solution of interest and properties such as the pH and the temperature of the solution. The code calculates the distribution of each element among possible dissolved species (given as concentrations, thermodynamic activities, and the proportions of the total quantity of that element), and whether the solution is undersaturated, saturated, or supersaturated with respect to minerals or other solids that contain that element. EQ3NR also creates an input file for the reaction-path code EQ6.

EQ3NR uses two measures of the degree of saturation of solutions. The saturation index (SI) is defined as the log of the quotient  $Q/K$ , in which  $Q$  is the ion activity product and  $K$  the equilibrium constant for a reaction, typically the congruent dissolution of a mineral. The SI is negative for undersaturated minerals, zero for saturated minerals, and positive for supersaturated minerals. The other measure, the affinity ( $A$ ), is defined as



the product of the SI and the factor  $-2.303 R T$ , in which  $R$  is the gas constant ( $0.0821 \text{ liter atm mol}^{-1} \text{ }^\circ\text{K}^{-1}$ ) and  $T$  is the absolute temperature ( $^\circ\text{K}$ ). Because  $\log(Q/K)$  changes sign when the reaction is reversed, the affinity to precipitate a mineral is defined as the product of the SI and the factor  $2.303 R T$ . Aprecipitation therefore has the same sign as the SI. Although one generally uses the chemical analysis of a solution to compute the degree of saturation of minerals or other solids, it is possible to assume that a mineral is in equilibrium with the solution and compute what constraints this places on certain components, given that the values for other components are known and correct.

For solutions with ionic strengths less than about 1 M, EQ3NR uses an ion-association model for the speciation of solutes. This model explicitly recognizes the reaction of oppositely charged species to form complexes, and applies mass-action, mass-balance, and charge-balance equations to calculate the relative activities of the free (dissociated) ions and complexes. EQ3NR uses the extended Debye-Hückel equation of Helgeson (1969), commonly referred to as the B-dot Equation, to determine activity coefficients for solute species.

The ion-association model, in conjunction with the B-dot Equation, has proven very successful in modeling dilute aqueous solutions of geochemical interest. Sufficient thermodynamic data now exist for modeling the behavior of several important radionuclides in such systems. However, in solutions with ionic strengths much above 1 M, these equations fail to predict activity coefficients accurately, and the ion-association model breaks down. These failures are especially apparent in the case of concentrated brines such as those at the WIPP Site.

For solutions with ionic strengths up to several molar, EQ3NR uses a mixed-electrolyte model for the speciation of solutes. In contrast to the ion-association model, this model explicitly recognizes only a few complexes in solution. For the mixed-electrolyte model, EQ3NR uses the equations of Pitzer (1973, 1975, 1979) and Pitzer and Kim (1974) to calculate activity coefficients as a function of the composition of the solution. These equations require empirical two- and three-ion-interaction parameters regressed from experimental data attributed to the interactions of the components of the solution. The use of Pitzer's equations to calculate accurate activity coefficients in multicomponent solutions over a wide range of ionic strengths requires appropriate interaction parameters for all of the components of the solution. It is therefore critical to determine whether the set of ion-interaction parameters adequately describes the composition of the system being modeled. Jackson (1988) added the Pitzer Tabulation Option to evaluate the adequacy of the ion-interaction parameters.

With the addition of the Pitzer Activity Coefficient Option and the ion-interaction parameters from Harvie, Møller, and Weare (1984) to EQ3NR and its data base (Jackson and Wolery, 1985; Jackson, 1988), this code can now simulate solubility equilibria between evaporite minerals and WIPP brines. The results of these simulations provide additional validation of EQ3NR with the Pitzer model. Eugster, Harvie, and Weare (1980), Harvie and Weare (1980), Harvie et al. (1980), Harvie, Møller, and Weare (1984), and Pabalan and Pitzer (1987) have already validated the mixed-electrolyte model, the Pitzer equations, and various ion-interaction parameters in other systems consisting

of brines and evaporite minerals. Jackson and Wolery (1985) and Jackson (1988) recently verified and partially validated the addition of the Pitzer equations and various ion-interaction parameters to the EQ3/6 software package.

