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BETWEEN AECL AND US/DOE
FOR A RADIOACTIVE WASTE MANAGEMENT
TECHNICAL CO-OPERATIVE PROGRAM**

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TABLE OF CONTENTS

FUNDAMENTAL MATERIALS INVESTIGATIONS.....	1
IN SITU STRESS DETERMINATION.....	22
DEVELOPMENT OF A SPENT FUEL DISSOLUTION MODEL.....	27
LARGE BLOCK TRACER TEST: EXPERIMENTAL TESTING OF RETARDATION MODELS.....	30
LABORATORY AND FIELD TESTS OF IN SITU HYDROCHEMICAL TOOL.....	35
CIGAR LAKE - ANALOGUE STUDY - ACTINIDE AND FISSION PRODUCT GEOCHEMISTRY.....	36
PERFORMANCE ASSESSMENT TECHNOLOGY EXCHANGE.....	40
DEVELOPMENT OF MULTIPLE-WELL HYDRAULIC TEST AND FIELD TRACER TEST METHODS...	44

ABBREVIATIONS

AECL	Atomic Energy of Canada Limited
LANL	Los Alamos National Laboratory
LLNL	Lawrence Livermore National Laboratory
SAIC	Scientific Applications International Corporation
URL	Underground Research Laboratory
USBR	United States Bureau of Reclamation
US/DOE	United States Department of Energy
USGS	United States Geological Survey
WL	Whiteshell Laboratories

FUNDAMENTAL MATERIALS INVESTIGATIONS

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Objectives

1. To provide sufficient thermodynamic and laboratory databases such that adequate modeling of the long-term chemical behavior of man-made sealing materials in the vicinity of waste packages can be accomplished.
2. To determine the effects of temperature on the mechanical and chemical properties of sealing materials.
3. To determine the types of interactions that may occur between sealing materials and rock.
4. To extend the available information regarding the thermodynamic properties of the chemical and mineralogical components of sealing materials.
5. To develop models that describe the consequences to the performance of waste packages in various scenarios of water flow and temperature.

PREAMBLE

The investigation into the long-term performance of cement-based sealing materials is being pursued along two parallel and interactive lines - experimental and numerical model. The experimental investigations are being carried out under the auspices of Atomic Energy of Canada Limited (AECL) and the numerical models are being carried out by the Lawrence Livermore National Laboratory (LLNL).

The laboratory program is designed to assess the performance of cement-based materials under the conditions of a repository, to develop an improved understanding of potential modes of degradation of cement-based materials, and to provide the fundamental data necessary to conduct and qualify the theoretical predictions. This was necessary because it was recognized that required data were either not available or not of sufficiently high quality to permit reasonable predictions. The task of the numerical analysis is to develop and apply appropriate thermodynamic models to better predict the long-term performance of cement-based materials in the vicinity of a waste package.

Technical Progress Report for 1992 October to 1993 September Inclusive

Laboratory investigations carried out at AECL for the assessment of the long-term performance of cement-based materials during the reporting period focused on:

1. Investigating the microstructure of the reference high performance grout (RHPG).

2. Studying the occurrences of the nine selected potential high temperature cement phases in selected grouts and concrete mixes.
3. Initiating an experimental program to develop low heat high performance concretes.
4. Studying the effects of high temperature on selected properties of concrete mixtures developed in support of the Yucca Mountain Project.
5. Measuring the heat capacities of the nonhydrated crystalline phases provided by LLNL.
6. Assessing the ability of the reference high performance grouts to self-seal.

Activities at LLNL in the past year focused on:

1. Synthesizing 11 Å tobermorite to use in the following experiments. Conducting X-ray diffraction (XRD), chemical analysis and nuclear magnetic resonance (NMR) spectroscopy for a detailed structural characterization.
2. Structural analysis of cement phases during heating and dehydration/rehydration.
3. Mechanistic and thermodynamic descriptions of the hydration/dehydration behaviour of hydrated Ca-silicates as a function of temperature, pressure and relative humidity.
4. Studying occurrences of tobermorite and other low-temperature Ca silicates at Crestmore to evaluate as potential natural analog.
5. Measurements of thermodynamic data for hydrated Ca-silicates.

Reference High Performance Grouts (RHPG) Tests

The RHPG contain both silica fume and superplasticizer. Specific features of the materials developed are the inclusion of pozzolanic materials (such as silica fume) to limit the amount of portlandite ($\text{Ca}(\text{OH})_2$) (CH)¹ in the hardened material and superplasticizers (water reducer) to enhance workability at low water to cementitious materials (W/CM) ratios. By their physical presence, these components naturally affect the development of the material microstructure; moreover, they will react with developing hydration products. Scanning electron microscopy (SEM) and mercury intrusion porosimeter (MIP) were used to investigate the microstructure. The results indicate that the microstructure of RHPG is completely different from that of ordinary cement paste. The addition of silica fume and superplasticizer led to the development of a dense microstructure. The basic structure appears to be amorphous Type III hydrated calcium silicates (CSH) gel particles compacted into a dense array with very few isolated small pores (Diamond, 1986). Although X-ray diffraction and infrared spectroscopy of the granulated grout revealed that some (~3%) $\text{Ca}(\text{OH})_2$ persists, the large layered deposits of calcium hydroxide intergrowing around the CSH gel and other paste components, a typical feature of hardened ordinary cement paste, were not observed.

1. The following nomenclature is used in cement chemistry C=CaO, S=SiO₂, A=Al₂O₃, F=Fe₂O₃ and H=H₂O.

The examination of the microstructure with both SEM and MIP indicated that addition of both silica fume and superplasticizer promoted the development of a dense homogeneous microstructure with extremely fine porosity (Figure 1). The results show the absence of pores with diameter larger than $0.1 \mu\text{m}$. The absence of pores with radius larger than $0.1 \mu\text{m}$ should have significant effects on the permeability and consequently on the durability of the developed grouts. In this respect Mehta, 1986, proposed a pore diameter of $1 \mu\text{m}$ (measured by MIP) as a somewhat arbitrary dividing point between "large" pores which contribute most to permeability, and "small" pores, which are much less significant. It is recognized that the properties of a material originate from its internal microstructure and that the properties can be modified by making suitable changes in the structure of the material. The low hydraulic conductivity ($<10^{-14} \text{ m/s}^{-1}$) and high strength (90 MPa compressive strength) of the RHPG developed can be related to the grout's dense microstructure and the lack of pores with diameters larger than $0.1 \mu\text{m}$ (Onofrei et al. 1993). It can be suggested from the results that the pore size distribution is more important than total porosity in determining permeability.

One of the possible functions of cement-based sealants is the long-term sealing of fractures that may contribute to the dispersal of dissolved nuclear waste to the environment. To accomplish this objective, the sealant must have acceptable low hydraulic conductivity (i.e., $<10^{-10} \text{ m/s}$). However, it is known that there are possible mechanisms that may lead to loss of hydraulic performance of cement-based sealing materials. These mechanisms include:

- microcracking under excessively high loads imposed by the rock mass,
- microcracking from shrinkage caused by drying,
- microcracking from differential thermal expansion,
- increases in porosity attributed to dissolution/leaching of solid phases,
- thermodynamic instability of phases, which may increase porosity by solid phase transformation.

Presence of any defects (cracks, capillary pores) in the structure of the grout and concrete has the potential to provide a more rapid transport pathway for the advection or diffusion of radionuclides. The presence of these defects could impair the performance of grouts and concrete as a barrier to radionuclide migration. If self sealing can be assured, particularly for the modified cement-based grouts (containing silica fume and superplasticizer) under the chemical conditions likely within an underground disposal vault, the cracks will be of much less significance.

Figure 1: Pore size distribution curves for the RHPG mixed at W/CM = 0.4 with 10% silica fume and 1% superplasticizer measured by MIP. a) cumulative pore volume and b) incremental intrusion.

It has been reported that cracks in concrete can self-seal in the presence of moisture by a process known as "autogenous healing". The process is now generally accepted to occur in concretes and cements. The self-sealing has been investigated by examining the recovery of mechanical properties in damaged concrete, the decrease of water flow through cracks or using petrographic techniques (Wagner 1974; Munday et al. 1974; Dhir et al. 1974). Self-sealing has only been observed when water is present (i.e., either in air at high humidity >95%) or during total immersion in water. A conclusion was that the sealing rate, as determined by measuring the apertures of cracks with a microscope, was reduced when water was allowed to flow through the cracks. The material infilling the cracks was examined and found to be CaCO_3 . It appeared that the most likely self-sealing process is calcite formation (CaCO_3) resulting from the reaction between aqueous Ca^{2+} ions from the cement and the dissolved CO_2 and/or the carbonate from the environment. A source of CO_2 is required for self-sealing to occur by carbonation. When a source of CO_2 is not available, as may be the case in a repository for heat-generating radioactive waste, it is not clear that self-sealing would occur by an alternative processes.

There is uncertainty concerning whether the conditions in a repository will be suitable for the potential imperfections (cracks, capillary pores) in the cement-based sealants to heal with time. Because of the limited knowledge of the sealing mechanism, particularly for modified cements containing additives such as water reducers (i.e., superplasticizer) and pozzolanic materials (i.e., silica fume) an improved understanding is required for the self sealing process, particularly in the chemical conditions within an underground repository.

A research program was initiated at the Whiteshell Laboratories to assess the ability of the Canadian cement-based grouts to self-seal. The self-sealing capabilities of both bulk grouts and thin films of grouts are being investigated with water flowing through the grout.

The autogenous sealing of cracks in thin films of grouts is being investigated in the cone-in-cone apparatus described in detail by Onofrei et al. (1989). The effect of self-sealing on the hydraulic properties of bulk grouts is being investigated on cylinder specimens used to determine the hydraulic conductivity of reference high-performance grouts RHPG and RHPG with imposed porosity. The autogenous sealing is being studied using changes in pore structure (decrease in pore radius and volume of pores), changes in the size of the induced cracks, and changes in the rate of water flow through the grouts.