### 8.2.2 EQ6

EQ6 (Wolery, 1979; Wolery and Daveler, in preparation) uses the model of an aqueous solution generated by EQ3NR as the starting point for simulations of reactions between the solution and minerals or other solids, gases, or other solutions. EQ6 calculates the extent to which these reactions occur, keeps track of the reaction products that precipitate or redissolve, and recalculates the species distribution and degree of saturation of the solution as its composition changes in response to the reactions.

Reaction-path codes generally assume that as a reactant or reactants are incrementally added to the solution, chemical equilibrium is maintained within the solution, as well as between the solution and any solids that precipitate. Conceptually, this is equivalent to a system in which a reactant dissolves at a finite rate, but all other reactions occur instantaneously; the dissolution of the reactant is thus the rate-limiting step for the system as a whole.

EQ6 operates in three modes: a titration mode, a closed-system mode, and a pseudo-one-dimensional "flow-through" mode which follows the evolution of a packet of solution moving through a reactant medium. There is no provision in EQ6 for modeling actual flow through a column. Currently, the "flow-through" only models what happens to the "first" packet of solution. The user can impose fixed fugacities for specified gases on all three of these reaction models (Delany and Wolery, 1984) to simulate systems open with respect to external reservoirs of these gases. This capability is useful in modeling systems open to the atmosphere, which contains highly reactive gases such as carbon dioxide and oxygen.

EQ6 allows the user to choose the function which describes the rates at which the reactants equilibrate with the solution. These functions may represent arbitrary, relative rates or actual, kinetic rate models. If the user employs arbitrary, relative rates, there is no time frame in the calculation, and the code measures the progress of the reaction with a progress variable  $\xi$  related to the quantities of reactants consumed. Each step of the calculation represents an equilibrium state of the system, the composition of which is changing as reactants enter the system. If the user specifies actual rate laws, the calculation includes a time frame. The rate at which a reactant dissolves can be negative, in which case the "reactant" is actually a product precipitating according to the rate law instead of instantaneously to satisfy solubility equilibrium. This is the principle behind the option to specify precipitation kinetics (Delany, Puigdomenech, and Wolery, 1986). Unfortunately, few kinetic data exist yet for geochemical precipitation reactions.

### 8.2.3 Thermodynamic Data and Other Supporting Files

The thermodynamic data base for EQ3/6 was originally a reformatted version of the data base for PATHI (Helgeson, 1968; Helgeson et al., 1970).

This data base included stability constants for many ion pairs and complexes. Subsequent versions of the PATHI data base included revised equilibrium constants for mineral dissolution reactions and a few aqueous redox reactions from the work of Helgeson and Kirkham (1974; 1976), Helgeson et al. (1978), and Helgeson, Kirkham, and Flowers (1981). Helgeson and his colleagues did not revise the stability constants for dissolved species. Since Wolery brought EQ3/6 to LLNL, personnel there have periodically expanded and updated the data base. They have continued to incorporate the results from the ongoing efforts of Helgeson and his co-workers to correlate and predict the thermodynamic properties of the major rock-forming minerals (exclusive of evaporite minerals) and many aqueous species found in geochemical systems. LLNL personnel have obtained data for evaporite minerals from Harvie, Møller, and Weare (1984). Rard (1983, 1985) has reviewed and incorporated data relevant to radioactive waste disposal.

The name of the file that contains the EQ3/6 thermodynamic data base is DATA0. A preprocessor creates DATA1 from DATA0, performs various mass and charge balances, and replaces equilibrium constants on a temperature grid with equivalent interpolating polynomials. EQ3NR and EQ6 then read DATA1. The preprocessor creates a special DATA1 to support the use of the Pitzer model. In this case, DATA1 contains an additional file with ion-interaction parameters, but omits those aqueous species that appear in DATA0 but not in DATA1 to maintain consistency between the activity-coefficient and speciation models.

LLNL personnel formerly maintained the DATA0 file by a combination of "hands-on" editing, a data-block editing code, and several data-generating codes, each of which had one or more of its own data files. They have now replaced this patchwork system with a system based on INGRES, a commercial, relational data base. They integrated the previously used data-base codes into the new system as INGRES "applications." Internal documentation of the data and how it was processed is now an integral part of the system. Additional modifications in progress include provisions for the correction of apparent equilibrium constants to standard-state values, a major revision to incorporate the results of Helgeson and his colleagues (for example, Schock and Helgeson, 1988; Tanger and Helgeson, 1988), and for ensuring compatibility with values recommended by other ongoing, outside reviews of thermodynamic data.

The EQLIB library supports both EQ3NR and EQ6. EQLIB contains mathematical routines, routines that perform various computer-system functions, and routines that evaluate chemical submodels, such as activity-coefficient models, that are used by both EQ3NR and EQ6.

### **8.3 STATUS OF EQ3/6**

Although EQ3/6 can now calculate the solubilities of evaporite minerals in WIPP brines, it cannot yet simulate reactions between these brines and silicates. This is because there are no ion-interaction parameters yet for aqueous Al(III) and Si(IV) species. EQ3/6 thus cannot predict reactions between WIPP brines and clay minerals in the Salado Fm., bentonite, or grouts. Investigators at the University of California at San Diego (UCSD) have recently obtained ion-interaction parameters for Si(IV) species, but

LLNL personnel have not yet incorporated them into the appropriate EQ3/6 data file. UCSD personnel are currently developing ion-interaction parameters for Al(III) species in the system  $\text{AlCl}_3\text{-HCl-H}_2\text{O}$ . This work will yield only the ion-interaction parameters necessary to describe this system, not the complete set required to describe the behavior of Al(III) species in complex, multicomponent systems such as WIPP brines. Nevertheless, it is possible that characterization of the interactions between  $\text{Al}^{3+}$  and  $\text{Cl}^-$  will be sufficient for Al(III) species in WIPP brines because  $\text{Cl}^-$  is the dominant anion in these solutions. When this work is published, LLNL personnel will incorporate the resulting ion-interaction parameters into EQ3/6 (the work at UCSD is not part of the WIPP research program). In addition, it would be useful to have ion-interaction parameters for Cu(II), Fe(III), Mn(II), and Mn(IV) species because these elements occur in proposed backfill additives (6.1) or possible corrosion products of steel containers or Fe and Fe-base alloys in the waste.

Because ion-interaction parameters are also unavailable for the important radionuclides in TRU waste, spent fuel, or high-level waste (HLW), EQ3/6 cannot predict the behavior of radionuclides in brines yet. The ion-interaction parameters required for mixed-electrolyte models such as that of Pitzer (1973) and Pitzer and Kim (1974) are empirical parameters which are applicable only over the compositional range of the experimental data from which they were obtained. Extrapolation of these parameters outside of this range is unlikely to produce reliable results. Because all of the relevant data for the actinide elements have been obtained at ionic strengths significantly below those of WIPP brines (Tables 2.1, 2.2, and 2.3), it would be difficult, if not impossible, to obtain useful ion-interaction parameters for the actinide elements without expensive and time-consuming laboratory experiments. Furthermore, the mixed-electrolyte model might not work at all for the actinides because this model of aqueous solutions explicitly recognizes very few complex species, but the actinide elements form complexes readily.

The Salt Repository Project (SRP) for commercial spent fuel and HLW was funding LLNL to develop alternative activity-coefficient models for brines. Unfortunately, development of these other models ceased with the termination of the SRP. The Yucca Mountain Project (YMP) is still funding LLNL to develop other aspects of the EQ3/6 software package (Wolery et al., 1990), but has no need for other activity-coefficient models because the currently available model based on the B-Dot Equation (Helgeson, 1969) is adequate for the dilute aqueous solutions in tuff at the Nevada Test Site.

#### **8.4 DESCRIPTION OF ADDITIONAL DEVELOPMENT OF EQ3/6**

The objectives of this work are to: (1) extend the Pitzer activity-coefficient model by adding ion-interaction parameters for aqueous Al(III), Cu(II), Fe(III), Mn(II), Mn(IV), and Si(IV) species to the existing data base (8.4.1); (2) develop an alternative activity-coefficient model based on hydration theory (8.4.2).