Reference High Performance Concretes (RHPC) Tests

New type, high performance, cementitious materials are being considered for possible use in the construction of seals for underground repositories for heat-generating, radioactive, nuclear waste (Johnson et al. 1994). With the rapidly expanding data-base on the properties of high-performance cement, grouts and mortars (Onofrei et al. 1993) there is increasing confidence that the new materials possess many of the physical and mechanical properties required of repository sealants. Studies (Alcorn et al. 1992) have shown that in an underground repository in granite rock, such as that being considered by the Canadian Nuclear Fuel Waste Management Program (CNFWMP), high-performance

cement-based grouts and mortars are quite thermodynamically stable and, hence, durable; hydraulic conductivity can remain very low ($<10^{-12}$ m/s) for hundreds of thousands of years. In light of these observations, high-performance concretes for use in the underground construction of mass concrete dams, which may be unreinforced, or possibly for completely backfilling underground openings, are being developed and investigated for the CNFWMP.

Typically, current generation high-performance concretes with low W/CM have cement contents between 450 and 500 kg/m³ (Table 1). This makes the materials unsuitable for use in mass-concrete structures. The materials shrink autogenously as the limited amount of water in the concrete is consumed by the cement hydration reactions. Moreover, the materials change volume with the significant changes in temperature that occur as heat is generated by the cement-hydration reactions and as the heat is congruently and subsequently dissipated.

TABLE 1
CONCRETE MIXTURES

Characteristics	SHPC ¹	LHHPC ²
Density (Kg/m ³):	2482	2424
Cement content (Kg/m ³):	497	97
Water content (Kg/m ³):	124	92
Minerals content (Kg/m ³):	1804	2128
Minerals content (% mass):	72.7	87.8
1. Normal (Standard) High performance Concrete		
2. Low Heat High Performance Concrete		

A high-performance concrete with a cement content of 97 kg/m³ has been developed. Less mineralogically complex and, hence, more amenable to thermodynamic analysis than pulverized fly ash (PFA-based) low-heat concretes, the new material has an unconfined compressive strength of 100 MPa 90 days after casting, exhibits a maximum temperature increase of 15°C during hydration and, compared to both conventional and high-performance concretes, is volumetrically stable. It can be inferred from the high strength and associated microstructural properties that low-heat, high-performance concretes possessing the durability properties required for repository sealants can be designed. The mechanical, microstructural and chemical properties of the new material will be evaluated.

Effects of High Temperature on Selected Properties of Cement-Based Materials.

A series of laboratory experiments was initiated at the Whiteshell Laboratories in collaboration with University of Sherbrooke, to determine the way in which selected properties of cement-based sealing materials will behave when subject to the thermal conditions expected in the vicinity of the waste package. The consequences of these thermal stresses on sealing materials are being considered and evaluated.

Two groups of cement-based materials are being studied in these investigations. The first one was developed and used in the laboratory tests at the Whiteshell Laboratories and in field trials at the Underground Research Laboratory (URL) in support of the CNFWMP (Onofrei et al. 1993) and another derived from the laboratory tests on cementitious materials in support of the Yucca Mountain Project repository sealing program (Licastro et al. 1990). Based on these laboratory studies, the Canadian and U.S. Task Managers agreed on two concrete mixtures (Table 1) and three grout mixes (Table 2) to be adopted for use in these laboratory investigations. These mixtures may be altered as required by the demands of the task. The time and the program budget will also be taken into consideration.

Concrete Mixtures

The compositions of the concrete mixtures (Table 2) were arrived at from the following criteria:

1. Compositions of the mixtures should reproduce those of Licastro et al. (1990) as closely as possible within the constraints of the present experiments in order to allow easy comparison and evaluation with the present study.
2. The chemical constituents should be simplified as much as possible during the initial experimental runs to provide a foundation for understanding progressively more complex chemical systems. In the future it will be necessary to investigate such complex systems.
3. The chemical interactions between aggregate and grout should be maximized by increasing the surface area of the aggregate. As a consequence the aggregate size will be between 5 μm and 10 μm .

The laboratory studies are being divided into the following activities:

1. Mechanical properties (strength and elastic parameters).
2. Hydraulic properties (radial permeability).
3. Microstructural stability.

The ranges of independent variables under investigation include:

1. Temperature, 20 to 200°C.

2. Curing time, 7, 28 and 90 d.

3. Mix composition. (See Table 2.)

Analytical methods will include the following:

1. Mechanical analysis: sonic velocity, compressive and tensile strength, elastic parameters.
2. Hydraulic permeability analysis at 20°C and 200°C.
3. Microstructural analysis.

The pore structure of thermally stressed specimens will be determined before and after test using mercury intrusion porosimetry (MIP) or gas absorption.

TABLE 2

CONCRETE MIXTURES SELECTED FOR USE IN LABORATORY STUDIES.

Component	Weight Percentage of Mixtures	
	Modified 82-22 mix ¹	Modified 84-12 mix ¹
Type K cement	21.5	-
Class H cement	-	11.9
Tap Water	8.7	8.7
Silica Fume	7.3	11.3
Silica Flour	-	-
Slag	-	13.4
Silica Sand ²	22.5	18.1
Fly Ash ³	4.2	-
Tuff ⁴	35.0	36.2
Superplasticizer ⁵	1.0	1.0

1) Licastro et al. (1990).

2) ASTM C 109 Ottawa silica sand.

3) Low calcium content.

4) Tuff aggregate between 5 mm and 10 mm.

5) Water reducer-sodium salt of sulphonated naphthalene formaldehyde condensate.

Microstructural analyses of thermally stress specimen will be performed by scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDAX).

Phase transformation observations (mineralogy) will be performed by a thermal analysis methods; differential thermal analysis (DTA) and thermal gravimetry (TG) and X-ray diffraction (XRD) at the termination of the tests.

Grout Mixtures

Cement-based grouts are fabricated by mixing water with portland cement and often with additives such as; superplasticizer and pozzolanic materials² to produce materials with the desired properties. Cement-based grout consists primarily of an assemblage of hydrated phases formed from calcium oxide (CaO), aluminum oxide (Al_2O_3), and silica (SiO_2). Common phases include CH (portlandite), hydrated calcium silicates (CSH), CAH and ettringite ($C_3A \cdot CaSO_4 \cdot 32H$) as well as unhydrated residual phases. The predominant phase is CSH, a semi- or cryptocrystalline material sometimes referred to as tobermorite gel because of similarities between the CSH gel and the natural mineral tobermorite. It is expected that curing time and the type and the proportion of the starting materials will produce grouts with different mineral phases assemblages. Also, the environmental conditions (temperature, dry or wet conditions, groundwater composition) in which the grout and concrete will function are expected to affect the mineralogical composition of the grouts.

Nine phases (hillebrandite, afwillite, foshagite, xonotlite, 9Å tobermorite, 11Å tobermorite, 14Å tobermorite, gyrolite and okenite) that may be found in or derived from cementitious materials at elevated temperature are presently under investigation. Two selection criteria were established for these phases. First, to minimize the complexity of the initial chemical system, the investigation was limited to the three most common chemical components, calcium oxide (CaO), silicate (SiO_2) and water (H_2O). The second criterion was to select phases that are favored at temperatures above 25°C.

A laboratory experimental program was initiated at the Whiteshell Laboratories to determine the occurrences of these phases in the cement-based grouts and concretes intended for use in Canadian Nuclear Waste Management Program and in the Yucca Mountain Site Characterization Project Repository Sealing Program. The experimental program involves monitoring changes that occur under the influence of temperature on the phase composition and in the microstructure of the selected hardened grout compositions (Table 2). Gradually these compositions will be altered by the addition of sand and tuff, the other two major components of the concrete mixtures, and the effects of these components

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2. Pozzolanas are silicious materials that, though not cementitious in themselves, contain constituents that will combine with lime at ordinary temperatures in the presence of water to form compounds which possess cementing properties and have a low solubility.

on the composition of the phases will be investigated. The investigations will be performed by means of thermal analysis (DTA and TG), XRD analysis, SEM/EDAX and MIP.

TABLE 3

GROUT MIXTURES SELECTED FOR USE IN LABORATORY STUDIES.

1. RHPG mixed at W/CM ratios of 0.4 and 0.6 with 10% silica fume and 1% superplasticizer.
2. Class H cement mixed at W/CM =0.3 with 15% silica fume and 1% superplasticizer.
3. Class K cement mixed at W/CM with 15% silica fume and 1% superplasticizer.

Three different types of test methods will be applied to study the effects of temperature, environmental conditions and mix composition on mineralogical transformation in the selected grout mixtures:

1. The grout mixtures will be heated in air at 25 to 250°C.
2. The grout mixtures will be heated in saturated steam at 25 to 100°C.
3. The grout mixtures will be leached under static conditions at 25 to 85°C.

Energetics of High Temperature Phases Found in Cementitious Materials

An experimental and modeling program has been designed to elucidate the structural and thermodynamic response of cement minerals to elevated temperature. The components of the program include: a) synthesis of hydrated Ca-silicates; b) structural analysis of cement phases during heating and dehydration/rehydration; c) mechanistic and thermodynamic descriptions of the hydration/dehydration behavior of hydrated Ca-silicates as a function of temperature, pressure and relative humidity; d) study of naturally occurring hydrated Ca-silicates; and e) measurements of thermodynamic data for hydrated Ca-silicates.

The purpose of this project is to determine the structural characteristics of the minerals that form in cement at elevated temperature, and to determine the thermodynamic properties of these phases. Knowledge of the structural properties of minerals allows us to model their physical and chemical properties more accurately. Information from this project will ultimately be incorporated into evaluations of the mineralogic response of cementitious materials to elevated temperatures and fluid movement, and into determinations of how cements modify or "condition" fluid chemistry.

Cements minerals and their thermodynamic properties

Hydrated cements prior to aging consist largely of Ca(OH)_2 and what is known as C-S-H gel (Taylor 1964; Glasser et al. 1985), which is weakly crystalline, hydrous, and composed of Ca(C), Si(S) and $\text{H}_2\text{O(H)}$. A form of reactive SiO_2 is often present as well. Upon aging and/or heating, these phases convert to a variety of hydrated Ca-silicates such as tobermorite, afwillite, hillebrandite, foshagite, xonotlite, reyerite, gyrolite and truscottite (Table 4, Figure 2).

The above minerals vary in their atomic structures, Ca-Si ratio, and H_2O and OH content. (The term "hydrated" as used in this paper refers to the presence of OH and/or H_2O in a mineral). We have initially focused on this suite of minerals as representative of chemical system $\text{CaO-SiO}_2\text{-H}_2\text{O}$, which is a primary component of cement-water systems. Future studies will expand the compositional system to include SO_4 , Al, Fe and other components found in typical cements.