Brush selected EQ3/6 for additional development because LLNL personnel have made considerable progress in the application of this code to brines and evaporite minerals. Furthermore, the YMP is funding additional development of the EQ3/6 software package at LLNL. These improvements

include: (1) solid-solution models for carbonates, chlorites, and smectites; (2) a linear-isotherm sorption model (LLNL will eventually add a surface-complexation sorption model); (3) a one-dimensional flow model; (4) optimization of computational aspects of the EQ3/6 software package. These features will be extremely useful to the WIPP Performance Assessment (PA) when the ability of EQ3/6 to model systems consisting of brines and evaporite minerals has been extended to include silicates and radionuclides.

K. J. Jackson and T. J. Wolery of LLNL are carrying out additional development of the EQ3/6 software package for the WIPP Project.

#### **8.4.1 Extension of the Pitzer Model**

Jackson and Wolery are attempting to extend the Pitzer model (8.2.1) by adding ion-interaction parameters for important aqueous Al(III), Cu(II), Fe(III), Mn(II), Mn(IV), and Si(IV) species to the data base of Harvie, Møller, and Weare (1984).

Jackson and Wolery will incorporate ion-interaction parameters for Si(IV) species recently obtained by investigators at UCSD into the appropriate EQ3/6 data file as soon as these data are published. They will also incorporate ion-interaction parameters for Al(III) species as soon as UCSD personnel determine them.

For Cu(II), Fe(III), Mn(II), and Mn(IV) species, Jackson and Wolery will carry out a literature search for ion-interaction parameters and incorporate any available data. If there are no published parameters, they will search for experimental data such as isopiestic or emf data for osmotic or activity coefficients in binary systems from which they can obtain these parameters by regression with a fitting code developed for the hydration-theory equations (8.4.2).

When adding ion-interaction parameters to the existing data base, Jackson and Wolery will ensure that all of the regressions used to obtain them are based on the same assumptions, conventions, and forms as the Pitzer equations. The speciation assumed for the solution and the number of electrostatic terms included in the equations, for example, can affect the regression significantly. Differences in the assumed speciation or the number of electrostatic terms can produce incompatible results even if each regression is legitimate.

#### **8.4.2 Additional Development of the Hydration-Theory Model**

Jackson and Wolery are continuing the development of an activity-coefficient model based on hydration theory. Their objective is to develop a model with which they can calculate activity coefficients for radionuclides and other aqueous species in WIPP brines at 30°C. If successful, this would extend the results of laboratory studies of radionuclide chemistry to other conditions without additional expensive and time-consuming experiments.

In their previous work for the SRP, Wolery and Jackson (1990) developed empirical procedures for modifying Debye-Hückel expressions based on a single value of the size of an ion to allow thermodynamically consistent use of

individual size values. They applied one of these approaches in a modification of the hydration theory of Stokes and Robinson (1948), thus allowing the application of the model to mixtures of aqueous electrolytes. In their modified model, they also derived separate equations for the activity coefficients of solutes and the activity of H<sub>2</sub>O, thus eliminating another drawback of the original model. They applied their modified model to published data for several pure aqueous electrolytes by using only two fitting parameters, the ion size and the hydration number, and ignoring complexes. They obtained excellent fits for the 1:1 electrolytes but generally poor fits for the 2:1 and 3:1 electrolytes. The poor fits probably resulted from ignoring complexing. If ion pairing is included, additional species appear, each with its own ion size, hydration number, and equilibrium constant. In the case of the system CaCl<sub>2</sub>-H<sub>2</sub>O, for example, this is conceptually equivalent to treating the system as pseudo-ternary with two CaCl<sub>2</sub> salts, one of which dissociates to the simple ions, the other to CaCl<sup>+</sup> and Cl<sup>-</sup>.

The previous equations of Wolery and Jackson (1990) incorporated a standard, "pure" Debye-Hückel model as the primary theoretical basis. In a review of the manuscript by Wolery and Jackson (1990), K. S. Pitzer criticized the omission of hard-core effects, correctly pointing out that the Debye-Hückel theory only uses the ion size to establish a limit of integration for the electrical forces and ignores its giving rise to hard-core repulsion. Although simple, first-order expressions for this effect are available (for example, Pitzer, 1973; 1977; Olivares and McQuarrie, 1975; Pailthorpe, Mitchell, and Ninham, 1984), empirical models of activity coefficients in aqueous electrolyte solutions often ignore hard-core repulsion. Pailthorpe, Mitchell, and Ninham (1984) point out that inclusion of this effect in the Debye-Hückel model produces results that compare favorably with predictions based on the hypernetted chain equation, the mean spherical approximation, and "exact" Monte Carlo calculations.

The inclusion of hard-core repulsion in the Debye-Hückel model raises the activity coefficient, an effect also produced by the hydration correction. The addition of a hard-core term in a hydration-theory model will thus result in smaller hydration numbers. The inclusion of a hard-core term does not increase any new variables to the model because this term depends only on the ion size and the total solute concentration. Because it does not depend on the total electrical charge, it affects the activity coefficients of neutral solutes as well as ionic species.

It is possible to add hard-core repulsion to the Debye-Hückel model by superimposing first-order results obtained from separate statistical mechanical analyses. Pitzer (1973, 1977) and Pailthorpe, Mitchell, and Ninham (1984), however, have derived a model from a single analysis with an integral equation approach. Pitzer (1973) showed that the usual truncation of the expanded exponential function describing the radial distribution function after the first two terms gave a first-order Debye-Hückel term and a first-order hard-core term. He also showed that carrying a third term (his "three-term" model) yielded a term which mixes electrostatic and hard-core effects. Pitzer (1973, 1979, 1989) used this three-term model as a conceptual guide in the development of his famous empirical equations. The pure Debye-Hückel

term became Pitzer's Debye-Hückel-osmotic (DHO) model. Pitzer used the other two terms to justify his formalism of making the second-order virial coefficients functions of the ionic strength. The mathematics of these two terms did not remain intact, making this a semi-empirical model. In their evaluation of Pitzer's three-term model as a theoretical basis of their model, Jackson and Wolery (LLNL, personal communication) concluded that there should be a fourth term not reported by Pitzer (1973, 1977). This is a second-order Debye-Hückel term and is zero for symmetrical electrolytes and mixtures of symmetrical electrolytes. They point out that including the two additional terms in the three-term model introduces no new variables.

The developments described above yield results for the "restricted primitive model," which uses a single ion-size parameter. It is possible to modify them for ion-size mixing with approaches used previously for pure Debye-Hückel models. It is also possible to modify them directly by relaxing the restriction of a single ion at the deepest theoretical level.

It is important to assess the consequences of upgrading the theoretical basis from a first-order Debye-Hückel term to a modified three-term model that includes the recently discovered fourth term. This should significantly increase the capability of treating higher order electrolytes, especially asymmetrical ones. It will probably still be necessary to include complexes. It will also be necessary to compare empirical ion-size averaging approaches with more recent rigorous results to see which would work best in the model. Equations for the latter are more complex, but should not be too difficult for modern computers to evaluate.

In testing complexes as component species, it may be necessary to modify the electrostatic model to include a description of ion-dipole and dipole-dipole interactions, inasmuch as some of these species are likely to possess significant permanent dipole moments. It will probably be possible to estimate these dipole moments from the ion-size parameters, the charges of the component ions, and their geometry. It will probably be safe to ignore other factors such as quadrupole moments and induced dipole moments.

To develop the hydration-theory model, Jackson and Wolery will: (1) compile an internally consistent data base (ion sizes and hydration numbers) which, when used in the model, gives activity coefficients in agreement with experimental values for simple solutions of strong electrolytes; (2) validate the model and data in complex, multicomponent solutions of strong electrolytes; (3) incorporate this model and data into the EQ3/6 software package; (4) verify and document the addition of the model for strong electrolytes to EQ3/6.

Initially, the compilation of an internally consistent data set is closely related to the final equation development and focuses on fitting or otherwise explaining published experimental data for simple systems such as solutions of one and two electrolytes. The efforts of Jackson and Wolery differ from previous work in that they are attempting to develop a more theoretical model with physically meaningful parameters that may be more amenable to prediction from corresponding-states algorithms such as those used by Helgeson et al. (1978) to predict parameters for equations of state for aqueous electrolytes. This is an essential prerequisite for extending

the model beyond mixtures of mostly strong electrolytes to components such as the actinides and transition metals.