Extensive literature reviews have revealed that thermodynamic data (e.g., Newman 1956; Taylor 1968) are sparse for these minerals, and when available, they are contradictory. The contradictions arise because minerals were not characterized adequately prior to measurements, and their hydration states were either guessed, estimated, or not controlled during the measurements. As a result, significant differences exist among experimentally determined thermodynamic values for minerals with the same reported chemical formula.

TABLE 4

MINERAL COMPOSITIONS

9.7, 11.3, and 14Å tobermorite ^a	$\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot n\text{H}_2\text{O}$
afwillite	$\text{Ca}_3\text{Si}_2\text{O}_4(\text{OH})_6$
hillebrandite	$\text{Ca}_2\text{SiO}_3(\text{OH})_2$
foshagite	$\text{Ca}_4\text{Si}_3\text{O}_9(\text{OH})_2$
xonotlite	$\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$
reyerite	$(\text{Na,K})_2\text{Ca}_{14}\text{-}$ $(\text{Si,Al})_{24}\text{O}_{58}(\text{OH})_8 \cdot 6\text{H}_2\text{O}$
gyrolite	$\text{Ca}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$
truscottite	$\text{Ca}_{14}\text{Si}_{24}\text{O}_{58}(\text{OH})_8 \cdot 2\text{H}_2\text{O}$
okenite	$\text{Ca}_{10}\text{Si}_{18}\text{O}_{46} \cdot 18\text{H}_2\text{O}$
nekoite	$\text{Ca}_3\text{Si}_6\text{O}_{12}(\text{OH})_6 \cdot 5\text{H}_2\text{O}$

^a referred to as 9Å, 11Å and 14Å tobermorite
in this paper

Thermodynamic data for some of the phases of interest have been estimated (Babushkin et al. 1985) based on structural interpretations and average bond energies obtained from minerals whose thermodynamic properties are known. However, we have several reasons to re-evaluate these estimated values even though the data have been used in thermodynamic calculations of cement stability at 25°C (Alcorn et al. 1991). The enthalpies of minerals used in the estimations differ from accepted values for those minerals today (Newman, 1956). In addition, the Ca-silicate hydrates are unique structures. No compositional or structural analogues to the hydrated Ca-silicate are known to exist (Taylor 1964). As a consequence, one is forced to question the appropriateness of estimation techniques based on the assumed similarity of bond energies, especially at elevated temperature.

The estimation techniques that have been applied to the hydrated Ca-silicates do not provide for the energetics of hydration/dehydration. Johnson et al. 1991, have shown that for hydrated phases such as zeolites, the energetic contribution of zeolitic H_2O is significant, but is unique to each mineral, is not constant and does not seem to follow a pattern.

Figure 2: Selected cement minerals in system $CaO-SiO_2-H_2O$ (mole percent). Compositional regions of C-S-H and silica gel (Glasser et al. 1985) are stippled.

Considered as an isolated group, the estimated data seem to agree with the relative stability of these phases. However, it has not been demonstrated that the data are consistent with that for other minerals included in the thermodynamic data bases associated with geochemical modeling codes. Assuring that our data set is internally consistent is critical to the successful evaluation of interactions among cement minerals and host rock minerals.

Experimental program

In view of the above needs, a multi-disciplinary experimental and modeling program has been designed to elucidate the structural and thermodynamic response of cement minerals to elevated temperature. The program includes: a) synthesis of hydrated Ca-silicates; b) structural analysis of cement phases during heating and dehydration/rehydration; c) mechanistic and thermodynamic descriptions of the hydration/dehydration behavior of hydrated Ca-silicates as a function of temperature, pressure and relative humidity; d) study of naturally occurring hydrated Ca-silicates; and e) measurements of thermodynamic data for hydrated Ca-silicates. The following sections summarize recent results in these areas except for a) and d), which are described elsewhere (Bruton et al. 1993).

Structural analysis

Structural changes in natural and synthetic phases that occur during heating/cooling and dehydration/rehydration are being assessed by computer-based molecular modeling, X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) spectroscopy.

Molecular modeling. We are using published atomic parameters and molecular simulation software (CERIUS) to construct a visual library of three-dimensional Ca-silicate hydrate crystal structures and their simulated x-ray diffraction patterns. The crystal structure library will be used to verify structural modifications that occur during the course of experiments. Structural modifications are apparent from changes in the relative intensities and positions of the peaks in X-ray diffraction patterns, which can be compared to simulated patterns (see X-ray diffraction).

The geometric relationship between an ion and its nearest neighbors reflects the cation-oxygen bonding relationship, which is fundamental to the thermodynamic characteristics of the material. This geometric relationship, or ion coordination, is the basis for thermodynamic estimation techniques that have been applied to the Ca-silicate hydrates (Babushkin et al. 1985). The applicability of these techniques requires verification because the calcium ion coordination of many of the Ca-silicate hydrates is thought to differ from other common silicate structures that contain calcium.

Previous thermochemical models for the Ca-silicate hydrates (Babushkin et al. 1985) use a Ca-O binding energy determined from wollastonite (β -CaSiO₃). The Ca-O bonding polyhedra in wollastonite (Figure 3a) contain six or seven oxygens at an average distance of 2.37 to 2.41 Å with a standard deviation of 0.07 to 0.12 Å. In contrast, Ca-silicate hydrates display a wide variety of Ca-O bonding polyhedra, some of which contain water molecules. For example, tobermorite (Figure 3b-d) contains three types of Ca-sites that vary greatly in both mean Ca-O distance (2.42 to 2.94 Å) and regularity (standard deviation 0.05 to 0.30 Å). The appropriateness of a thermochemical estimation technique based on wollastonite must therefore be questioned.

X-ray diffraction. XRD is being used to determine whether structural changes accompany dehydration/rehydration. Knowledge of the hydration state is required to quantify the amount and timing of water released to the repository from these

materials, and to evaluate of the energetics of the materials throughout the repository lifetime. Documentation of the dehydration characteristics of the Ca-silicate hydrates will constitute a major part of the present investigation.

Changes in hydration state (structural OH and H₂O) can modify the atomic structure of a material to various degrees depending on a number of factors. For example, it is known that the removal of water from tobermorite appears to decrease the spacings of one set of parallel layers to a far greater extent than for other layers. Thus, the three identified tobermorite phases are named 9 Å, 11 Å, and 14 Å after those diagnostic layer spacings.

Figure 3: Ca-O bonding polyhedra for wollastonite (a) and tobermorite (b, c, d; after (Hamid, 1981)). Small circles are oxygen atoms and large circles are H₂O molecules.

Preliminary studies suggest that material originally synthesized as a mixture of 14Å and 11 Å tobermorite dehydrates to 11 Å tobermorite upon heating to 110°C. Comparison of the XRD patterns of the post-heating sample and the simulated 11Å tobermorite (Figure 4) to the air-dried 42 day sample (not shown) illustrates the structural change upon dehydration. Our preliminary results suggest that in agreement with previous studies, 11 Å, rather than 14 Å tobermorite, will be the dominant phase at elevated temperature in the repository environment.

Figure 4: X-ray diffraction pattern of the 42 day synthesized sample dried at 110°C (solid line) superimposed upon a simulated pattern of 11Å tobermorite (dotted line).

Nuclear magnetic resonance spectroscopy. NMR spectroscopic data are being collected for hydrated Ca-silicates under ambient conditions to deduce the structures of materials on a molecular level. Such data form the basis from which structural changes during dehydration/rehydration can be assessed. ^{29}Si and ^1H NMR data have been collected for gyrolite, okenite, xonotlite, hillebrandite and a synthetic tobermorite, and ^1H data have been collected for portlandite and ettringite.

For ^{29}Si , two basic magic-angle-spinning (MAS) experiments were performed—single-pulse (SP) and $^{29}\text{Si}\{^1\text{H}\}$ cross-polarization (CPMAS). All ^1H MAS spectra are from SP experiments. ^{29}Si peak positions for the hydrated Ca-silicates depend mostly on the degree of polymerization (i.e. number of bridging oxygens), and are designated Q^n , where n is the number of bridging oxygens.

The crystal structure of gyrolite is shown in Figure 5. The ^{29}Si SP and CPMAS NMR spectra of gyrolite (Figure 6, top and bottom, respectively) contain strong Q^3 peaks at -91.8, -93.5 and -98.8 ppm, consistent with the proposed sheet silicate structure (Merlino, 1988). For a synthetic gyrolite, Bell et al. 1990, observed additional, relatively intense peaks at -80 and -86 ppm due to Q^1 and Q^2 environments, respectively. Our spectra show only a small Q^2 peak at -84.6 ppm (0.4 ± 0.1 percent) and another, broader peak at about -88.5 ppm that is probably also due to Q^2 . The much lower concentration of Q^2 Si sites and the narrower peaks for the natural material indicate that it is more ordered than the synthetic sample examined by Bell et al. 1990. These ordering differences could translate into significant energetic differences. This finding underscores the need for careful sample characterization before thermodynamic or other analyses are conducted.

Figure 5: Atomic structure of gyrolite (after Merlino, 1988). Samples contain small amount of Na.

^1H MAS NMR spectra for xonotlite and gyrolite are shown in Figure 7. Xonotlite gives a single hydroxyl peak at +2.4 ppm, in agreement with the accepted structural formula. Gyrolite has a broad peak at +5.1 ppm for structural water, a narrow peak at +1.5 (width 0.6 ppm) due to isolated hydroxyls, and a broader hydroxyl peak at +2.2 ppm (width 1.6 ppm). The main hydroxyl peaks are probably from the octahedral sheet and the structural water from the interlayer. These ^1H results indicate that it will be possible to determine the changes in the hydrogen speciation upon dehydration.

Dehydration/rehydration behavior

The thermodynamic behavior of the hydrous Ca-silicates as a function of temperature, pressure and relative humidity will be deduced from experimentally determined water sorption isotherms. Hydrated Ca-silicates will be also equilibrated at varying relative humidities within an environmental chamber attached to the XRD. Water is associated with the external (intercrystalline water) and internal (intracrystalline water) surfaces of these hydrates. Loss of external, interparticle water will be reflected by weight loss without associated structural changes. Loss of such water can, however, affect the release of water into the environment surrounding cements.

Figure 6: ^{29}Si SP and CPMAS NMR spectra of gyrolite are consistent with proposed sheet silicate structure (see Figure 4).