In their model development, Jackson and Wolery are restricted to the use of previously obtained experimental data, including data for mostly strong electrolytes that have been used in the development of models based on Pitzer's equations. These include osmotic pressure, emf, and some solubility data. Corresponding data for "electrolytes" consisting of actinide elements are scarce and of limited utility because of the strong tendency of these metals to form complexes. For the actinides, they are mostly restricted to electrical conductivity, spectrophotometric, and solubility data. In many cases, these data are apparent equilibrium constants obtained in solutions with ionic strengths of 0.1 to 3 M and extrapolated to infinite dilution to estimate the true equilibrium constants. It is possible to use these true equilibrium constants to model the behavior of actinides and transition metals in dilute solutions, including the formation of complexes and their effects on solubilities. Studies that yield osmotic coefficient and emf data for "strong" electrolytes have largely ignored complexation. Their model development will require integration of all of these types of data.

Jackson and Wolery will fit their equations to data for simple systems consisting of solutions of one strong electrolyte. They will use their HTFIT code and osmotic-coefficient data from Stokes and Robinson (1965) and other sources. HTFIT uses a weighted least squares minimization technique to determine the optimum fit of equations to a data set. This leads to a preliminary data set and provides an opportunity to test the equations and the assumed component species. Initially, they will include as component species those complexes that seem likely from experience modeling dilute solutions, and assume reported values of the true equilibrium constants. This will leave only ion sizes and hydration numbers to produce by fitting. They will not adjust the values of these equilibrium constants unless they have to, but will test the sensitivity of the results to the values of the equilibrium constants. Once they have gained confidence in the equations, they may use them to extrapolate the measured apparent equilibrium constants to the true equilibrium constants in a fully consistent manner. Two tests will be possible at this stage. First, they will require good fits to the data. Second, their parameters are physically meaningful; therefore, their values should follow regular patterns predicted by corresponding states algorithms such as those developed for other activity-coefficient equations (for example, Helgeson et al., 1984).

Next, Jackson and Wolery will apply the model to mixtures of strong electrolytes. They will again emphasize osmotic-coefficient and emf data. Most of these data pertain to mixtures of two electrolytes. Because their model has fewer parameters than the model based on Pitzer's equations, they can make predictive tests with most of these data sets. For mixtures of two electrolytes with a common ion, their model introduces no additional parameters beyond those required for the constituent pure electrolytes; all of the parameters for mixtures appear in the models for the constituent pure electrolytes. This is true even if they include complexes as component species. In Pitzer's model, an additional fit parameter would be necessary. For pure electrolytes their model has more parameters than Pitzer's model. Furthermore, the values of some of their parameters may not be very sensitive to the



experimental data for pure electrolytes. This is especially likely in the case of the parameters for complexes of 1:1 electrolytes, such as the NaCl<sup>o</sup> species. Preliminary calculations suggest that in saturated, pure NaCl solutions at 25°C, this complex accounts for only about 1 to 10% of the dissolved NaCl. Data for this system at 25°C will therefore probably not be very useful for determining the parameters for this species. In this case, they will obtain the parameters for 25°C by extrapolating data from high temperatures, where complexing is generally more extensive. However, for other complexes, data from mixtures of electrolytes may be more sensitive to associated parameter values; therefore, they may adjust their parameters for pure electrolytes in these cases. Because the temperature in WIPP disposal rooms will not significantly exceed 30°C (1.10), they will fit their equations mainly to data obtained at 25°C, with a few exceptions such as that discussed above for NaCl.

Jackson and Wolery will then attempt to incorporate the actinide elements into their model. This will require a different approach, based on predictive corresponding-states relationships, because osmotic-coefficient and emf data will not predict the complex behavior of the actinides. There may be insufficient experimental data to extend their model to the actinides.

To be validated, a model must calculate realistic values for measurable parameters of a system (Silling, 1983). The point at which the user should be satisfied that the model is valid necessarily depends on the type of problem to be solved and the degree of accuracy specified for the solution. Thorough testing on problems similar to the desired applications may validate the model under those conditions, but not necessarily under different conditions. It is often a matter of careful judgment whether a model is valid under other conditions.