Thermodynamic models

Standard experimental techniques designed to obtain thermodynamic data for anhydrous minerals will encounter problems when applied to hydrated minerals owing to the changes in hydration state that can occur during the course of a measurement. Such behavior confounds interpretation of the results. We must therefore develop an understanding of the hydration/dehydration behavior of hydrated phases as a function of temperature, pressure and relative humidity. Current work in this area is directed to controlling the hydration state of phases during the differential scanning calorimetry (DSC) scan, and to determining properties of phases with limited water loss.

During the reporting period very pure, single-crystal synthetic and natural quartz, natural calcite, natural gypsum, and wollastonite, supplied by LLNL, were used to calibrate a DSC at Whiteshell Laboratories (WL). The heat capacities of the natural and synthetic materials derived from this work together with experimental results of Robie et al. (1979), are shown in Table 5. From the data, it can be seen that the values determined at WL were, in most cases, lower than those obtained by Robie et al. (1979). The results showed that the C_p values were affected by sample preparation procedures. The

differences between the measured C_p values and those reported by Robie et al. (1979) decreased markedly when the specimens were finely ground and tamped in the aluminium pan. However, as shown in Table 5 the C_p values were still lower than those reported by Robie et al. (1979). In addition to differences in preparation procedures, the differences between the measured C_p values may be due to differences in the degree of purity of the samples.

TABLE 5

COMPARISON OF HEAT CAPACITIES OBTAINED BY DSC FOR A NUMBER OF MINERALS

Material	Temperature °K	Heat Capacities (C_p) in J/mol.K	
		present tests	Robie et al.
Ground Synthetic Quartz	323.15	45.38	47.21
	373.15	50.25	51.50
	423.15	54.16	54.98
	473.15	56.67	57.99
	523.15	58.80	60.69
Ground Natural Quartz	323.15	44.78	47.21
	373.15	49.23	51.50
	423.15	53.09	54.98
	473.15	55.56	57.99
	523.15	57.78	60.69
Ground Natural Calcite	323.15	83.48	87.75
	373.15	89.80	94.26
	423.15	95.41	99.06
	473.15	98.26	102.81
	523.15	100.31	105.91
	573.15	103.12	108.58
Ground Natural Wollastonite	323.15	87.02	90.23
	373.15	95.25	97.54
	423.15	101.05	102.64
	473.15	103.72	106.42
	523.15	107.63	109.36
Ground Natural Gypsum*	473.15	123.29	117.63
	523.15	124.35	122.61

* Assuming anhydrite above 473.1°K.

In the view of the high sensitivity of the predictions of longevity to the precision of measured parameters, work for immediate future will focus on ensuring the accuracy and precision of the DCS measurements. A standard will be run after each sample in the experimental sequence, as suggested by Callanan and

Sullivan (1986), and an attempt will also be made to determine a correction factor to compensate for the differences in empty pan mass (using the procedures suggested by Luebke and Tria (1984), and the differences between the recorded temperature and that actually experienced by the sample (Callanan and Sullivan 1986; Richardson and Burrington 1974). For comparison, the heat capacities will be also measured by the drop calorimetry technique at temperatures up to 80°C.

Figure 7: ^1H MAS NMR spectra of xonotlite and gyrolite illustrating the distinction between structural water and hydroxyls.

A data base of the thermodynamic properties of the main silicate phases in hardened cement has been established and is being expanded to provide the information needed to model, numerically, the processes of the phase transformation that will occur in cement-based materials used to seal a vault. Work is in progress to build confidence in the measured thermodynamic properties used in the modelling exercises. This necessarily involves advancing DSC techniques and improving the precision of measurements.

Data from the above studies should provide the basis for describing the high-temperature behavior of cement minerals, their impact on water chemistry and their interactions with the surrounding host rock and waste canisters. Our preliminary studies demonstrate the limitations of available thermodynamic data,

and emphasize the importance of determining cement mineral behaviour as a function of temperature, pressure, and relative humidity.

In agreement with previous studies, 11Å tobermorite should become the dominant tobermorite phase as temperatures increase. NMR spectroscopy suggests that significant energetic differences could exist between synthetic and natural samples selected for calorimetric studies. NMR has also proven capable of determining changes in hydrogen speciation during dehydration of cement minerals.

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IN SITU STRESS DETERMINATION

Task Managers

P.M. Thompson (AECL)

W.G. Austin (USBR)

Objectives

1. To develop improved stress determination instruments and techniques that are more reliable and cost-effective than ones that are currently available.
2. To evaluate stress determination instruments and techniques by direct comparison with each other in situ.
3. To increase understanding of the three-dimensional state of stress in rock by improved analytical techniques and to improve presentation of the stress tensor.
4. To improve interpretation of stress determination results, including effects of scale, structure, and anisotropy.

Technical Progress Report for 1992 October to 1993 September Inclusive

Instrumentation Development

During the early part of this reporting period some additional rosettes were fabricated for the improved triaxial strain cell. The mold for the rosettes was modified to reduce the thickness of the rosettes by about 1 mm so that the cell can be installed in a 38-mm-diameter borehole without the strain gauge adhesive on the rosettes contacting the borehole walls prior to setting the rosettes. Other items on the cell that were modified were the cable sealing mechanism, and the attachment of the nosecone. The front of the cell was drilled out to facilitate wiring of the rosette pistons. The nosecone is now installed by screwing it in place against an O-ring seal at the front of the cell.

Overcore Training at the (URL)

A five member team from US/DOE visited the URL the week of 1993 January 16 for training in the use of the Continuously Monitored Council for Scientific and Industrial Research (South Africa) (CSIR) triaxial strain cell in borehole 209-005-OC1, located on the 240 Level at the corners of Rooms 209 and 207. The hole was drilled into the back of the tunnel at an upward plunge of 30°. Unfortunately the hole penetrated some tight, water-bearing fractures, causing water seepage in the hole which hindered efforts at obtaining a successful test. This did not affect the training, however in order to test the prototype Improved Triaxial Strain Cell it was decided to move the overcoring to an existing hole, 210-003-OC1 where several successful tests were performed.

Hydraulic Injection Testing

Triaxial overcore stress measurements were previously made in borehole 209-032-OC3, on both sides of the Room 209 fracture. The magnitude results from this hole indicate that the normal stress across the fracture ranges from 6.6 to 11.7 MPa and that close to the fracture the normal stress is about 8 MPa. It is generally accepted that hydraulic injection tests can be used to determine the in situ stress acting normal to a fracture. A packer system was installed in OC3 and hydraulic injection tests were carried out in pressure steps of 0.7 MPa. The fracture opened at 13.2 MPa which is somewhat higher than the overcore results mentioned above. The difference between the stress magnitude from the overcore testing and the hydraulic opening pressure may be a function of the scale of the measurement, i.e., the overcore test is a point measurement, whereas the hydraulic injection test influences a much larger area.

Triaxial Testing at United States Geological Survey (USGS)

Calibration testing revealed that the displacement transducers on the triaxial cell were inadequate. Special custom made ceramic transducers were purchased. A computer-controlled pressure system was acquired to improve the control of the three loading axes.

Borehole Breakouts

Laboratory work was conducted at the University of Wisconsin to examine the relationship between the extent of core discing and applied stress, and the dimensions of borehole breakouts and applied stress. This work was carried out on samples of Lac du Bonnet granite taken from the 240 Level of the URL. The tests were unique, in that the loads were applied to the sample as the borehole was being drilled.

The major objectives of the study were to characterize the failure mechanism in the rock and to establish the limiting in situ stress conditions leading to the onset of borehole breakouts. It was demonstrated experimentally that breakouts in Lac du Bonnet granite occur in two diametrically opposed zones of the borehole along a line parallel to the direction of σ_h . Laboratory induced breakouts are deep and pointed (V-shape), and dramatically similar to those observed in a large circular tunnel in the same rock at the URL. This deep and pointed shape contradicts the broad and flat bottomed breakouts interpreted for deep granitic rocks from televiewer logs, and predicted based on shear failure zone model calculated linear elasticity and the Mohr-Coulomb failure criterion. Extensile cracking has been found to be the basic mechanism of breakout initiation. Progressive failure of detached flakes bounded by these extensile cracks leads to deep and pointed breakouts.

With respect to stress magnitudes leading to breakouts, σ_h values at which incipient failure occurs and those at which breakouts initiate, generally increase linearly with the magnitude of the least horizontal stress. This result suggests that the occurrence of breakouts at URL can provide, in principle, a means of estimating the magnitude of σ_h responsible for breakout initiation if σ_h is independently measured or estimated.

A paper describing this work by M.Y. Lee and B.C. Haimson entitled "Laboratory Study of Borehole Breakouts in Lac du Bonnet Granite: a Case Study of Extensile Failure Mechanism" was presented at the 34th U.S. Symposium on Rock Mechanics in Madison, Wisconsin.

Hydraulic Fracturing Research

Laboratory work is also being conducted for hydraulic fracturing research. Diametral measurements made in a borehole during laboratory hydraulic fracturing can be used to pin-point the fluid pressure at the instant of rock fracturing. Correct identification of the fracturing pressure has important implications with respect to the calculation of the in situ stress magnitudes from hydraulic fracturing results.

Evaluation and Testing of Overcoring Equipment Acquired by USDOE

The overcoring instrumentation acquired by the US/DOE for the field testing/training exercise at the U.S. site (Amethyst Mine in Creede, Colorado) was assessed and evaluated prior to using it in the field. A number of deficiencies with the equipment were identified and rectified. Among the problems identified were the following:

- The quick-coupled 2-m-long emplacement rods supplied were in fact approx. 2.03-m-long.
- The internal connector in the installation head for attachment of the CSIR gauge was 60° out of proper alignment.
- No internal stable resistor was supplied in the installation head (for channel 12).
- Software to operate the data logger was not provided.
- No dedicated current users manuals were provided for the equipment.
- Six doorstopper gauges, the installation head and the drilling accessories are either defective, or are not sized correctly.

Thin-section Microscopy

A program of petrographic examination of thin-sections of URL granite is underway at USBR in Denver. The program is investigating the microfabric of the Lac du Bonnet granite in order to determine the influence of microfracture orientation on rock deformation and in situ stresses. Microscopic techniques have revealed abundant microfracturing in the granite as expected based on the known anisotropy. The microfractures are believed to have influenced the directional dependence of overcoring stress measurements.

Overcoring Field Trials/ Training at Amethyst Mine

The use of the Amethyst Mine at Creede, Colorado, for training of US/DOE staff at a US site, was confirmed with the mine owner during the first quarter of the

US Fiscal Year. The training and field testing program was subsequently deferred to 1993 September, with 3 AECL staff members on site to conduct the training between September 20-24.

During the testing at Creede, several deficiencies with the equipment (in addition to those identified previously) were identified. Among the problems identified were the following:

- The data logger supplied to monitor the CSIR cell during an overcore test was not properly set up. There was no compensation for temperature change and as a result the readings were meaningless.
- The flattening and polishing bits for the Doorstopper Gauges were somehow damaged (the central diamonds were worn away), and a small protrusion of rock resulted at the base of the flattened holes which damaged the strain gauge rosettes as the Doorstoppers were installed. This prevented any successful Doorstopper tests.

All other components required to successfully install and overcore a Continuously Monitored CSIR Triaxial Strain Cell had been brought up to acceptable standards (mainly by U.S. staff working on the project). In order to solve the problems with the data logger, it was agreed that it would be returned to the factory for modifications at no cost. After the manufacturer has finished with the datalogger they will ship it to AECL (at the URL) who will perform a complete evaluation on the logger with respect to the effect of temperature changes, and comparing it to AECL monitoring equipment. If the data logger is determined to be acceptable, it will then be forwarded to US/DOE. If not, either the manufacturer or AECL will rectify the situation so that the logger provides accurate, temperature compensated readings.

With respect to the polishing and flattening bits for the Doorstopper tests, AECL will evaluate bits from 2 separate manufacturers at the URL to determine which performs best. AECL has not experienced problems with Doorstopper bits at the URL in the past.

The field testing and training program at Amethyst Mine was very successful in terms of a training exercise, and at identifying shortcomings in the present design of the Continuously Monitored CSIR Triaxial Strain as it relates to use in vuggy tuff. It was noted that vugs present in the rock greatly reduce the likelihood of a water seal between the outside of the overcore rock cylinder and the pilot hole interior over the length of an overcore test (30-40 cm). This results in flooding of the pilot hole during the overcoring process which shorts out the CSIR installation head, ruining the test. Since nothing can be done about the presence of vugs in the rock, AECL will continue the development of the sealed "improved" triaxial strain cell at the URL. Design changes to this instrument will include locating the installation head packer as close to the strain gauge rosettes as possible, to reduce the length of sealed pilot hole required to conduct a test. It is planned to perform additional trials at the Amethyst Mine site in 1994 July to evaluate the design changes together with the modified Sens-Log data logger. It was also noted that the high fracture frequency in the rock makes it difficult to find sections of rock long enough to

conduct triaxial overcore tests (or any overcore test requiring a pilot hole - including the USBM Borehole Deformation Gauge).

Another pertinent observation was that the rock temperature at the test location at Amethyst Mine was about 1.5°C which is much colder than that expected at the Yucca Mountain site. Such low temperatures are not conducive to successful cell installations which involve the use of temperature-sensitive epoxy glue. In fact the ambient rock temperature at the Amethyst Mine test site is actually 8-10°C colder than the rock at the URL. The rock temperature was measured deeper in the Amethyst Mine (several hundred metres from the portal) and was about 10°C, which is closer to temperatures expected at Yucca Mountain. Future tests at Amethyst Mine should be done further from the portal. This would require the installation of a temporary ventilation system.

DEVELOPMENT OF A SPENT FUEL DISSOLUTION MODEL

Task Managers

L.H. Johnson (AECL)

R. Stout (LLNL)

Objective

To develop a mechanistic model for the rate of oxidative dissolution of uranium dioxide that can be used to support the assessment of long-term dissolution behaviour of spent fuel in a repository.

Technical Progress Report for 1992 October to 1993 September Inclusive

1. UO₂ Electrochemistry and Spectroscopy Studies

Electrochemical studies at Whiteshell Laboratories (WL) and Lawrence Berkeley Laboratory (LBL) have used a variety of electrochemical and surface analysis techniques to examine the dissolution of both UO₂ and SIMFUEL (SIMulated high burnup UO₂ FUEL) over a wide range of redox potentials. The SIMFUEL contained inactive fission products at the 1.5, 3 and 6 atom % level. An X-ray photoelectron spectroscopy (XPS) study indicated that Ru, Rh, Mo and Pd were present as metals, while Sr, Ba, Y, La, Zr and Ce were present as oxides.

Studies of O₂ reduction on SIMFUEL indicate that surface reactivity is significantly enhanced, compared to similar behaviour for UO₂, by the presence of the simulated fission products. The initial stages of uranium oxidation are also accelerated for SIMFUEL; however, the steady-state corrosion potentials measured for SIMFUEL and UO₂ are equivalent. These results suggest that the variations in fission product and actinide content that occur as a result of variability in fuel burnup are unlikely to be a reason for differences in corrosion rates for different fuel assemblies.

At LBL, photo-thermal deflection spectroscopy (PDS) is being used to measure uranium concentration gradients in solution adjacent to polycrystalline and single crystal electrodes. The results obtained with polycrystalline electrodes indicate that the sustained dissolution that occurs at strongly oxidizing potentials (+300 mV) continues for several minutes after the potential is decreased to a reducing value. It appears that an oxide film is produced at high potentials and the film slowly dissolves even when a reducing potential is applied (Rudnicki et al., in press). Preliminary results obtained with a single crystal UO₂ electrode show no sign of this behaviour, suggesting that the grain boundaries in polycrystalline material are responsible for the chemical (non-oxidative) dissolution that occurs at reduced potentials. This likely arises as a result of dissolution, followed by precipitation, at grain boundaries. This precipitated material subsequently continues to slowly dissolve, even when a reducing potential is applied.

2. Effects of Radiolysis

Radiolysis of water may result in redox conditions at the fuel surface being more oxidizing than in the surrounding environment. Because this may have a greater effect on spent fuel dissolution in a reducing environment (granite) than in the oxidizing environment at the Yucca Mountain repository, studies in this area are performed by WL staff. Previous investigations (Shoesmith and Sunder 1992) suggested that oxidative dissolution of used CANDU fuel as a result of alpha-radiolysis of water may continue for periods of up to ten thousand years after disposal. More recent experiments indicate that alpha-radiolysis is likely to be significant for only the first six hundred years.

3. Flow-Through Dissolution Studies

Flow-through cells are being used to measure dissolution rates of both UO_2 and spent fuel. The UO_2 dissolution rates are being measured by WL, LLNL and Pacific Northwest Laboratory (PNL) on samples from the same well-characterized batch of UO_2 powder.

Dissolution rates under aerated conditions in a bicarbonate (0.01 M)/chloride (0.1 M) appear to be similar (i.e., within a factor of 3) for all three laboratories. A paper comparing the results from these studies and relating them to electrochemical results is in preparation.

Experiments measuring the dissolution rate of UO_2 powder in deoxygenated solutions (2 ng/mL O_2) at WL have measured rates of $0.001 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, three to four orders of magnitude lower than rates measured for aerated solutions. Similar experiments on used fuel samples under the same conditions give rates ten to fifty times higher than for UO_2 , suggesting that gamma-radiation may be enhancing dissolution rates.

Analysis of data on UO_2 and spent fuel dissolution experiments performed at LLNL and PNL for a test matrix involving a range of temperature, dissolved oxygen, carbonate and pH conditions is continuing. The apparent activation energies for the two materials differ, although, as expected, rates increase with temperature. The pH and carbonate dependencies are still under study. For aerated conditions, the overall averaged dissolution rates of UO_2 and spent fuel samples are 4.3 and $2.5 \text{ mg/m}^2 \cdot \text{day}$ respectively.

Progress Meetings

A meeting between WL, PNL and LLNL staff involved in developing the spent fuel dissolution model was held in Santa Fe on Sept. 26, 1993. It was clear that excellent progress had been made in obtaining dissolution rates that are reproducible. These results will be documented in a paper for the 1994 May High-Level Waste Meeting in Las Vegas. Reasonable agreement has also been obtained in some cases with the electrochemical model. Furthermore, spectroscopic and electrochemical studies are providing valuable insights into methods of incorporating reactivity effects (variation in burnup and preferential grain boundary dissolution into a model for spent fuel dissolution).

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LARGE BLOCK TRACER TEST: EXPERIMENTAL TESTING OF RETARDATION MODELS

Task Managers

T.T. Vandergraaf (AECL)
R.S. Rundberg (LANL)

Objectives

1. To apply and further develop the AECL methodology developed for the Large Block Radionuclide Migration Facility (LBRMF) to test models for radionuclide migration in igneous rock
2. To develop intermediate and field-scale methodologies for both near- and far-field radionuclide migration.
3. To develop techniques to measure concentrations of tracers sorbed on fracture surfaces and in the porous rock matrix.
4. To calibrate and test appropriate mathematical models, which could lead to greater confidence in these models.

Technical Progress Report for 1992 October to 1993 September Inclusive

1. Selection and Procurement of the Granite Material

This milestone was met during the previous reporting period and was described in the previous Annual Report. Six slabs, polished one side, with dimensions of 100 x 100 x 10 cm have been procured.

2. Plan and Cost Tuff Block Sampling

Field trips to Busted Butte and to Yucca Mountain at the Nevada Test Site during 1992 to survey rock outcrops showed that no surface blocks of appropriate size were available from the Topopah spring member tuff on Yucca Mountain. The largest surface outcrop of Topopah spring member tuff was found at Busted Butte but lack of access ruled out this source for a tuff block. During the reporting period, the feasibility of procuring a block from the Exploratory Studies Facility was investigated. The possibility of retrieving a suitable block of Topopah Spring tuff from the access tunnel to the proposed Exploratory Studies Facility in Yucca Mountain has been investigated. However, as the excavation of this Facility will not be located in the Topopah Spring tuff member, an alternate location for a source of a block of Topopah Spring tuff has been located on Fran Ridge, where a block of tuff will be excavated for the Lawrence Livermore Laboratory heated block test.

3. Selection of Tracers

This milestone was met in 1992 May. The following nonradioactive and radionuclide tracers were selected for the migration experiments: Br, $^3\text{H}_2\text{O}$, ^{85}Sr , ^{137}Cs , U, and ^{237}Np .

4. Complete Geochemical Characterization of Tracers and Granite

This milestone has also been completed and reported on in the 1992 Annual Report. A decision was made to issue only one report on the chemical, physical, and mineralogical composition of the geological material to be used in the joint radionuclide migration experiments. A preliminary draft of the report has been written and has been circulated for comments.