Jackson and Wolery will validate the hydration-theory model by demonstrating that it can predict the solubilities of the chemical components in WIPP disposal rooms under expected repository conditions, or at least the solubilities of these components in natural systems under similar conditions. Because the primary purpose of additional development of EQ3/6 is to predict the solubilities of actinide elements in WIPP brines, they will test the model by using it to predict actinide solubilities under expected WIPP conditions. The solubility products for actinide-bearing phases, or even the identities of the stable actinide-bearing phases, are poorly known; they will therefore exercise considerable caution in choosing solubility data for model validation. Because there are usually large uncertainties in the interpretation of the concentrations observed in complex, empirical, materials-interaction tests, they will mainly use data from carefully controlled laboratory experiments specifically designed to yield solubility data. They will also attempt to test the model with results from materials-interaction tests carried out either in the laboratory or the WIPP underground workings.

To demonstrate that the hydration-theory model can predict the solubilities of actinide-bearing phases under the conditions expected in WIPP disposal rooms, Jackson and Wolery must obtain data for the actinide-bearing phases expected to be stable under these conditions. The stable actinide phases under these conditions are more likely to be oxides, hydroxides, carbonates, and silicates than chlorides or sulfates. They will carry out a

literature search for previously obtained solubility data, and evaluate the quality and thermodynamic consistency of any such data prior to use. Because these data are probably still scarce, they may have to carry out additional laboratory experiments specifically for model validation.

Jackson and Wolery must validate the hydration-theory model for strong electrolytes by demonstrating that it predicts the solubilities of evaporite minerals in WIPP brines successfully.

Once validated, addition of the Hydration-Theory Option to EQ3/6 will require relatively minor code modifications. These modifications will make it possible to use EQ3NR and EQ6 in conjunction with the necessary data files (ion sizes and hydration numbers generated by fitting their equations to previously obtained data and using corresponding-states algorithms) to compute activity coefficients for a wide variety of solutes, especially radio-nuclides, over a wide range of ionic strengths.

To select the Hydration-Theory Option, the user will set the IOPG option switch on the EQ3NR and EQ6 input files and provide an appropriate DATA1 file. During the initial development of this option, a supplemental data file containing the ion sizes and hydration numbers may also be necessary. Eventually, Jackson and Wolery will append this file to DATA1 with the EQPT preprocessor, and the operation of this option will be transparent to the user.

The code modifications required for the incorporation of the Hydration-Theory Option will be mainly associated with the EQLIB library routines. This will allow EQ3NR and EQ6 to access the same coding to compute activity coefficients. The subroutine GCOEFF in EQLIB directs the calculation of activity coefficients. Various subroutines and subsidiary functions calculate factors required in the expressions for the activity coefficient, such as average ion size for the solution. Jackson and Wolery will insert an additional loop in GCOEFF to evaluate the hydration-theory equations. This loop will in turn necessitate additional arrays, logical variables, and flags throughout the other codes to carry information specific to this option, but will not require restructuring the logic in these codes. They will modify EQ3NR and EQ6 to read the new data files and to accept and produce new input and output files, respectively.

Jackson and Wolery will not modify the master iteration variables used in EQ3NR and EQ6 for the Hydration-Theory Option. Wolery (1983) and Wolery and Daveler (in preparation) describe these variables and the residual functions used in EQ3NR and EQ6. The codes will solve for the hydration-theory expressions as dependent variables analogous to the method used by the codes to solve for these expressions with the Pitzer model (Wolery and Daveler, in preparation). During each iteration, the codes will assume that the activity coefficients and the activity of H<sub>2</sub>O are constants, and recalculate them after each step. If the recomputed values differ significantly from the previous values, the codes will modify them and repeat the iteration. Based on their experience with the addition of the Pitzer Option to EQ3/6, they think that this will be the most efficient way to add the Hydration-Theory Option, and will result in a faster code relative to the possible inclusion

of the activity-coefficient expressions in the list of master iteration variables.