A synthetic reference groundwater was selected, consisting of a dilute Na/Ca/Cl/HCO₃ solution with a TDS (Total Dissolved Solids) concentration of 500 mg/L. Fifty-litre volumes of this synthetic groundwater are conditioned with 1 kg crushed rock for periods upwards of one year. This procedure introduces small amounts of other rock-forming elements, including K, Mg, SO₄ and Si into the groundwater. Sampling of the groundwater was started as a function time to obtain information on the evolution of the groundwater.

5. Develop Inverse Code for Multiple Outlet Experiment

Development of an inverse code, TRACRI, has been completed. The code has been tested using the data obtained in the hydraulic characterization of the natural fracture in quarried block LB-3. The data have been converted into a format that is compatible with the inverse code. Major modifications have been made to this code to allow the inversion of the pressure data.

Additional modelling of contaminant transport has been performed at LANL using code TRACR3D. Modelling included different sorption/desorption kinetics, diffusion into the interconnected pore space of the rock, and transport of dissolved species and colloidal particles in a grooved fracture. The results from the final modelling exercise suggest that the effect of the grooves on the transport of colloids is much greater than that of the dissolved species and that this difference should be observable experimentally.

6. Select Image Enhancement Technique

The development of the image enhancement technique at LANL has been completed. A two-dimensional inverse code has been developed, based on the Tikhonov regularization method. It has been tested successfully on a two-dimensional image. Further testing of the 2-D inversion code for gamma scans was carried out at LANL using synthesized data and a kernel function which is thought to approximate the actual kernel. That code will next be applied with the true kernel function, which has been determined experimentally by AECL at Whiteshell by gamma scanning an ion exchange bead containing ^{137}Cs .

7. Acquire Tuff Block Samples

Completion of this task has been postponed intentionally to take advantage of the excavation for the Lawrence Livermore National Laboratory heater test block at Fran Ridge. Earlier exploration had shown that zones of relatively low fracture density exist in this area compared to that observed at Busted Butte in two previous field campaigns. The location of Fran Ridge is in the centre of the Topopah Spring member, the host horizon for the proposed repository. The heater block test will consist of a 3 x 3 m block of tuff that will remain attached to the formation. To prepare this 3 x 3 m block of tuff, extraneous material surrounding the block must be excavated. It was felt at that time that the excavation would yield large intact blocks suitable for the proposed radionuclide tracer tests.

8. Complete Geochemical Characterization of Tuff

This milestone has been delayed due to delays in procuring the tuff block from the Nevada Test Site. These delays are described in Section 7, above.

9. Experimental Migration Program

Migration experiments to provide data to validate inverse code TRACRI

The natural fracture in quarried block LB-3, used by AECL at Whiteshell to study radionuclide migration, has been characterized hydraulically at imposed pressures of 0, 1.7, and 3.4 bar. Characterization was performed between pairs of boreholes for all 11 boreholes. The data obtained in the hydraulic characterization of the natural fracture in quarried block LB-3 have been transmitted to LANL and will be used to test the inverse code TRACRI to determine the fracture aperture distribution.

To follow the plume of injected radionuclides in LB-3 in real time, eight end-window Geiger-Müller counters were successfully installed into eight unused boreholes. These counters have been used to map the plume of an injected radionuclide during the migration experiment. The counting equipment and the data acquisition software have been tested during a preliminary injection with ^{131}I and used in successive migration experiments of ^{131}I and ^{22}Na . These data obtained with these detectors will be used to validate the inverse code TRACRI, developed at LANL.

Refurbishing has been completed of the gamma scanner at the Whiteshell Laboratories. This gamma scanner is used to obtain sorbed radionuclide concentration profiles on the flow path along fracture surfaces used in migration experiments after the experiments have been completed and the block separated along its fracture. The motion control for the detector, multichannel analyzer, gamma spectra analysis, and data storage has all been centralized in an MS-DOS 80486 computer. To calibrate the scanner, a single ion exchange bead, loaded with ^{137}Cs and mounted on a slab of rock, was scanned and the results transmitted to LANL for use in their image enhancement techniques.

Migration experiments in artificial fractures

A 60 x 60 cm slab of polished rock and a similar 10 cm thick slab of acrylic have been received. These two items have been assembled to form a fracture with a regular rectangular cross section, to be used to observe the flow of a non-sorbing dye through the fracture visually. The use of time-lapse photography is being considered to record the flow of the dye through the fracture. A sample of polished rock has been coated with a white epoxy paint and submitted for surface profilometry. If the paint does not adversely affect the surface, the surface of the 60 x 60 cm slab will be spray painted to observe the movement of the non-sorbing dye through the fracture visually.

A visit was made to the Lawrence Berkeley Laboratory during November to observe and discuss the techniques used to study unsaturated flow through acrylic replicas of natural fractures. The recording of images with a video camera and subsequent image analysis with commercially available software, as used at LBL, have potential application to study the flow of conservative dyes through the acrylic fracture by AECL at Whiteshell. This approach will be pursued when resources to acquire the necessary equipment become available.

Design and construction of a plenum for the outlet of the machined fractures have been completed. The design consists of a plenum extending along the width of the fracture. The bottom of this plenum consists of eight wedge-shaped chambers, with narrow tubes leading from the apices of the wedges to fraction collectors. A small-scale prototype plenum has been constructed out of plexiglas and fitted to a fracture constructed from a 60 x 60 cm slab of rock and a plexiglas cover, separated from each other by a 1 mm thick spacer.

The difficulties encountered in establishing a uniform flow across a fracture with a rectangular cross section have been solved successfully. By replacing the porous membrane between the inlet reservoir and a fracture created from a slab of rock and a slab of acrylic plastic, a much more uniform injection of a dye tracer across the width of the fracture can be obtained. The flow at the outlet of the fracture is regulated by "tuning" long sections of extremely fine bore tubing that are attached to the eight chambers in the outlet reservoir.

The first experiments in the acrylic fractures have been completed using a conservative dye tracer, uranine. The experiments were performed in the fracture with a regular rectangular cross section and with a wedge-shaped cross section. The results showed good agreement with those predicted using TRACR3D, when allowances were made for the deviation from a truly uniform cross section, caused by a slight concavity of the rock slab. An abstract of the experimental procedure and the results has been accepted for presentation at "Migration '93" in Charleston, SC, USA in 1993 December.

Design and construction have been completed by AECL at Whiteshell for a jig to cut grooves in a slab of rock. The design requirement for this jig is

to cut 5-mm wide grooves, 5 mm apart and 1-mm deep. The diamond saw is driven along the face of the slab by an electric motor. Positioning of the saw blade across the face of the slab will be done manually. Commissioning of equipment designed to cut grooves in rock slabs has also been completed and cutting of the grooves in one of the rock slabs is in progress.

The first set of two rock slabs has been inserted in the flexible plastic bag, evacuated and backfilled with synthetic groundwater.

REFERENCE

A.N. Tikhonov and V. Arsenin. Solution of ill-posed problems. V.H. Winston & Sons, Washington, D.C., 1977.

LABORATORY AND FIELD TESTS OF IN SITU HYDROCHEMICAL TOOL

Task Managers

M. Gascoyne (AECL)
W. Steinkampf (USGS)

Objectives

1. To describe the performance of the SKB in situ hydrochemical tool under conditions of varying temperature, pressure, and ionic strength.
2. To test preliminary procedures for use of the USGS data-collection and sampling equipment system, and attendant hardware and software, in (an) existing borehole(s).

Technical Progress Report for 1992 October to 1993 September Inclusive

The contract for procurement for the SKB hydrochemical tool was awarded on 1993 June 23. Tool delivery was anticipated for early in fiscal year 1994.

The USGS task manager visited Whiteshell Laboratories on 1993 September 28-30 to examine the physical aspects of the Borehole Instrumentation Test Facility with AECL staff. It appeared that minimal preparatory work, beyond cleanup after the pump failure and subsequent flooding, and verification of the integrity of the electrical and hydraulic systems, will be needed to prepare the BITF for use. An estimate was also made of equipment and supplies that will be needed. A preliminary testing plan for the laboratory work was jointly prepared following the physical inspections, and received concurrence from the AECL task manager. The USGS task manager also met with several AECL investigators to discuss technical matters of common interest and of direct relevance to the Canadian and US waste-investigations programs.

Following the visit to Whiteshell Laboratories, the USGS task manager travelled to Oskarshamn, Sweden to receive from the manufacturer 5 days of training in the maintenance and use of the hydrochemical tool.

CIGAR LAKE - ANALOG STUDY - ACTINIDE AND FISSION PRODUCT GEOCHEMISTRY

Task Managers

J.J. Cramer (AECL)
D.B. Curtis (LANL)

Objective

To provide observational information about natural plutonium, technetium and radioactive iodine, to be used to evaluate the uncertainties associated with the assessments of performance of the Yucca Mountain Repository.

Technical Progress Report for 1992 October to 1993 September Inclusive

1. General

The second year of this Task included many laboratory and modeling activities, as well as a Technical Information Meeting to review the progress and status of the Task. The Meeting was held on 1993 July 13 and 14, in Santa Fe, New Mexico.

The laboratory work by LANL and AECL included the preparation and analysis of water and rock samples from Cigar Lake. New data have been obtained for these samples on the contents of major and trace elements, and of isotopes pertinent to this Task, i.e., ^{99}Tc , ^{129}I and ^{239}Pu . In addition, selected water samples were analysed for the abundance of noble-gas isotopes of He, Ne, Ar and Xe, and a suite of water and rock samples was also analyzed for the abundance of ^{36}Cl .

The modeling work for this Task included modeling of the geochemical controls on U concentrations, of the redox geochemistry and evolution of groundwater compositions, of the hydrologic regime of the deposit through use of isotopic constraints, and modeling of radionuclide production and retention in the high-grade U mineralization.

Fieldwork was carried out by AECL staff at Cigar Lake as part of the analog study on fission product geochemistry, and included the collection and preparation of large water samples from various locations in the deposit. A total of 12 large water samples was collected by the end of 1993 September, and these samples were shipped to LANL for analysis.

2. Hydrologic Regime and Mass Transport

Through collaboration with Jack Cornett of AECL in Chalk River, Ontario, measurements were made of the $^{36}\text{Cl}/\text{Cl}$ abundance ratios in waters and rocks from Cigar Lake. A good-to-acceptable correlation was obtained for the measured $^{36}\text{Cl}/\text{Cl}$ values and those modelled from production-rate calculations carried out at LANL. Because some limited leaching of ^{36}Cl from the ore by groundwater may occur, the calculated residence time of Cl in the mineralized zone may not be the same as the residence time of the groundwater in this zone. However, it is estimated that groundwater residence times in the mineralized zone are on the order of 10^5 a.

A comparison of the modeling results for production rates of noble gas isotopes with the values obtained from noble gas analyses of Cigar Lake groundwaters showed quite variable results for the different nuclides. The main conclusion at this time is that the mineralized zone may not be a closed system for gaseous elements and nuclides.

3. Radionuclide Retention In Spent Fuel Analogs - Uranium Minerals

The determination of ^{99}Tc , ^{129}I and ^{239}Pu abundances in samples from Cigar Lake core 220 is being undertaken to understand processes of radionuclide release from their uranium host minerals.

Preliminary results for ^{129}I analyses of groundwaters show, as expected, low values for $^{129}\text{I}/\text{I}$ in the host sandstone (10^{-12} to 10^{-11}) compared with those within the ore zone (10^{-10} to 10^{-9}). Although the elevated ^{129}I content of groundwater in the mineralized zone suggests that ^{129}I is preferentially released relative to uranium, the amount of ^{129}I released still only represents $<1\%$ of the ^{129}I produced in the solid uranium phase.

The concentration of ^{99}Tc has been measured in five samples of Cigar Lake ore and two samples from the altered region of the Koongarra, Australia ore body. We see no identifiable deficiency of ^{99}Tc in any of these samples. At this time, the only evidence of ^{99}Tc release or retention at any site is the preliminary identification of excess ^{99}Tc at Cigar Lake as measured in sample CS-609. One interpretation of this result suggests that processes active in the mineralization in the last million years have resulted in preferential accumulation of technetium relative to uranium. Further careful evaluation of these data is ongoing.

Ongoing considerations of ^{239}Pu production in uranium-rich rock suggest that, within our ability to distinguish deviations from secular equilibrium concentrations - about a factor of two -, there is no evidence of ^{239}Pu release or mobilization in any of the Cigar Lake or Koongarra samples.

4. Geochemical Modeling

Modeling was carried out at the Lawrence Livermore National Laboratory (LLNL) on the speciation of U and Tc in the set of representative Cigar Lake groundwaters. This work involves evaluation of solubility trends in pH- $f\text{O}_2$ space for various compositional parameters ($f\text{O}_2$, $\text{SiO}_2(\text{aq})$, etc.). The results of the modeling for U-speciation suggest that U-silicates may provide important controls on aqueous concentrations of U in a Si-rich environment such as at Cigar Lake. The results for Tc predict that the number of aqueous Tc-species is limited in the near-neutral pH waters under the reducing conditions of the mineralization at Cigar Lake. Modeling has also been initiated on the rate and progress of reactions for U, Tc and Pu species upon ore dissolution under mildly oxidizing conditions.

Modeling of the water-rock interaction and evolution of groundwater compositions indicates that the clay and iron mineral phases in the mineralization play an important role in maintaining reducing conditions in the deposit. These reducing conditions in the ore zone correspond with the observed compositions of the uranium minerals. The composition of the uraninites is characterized by: a)

a surface-oxidation layer composition corresponding to U^{VI}/U^{IV} values in the range of 0.20 to 0.57, b) $^{234}U/^{238}U$ and $^{230}Th/^{234}U$ activity ratios ranging between 0.98 and 1.00, and between 1.05 and 1.11 respectively, c) high contents of radiogenic Pb, and d) relatively high contents of ^{129}I and ^{239}Pu from naturally occurring nuclear reactions. These four characteristics suggest both good retention of the isotopes in the natural- UO_2 matrix, and congruent dissolution of the matrix, at least over a period of 10^6 a.

5. Quality Assurance

As part of our quality assurance program for the ^{99}Tc measurements we have measured eleven blanks. (Blanks are samples that contain no indigenous ^{99}Tc .) Two of these samples contained what appear to be anomalous quantities of ^{99}Tc . Omitting these two, the average measured blank was 0.086×10^{-12} g of the nuclide. One standard deviation of this value is 0.035×10^{-12} g, and one standard deviation of the means is 0.012×10^{-12} g. Defining as three standard deviations of the average blank, our current detection limit is 0.1×10^{-12} g ^{99}Tc . All measured abundances of ^{99}Tc are blank-corrected and evaluations of the uncertainty of a measurement include the uncertainty associated with the correction for blank.

An additional component of our quality assurance program is evaluation of the precision of the ^{99}Tc analysis determined by replicate determinations of aliquots of a homogenous sample. The material used for this purpose is a Canadian Reference Material BL-5, which is a standard homogenized sample of rock containing 7% uranium. Three analysis of BL-5 for ^{99}Tc determined an average concentration of $0.050 \pm 0.010 \times 10^{-12}$ g/g of ^{99}Tc . The 1σ uncertainty of the three measurements is an order of magnitude larger than the uncertainty that we evaluated for individual results. The relative standard deviation associated with multiple measurements of BL-5 will be assigned as the uncertainty associated with all single measurements of ^{99}Tc abundances in uraniferous rock.

6. Reports and Presentations

- June Fabryka-Martin and David Curtis made presentations at the Natural Analogue Working Group Meeting in Toledo, Spain, on 1992 October 4-9. Talks were titled: Uranium orebodies as source terms for radionuclides: measurements and models, presented by June Fabryka-Martin; Natural constraints on radionuclide release rates, presented by David Curtis. The full text of these presentations will be published in the proceedings of this meeting in the CEC Publications Series under # EUR 15176 EN.
- A report, titled "Geochemistry of ^{239}Pu , ^{129}I , ^{99}Tc and ^{36}Cl " by June Fabryka-Martin and David Curtis, was submitted to the Australian Nuclear Science and Technology Organization for publication in the final report of the Alligator Rivers Analogue Project.
- David Curtis provided an overview of Natural Analogue Project work to individuals attending the Yucca Mountain Project performance assessment information exchange at LANL on 1993 March 17.

- An internal project report on geochemical controls of U-speciation in Cigar Lake groundwaters was prepared by LLNL staff.
- A total of 12 presentations were made at the Technical Information Meeting in Santa Fe, NM, on 1993 July 13 and 14, and summaries of these presentations and the discussions have been reported in the Proceedings of this Meeting issued by LANL in 1993 August.
- A manuscript, entitled "Natural nuclear products in the Cigar Lake deposit" by June Fabryka-Martin, David Curtis, Paul Dixon et al., was completed and included as a contributed section in the Final report of the AECL/SKB Cigar Lake Analog Study to be published by AECL under report AECL-10851.
- David Curtis made a presentation on 1993 September 22, entitled "Natural Nuclear Product Geochemistry", to the Symposium on Actinides and the Environment at the Actinides-93 Conference in Santa Fe, New Mexico.
- The Actinides-93 presentation was reconfigured and presented by David Curtis on 1993 September 28, to the Spent Nuclear Fuel Workshop in Santa Fe, New Mexico. This presentation was entitled "Natural Leaching Experiments of Spent Nuclear Fuel Analogues".
- A manuscript, entitled "Hydrogeochemistry of the Cigar Lake uranium deposit: Hydrologic and isotopic constraints" by Jan Cramer and Wayne Nesbitt, has been completed for journal publication.
- A manuscript, entitled "³⁶Cl measurements by AMS: A hydrogeological assessment tool" by Jack Cornett, Jan Cramer et al., has been completed for journal publication.

PERFORMANCE ASSESSMENT TECHNOLOGY EXCHANGE

Task Managers:

Steve E. Oliver (AECL)
Keith M. Kersch (SAIC)

Objectives

1. To verify the submodel code in accordance with sound software engineering principles.
2. To identify, document and classify defects within the SYVAC submodels.
3. For the US/DOE to learn from the AECL experience in total system performance assessment with a totally integrated software package from waste package release through radiation dose, with associated uncertainties.
4. To make the SYVAC3 software package available to the US/DOE, including the Yucca Mountain Site Characterization Project(YMP).
5. For the US/DOE to learn from the AECL experience in developing, testing, documenting, applying, and quality-assuring total system and related performance assessment methodology.
6. For the US/DOE to learn from the application of underlying AECL research and development to SYVAC3.
7. To increase confidence in future total system performance assessments through international cooperation and peer review.
8. To recommend further developments and improvements to the AECL and YMP performance assessment models based on experience gained with the SYVAC3 software package acquisition and verification.

Technical Progress Report for 1992 October to 1993 September Inclusive

First Quarter

AECL updated and reviewed biosphere model design specifications, and transferred the Biosphere model code specifications to the DOE subcontractor (SAIC).

Verification was completed on fourteen of 61 Biosphere modules.

An expanded version of BARIER was developed for probabilistic barrier analysis. In addition to a table of means of barrier effectiveness parameters for each nuclide (similar to the median value table), it was necessary to generate a data file of individual values from each simulation, for every nuclide-barrier combination, for statistical analysis.

Second Quarter

Verification of the pilot phase has been completed. In this phase AECL placed errors in 10 vault model modules to evaluate the efficiency of error detection. The DOE contractor completed this work and shipped the final report on 1992 October 15.

Verification has been started on the Biosphere Model. This model consists of 61 modules.

Functional specifications and data dictionary were updated for the soil, atmosphere, mass balance, food-chain/dose, and consequence submodels of the biosphere model. These functional specifications are being used in creating the biosphere design specifications.

Work continued on the reverse-engineering of Design Specifications for the Vault and Biosphere sub-models.

File format specifications have been prepared for three SYVAC3-CC3 optional output files: SVCDS.FFD (now used for vault model output), SVNDS.FFD (now used for geosphere model output), and SVSUB.FFD (now used for biosphere model output).

The CC305 design data dictionary was reviewed and merged with SV309 and ML303 dictionaries. Inadequate and inappropriate definitions were revised, to avoid failure of the tools used in creating module specifications.

Function testing of the vault submodel function for the normalized instant source release of nuclides from the titanium containers was completed.

Creation of the SYVAC3-CC3 system test plan was completed, identifying general functions and options to be tested. A total of about 50 test cases were set up, and over half of these were run.

An outline for the user's manual for the CC3 code was prepared, and a significant portion of the manual was drafted. Peer review of this material is also proceeding.

The CC3 database was expanded to include two indices to aid in locating data. One index uses the parameter "short name" (the FORTRAN variable name) as the primary key. The second index uses common English terms derived from the "Definition" field in the CC3 database. Program DBINDEX (DataBase INDEX) has been expanded to generate these indices.