Preliminary efforts by Jackson and Wolery to incorporate the Hydration-Theory Option have shown that there will be no major problems adding it once they validate it. These efforts also yielded several prototype versions of subroutines that may be used in the actual implementation of the Hydration-Theory Option.

Verification of a computer code consists of demonstrating that it evaluates a set of equations correctly (Silling, 1983). Although verification and validation have different definitions, many of the test runs used to verify a code also contribute to the validation of the model on which it is based.

Jackson and Wolery will verify the Hydration-Theory Option by showing that it evaluates the hydration-theory equations correctly and conforms to various specified conventions. Verification that the coding is correctly implemented will consist of comparing the results of a series of carefully designed test runs with results from selected hand calculations and results obtained using other code options such as the Pitzer Option. In general, they will verify the Hydration-Theory Option with the same procedures used to verify the implementation of Pitzer's equations (Jackson and Wolery, 1985; Jackson, 1988). They will carry out test runs designed to compare activity and osmotic coefficients for binary and ternary systems to verify the accuracy with which the Hydration-Theory Option reproduces the experimental data. They will also use any available activity- and osmotic-coefficient data for more complex systems (for example, Chan, Khoo, and Lim, 1979) to evaluate the accuracy of the coding in multicomponent systems. Finally, they will use solubility data for these test runs. All of these test runs will also contribute to the validation of the Hydration-Theory model.

Because the coding for the hydration-theory calculations will reside in the EQLIB library routines, it will be separate from EQ3NR and EQ6. Tests run using EQ3NR will therefore verify many of the same code modifications as tests run with EQ6, and duplicate tests run using both codes to solve the same problem must yield identical results.

After verification of the addition of the Hydration-Theory Option, Jackson and Wolery will prepare: a supplemental user's manual with sample input and output files for both EQ3NR and EQ6; documentation of the code modifications, and additions or revisions to the data files; technical details about the use of this option. This will supplement previous EQ3/6 user's manuals (Wolery, 1983; Delany and Wolery, 1984; Delany, Puigdomenech, and Wolery, 1986; Wolery and Daveler, in preparation).

### **8.4.3 Quality Assurance**

Jackson and Wolery are carrying out additional development of EQ3/6 (8.4.1 and 8.4.2) in accordance with all applicable sections of the overall quality assurance (QA) plan described by LLNL (1988) and approved by Pickering (1990c). This QA plan meets requirements of the American Society of Mechanical Engineers (1986) imposed by Sandia National Laboratories (1984b).

## 8.5 SCHEDULES FOR ADDITIONAL DEVELOPMENT OF EQ3/6

Jackson and Wolery started to extend the Pitzer model to Al(III), Cu(II), Fe(III), Mn(II), Mn(IV), and Si(IV) species at LLNL in late February 1989. Because ion-interaction parameters already exist for aqueous Si(IV) species, extension of the model to this element will be straightforward. A study to obtain ion-interaction parameters for Al(III) species in the system AlCl<sub>3</sub>-HCl-H<sub>2</sub>O is in progress at UCSD. It is unclear whether these parameters will be applicable to WIPP brines. Furthermore, neither Brush nor Jackson and Wolery have control over the direction and schedule for this study, because neither LLNL nor the WIPP Project is funding this research. It is also unclear whether there are existing parameters or data that can be used to obtain them for Cu(II), Fe(III), Mn(II), and Mn(IV) species. Jackson and Wolery will complete a literature search by the end of February 1990 to determine whether any data exist for these ions. At that time, they will reassess the prospects for extending the Pitzer model and, if possible, Brush will provide a schedule for this work.

Jackson and Wolery also restarted the development of the hydration-theory model at LLNL in late February 1989. They will compile an internally consistent data set (ion sizes and hydration numbers) for simple solutions of strong electrolytes, validate the model and data in complex, multicomponent solutions of strong electrolytes, if possible, and incorporate this model and data into the EQ3/6 software package by the end of February 1990. At that time, Brush, Jackson, and Wolery will review the model to determine whether they can extend it to the important radionuclides in TRU waste in time for use by the WIPP Project. If so, Jackson and Wolery will continue the development of the model. They will verify and document the addition of the model for strong electrolytes to EQ3/6 by the end of February 1991.

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