DSTRUC, a tool to produce SYVAC3-CC3 software calling tree structure and I/O status of passed variables, has been modified to correct deficiencies and improve performance.

DDCONV, the program used to convert an ASCII format data dictionary into Mass-11 format, was revised to make it easier to use and less prone to failure. ASCII format is used for code dictionaries, whereas the Mass-11 form is superior for module design specifications.

DDMERG, the program used to merge two or more data dictionaries, was improved so blank lines on input do not cause problems, and blank lines are not generated by the program at the top of the output dictionary.

Third Quarter

Verification of 45, out of 61, Biosphere Modules was about 85% complete. All that remained was the final quality check on the testing and inspection results, which was in progress. AECL began examination of completed module reports and supplied some comments to the DOE subcontractor.

AECL continued to work on design specifications, concentrating on the vault sub-model. The analytical specifications for the vault and biosphere are being revised, while the geosphere specifications entered an initial stage of development. Development of the BARRIER program continued. This program was developed to permit probabilistic analysis of barrier effectiveness.

Fourth Quarter

Verification of the Biosphere Model was nearly completed.

The majority of the Vault Model module design specifications were completed and transferred to US/DOE.

SCHEDULES AND DELIVERABLES

The following gives the schedule, milestones, and organizational responsibilities for this activity.

TABLE 1
SYVAC VERIFICATION SCHEDULE

Milestones	Schedule
1 AECL: Complete training workshop	03/01/92
2 AECL: Define test products for pilot project	11/01/91
2a AECL: Transfer entire source code except vault model	04/01/92
3 DOE: Complete pilot project-testing 10 modules	10/15/92
4 AECL: Complete review of pilot project	11/23/92
5 AECL: Transfer source code of vault model	01/10/93
6 DOE: Complete generation of test harnesses	continuing
7 AECL: Transfer Completed Biosphere model specifications	11/01/92
8 AECL: Transfer completed Vault model specifications	90% 9/28/93 10% 2/14/94
9 DOE: Complete Biosphere model testing	11/01/93
10 AECL: Transfer completed Geosphere model specifications	07/01/94
11 DOE: Complete Vault model testing	06/01/94
12a AECL: Transfer SYVAC3 PSCODE. specifications	11/01/95
12b AECL: Transfer SYVAC3 TSCODE. specifications	11/01/95
12c AECL: Transfer remaining SYVAC3 specifications	01/01/96
13 DOE: Complete Geosphere model testing	10/01/94
14 AECL: Complete system testing	01/01/94
15 AECL: Complete functional testing	03/01/95
16 AECL: Complete draft documentation of system testing results	10/01/94
17 AECL: Complete draft documentation of functional testing results	05/01/95
19 AECL: Complete SYVAC3 documentation including user manuals	01/01/95
20 AECL: Transfer remaining SYVAC3 documentation and corrected source code	03/01/96
21 DOE: Complete draft documentation of unit testing	12/01/94
22 DOE: Complete final documentation of unit testing	03/01/95
23 AECL: Complete final documentation of all software verification	03/29/96

DEVELOPMENT OF MULTIPLE-WELL HYDRAULIC TEST AND FIELD TRACER TEST METHODS

Task Managers

C.C. Davison (AECL)
M.J. Umari (USGS)

Objective

To develop testing and analytical capabilities for multiple-well hydraulic and tracer tests in complexly fractured and faulted groundwater reservoirs, ensuring relevance to both YMP and AECL.

Technical Progress Report for 1992 to 1993 September Inclusive

This report describes all work performed in FY93 at the U.S. site (Raymond Quarry, near Oakhurst, CA) and at Canada's URL site of the U.S. Department of Energy (US/DOE)/Atomic Energy of Canada Limited (AECL) international project. It is intended that the hydraulic and tracer tests planned for the c-well, at the Nevada Test Site (NTS), be prototyped at the Raymond site.

1. Report of US/DOE Activities at the Raymond Site

Borehole array at the Raymond Site

The staff of the Saturated Zone Fractured Rock Hydrology Project (SZFRHP), Hydrologic Investigations Program, USGS-Yucca Mountain Project (YMP), which, along with LBL, is in charge of the present task (Development of Multiple-Well Hydraulic Test and Field Tracer Test Methods) under the US/DOE-AECL International Project, was increased by one hydrologic technician. This brings the total to four hydrologists and two hydrologic technicians.

In two of the 6-inch holes at Raymond, SW2 and SE2, which had been enlarged to 10 inches to accommodate the multi-zone packer string being built for the c-holes complex (so that the string can be tested prior to being used at the c-holes), non-oriented T.V. logs were conducted.

Project hydrologist Art Geldon synthesized all the information from caliper, temperature, resistivity, acoustic televiewer, and intraborehole flow logs, obtained at the 9 Raymond holes by the Borehole Geophysics Unit (BGU) of the U.S. Geological Survey's Water Resources Division, and the above mentioned non-oriented T.V. logs. The synthesis led to a preliminary conceptualization

of a three zone system: an upper unconfined aquifer, a middle semiconfined or confined aquifer, and a lower confined aquifer.

All the components of the two 3-zone packer string systems to be prototyped at the Raymond site prior to use at the c-holes (on the Nevada Test site) were shipped to Raymond in November 1992. In preparation for placing the c-holes-bound packer strings of the USGS in the two 10-inch holes, SW2 and SE2, a simulation packer (a rigid cylinder in the shape of, but a 1/2" larger in diameter than, a packer) was lowered to determine if there are any hole obstructions that could interfere with lowering the actual packer string. (The extra diameter size of the simulation packer over that of the packer is to simulate the residual rubber stretching that occurs after the packer is inflated for use in the hole, and then deflated for removal from the hole.) The simulation packer encountered obstructions in both holes and was not able to travel to the bottom of the holes.

In 1993 January, Arrangements were made with Bannon Drilling, of Oakhurst, Ca., to ream the two holes. USGS personnel were able to lower a single packer down each of the two holes, and then bring it back to the surface successfully.

Data acquisition systems were purchased by the USGS and LBL. The software package is LabView from National Instruments Inc.). This package allows for the construction of tailored data acquisition programs written in graphical-programming language. LBL developed such a program for the tracer test conducted at Raymond in 1993 August and September (described below), and the USGS has also developed one for use at the upcoming tests at the c-hole complex.

The USGS placed the two 10-inch-hole packer strings in wells SE2 and SW2: During 1993 February, USGS personnel assembled the 2 packer strings on the ground, and then used a drill rig (on loan from the USBR) to install the strings in 2 of the 9 Raymond Quarry prototyping holes.

During 1993 April, the multi-zone packer string in SW2 was pulled out, and it was discovered that the water-tight protective casing, or "canister", that houses the motor for the downhole ball valve, that opens and closes the bottom of the transducer reference line, had developed a leak. The canister was replaced with a spare one, and the string lowered back into the hole. As a result of this leak, however, the design of this protective canister has been modified to include additional O-rings, and it is currently being laboratory-tested. This problem identification and resolution satisfies the objective of prototyping the c-holes-bound strings in Raymond.

During 1993 March, M.J Umari, Arthur Geldon, and Gary Patterson gave a presentation to Robert Levich, YMP International Program Director, on AECL project progress and planned activities.

During 1993 March, LBL performed "site development" activities at Raymond. This included excavating trenches for laying of multi-conductor cables between well head and "office" trailer, placing a culvert for easy passage over surface drainage features, and leveling ground for placement of "office", and "storage" trailers.

During 1993 April, Gary Patterson and John Earle, U.S. Geological Survey (USGS) accompanied Cliff Davison, AECL task manager for SA2, Task 8, to the Nevada Test Site (NTS) on a field trip during which they visited the c-well complex, site of the planned cross-hole hydraulic and tracer tests that are being prototyped at the U.S. site in Raymond, CA. Mr. Davison was in the U.S. to attend, and chair a session at, the Fourth Annual International High Level Radioactive Waste Management Conference and Exposition held in Las Vegas, NV.

During 1993 May, the two 10-inch-hole packer strings in SW2 and SE2 were removed to allow for cross-hole radar surveys to be conducted between the nine Raymond holes by a team from Finland. The surveys were conducted and the results are being analyzed. Also, Ernie Majer, Lawrence Berkeley Laboratory (LBL), attempted to carry a cross-hole seismic survey between the same holes but encountered technical difficulties and was unable actually to conduct the survey.

At the same time that the above field activities were proceeding in, the annual meeting for Fiscal Year 1993 between the U.S. team on SA2, task 8 (USGS and LBL) and the US/DOE project director Robert Levich took place in Oakhurst, CA near the U.S. site at Raymond CA. Lorrie Frost from the AECL team working on SA2, Task 8, who was visiting the U.S. during that time, participated in a field trip to the Raymond site that was arranged as part of this annual meeting.

The above meetings between the U.S. and AECL teams working on SA2, Task 8 were a welcome chance to have face-to-face contact and to compare respective activities, sites, and approaches.

During 1993 June, the two 10-inch-hole packer strings previously removed from wells SE2 and SW2, were placed back in the holes in preparation for conducting hydraulic and tracer tests. The two packers in each string were located in the holes so as to isolate three "aquifers" that were tentatively identified from geologic and geophysical logs. These "aquifers" were associated with zones of moderately, to very fractured, weathered granite. The other seven 6-inch-diameter holes were also instrumented with packer strings and all transducers were connected to the LBL LabView-software-driven data acquisition system.

Also during 1993 June, the packer string in SW2 was pulled up to the point where a leak, appearing to originate from the top Argon-gas-inflated packer, could be repaired. It turned out that the leak was from a pin-size hole in the steel-reinforced, rubber, packer inflation hose. A section of the hose was replaced to fix that problem. The problem indicated that the inflation hose should be pressure-checked prior to installation of packer string at the c-holes, where raising a string to repair a leak would be very costly due to the deep water table (around 1,320 Feet).

During the last three weeks of 1993 June, LBL conducted a series of single-hole, packed-off, short duration, pressure injection tests in the seven 6-inch-diameter holes. The injected zone was moved along the wellbore so as to obtain (after analysis of the test results) a "permeability profile" indicating changes in the horizontal permeability with depth for each of the

tested wells. Although these are near-well tests with the results only applicable to a relatively small radius around the well, permeabilities obtained from them can be very useful initial results that can guide in the design of the tracer test planned for 1993 August.

During late 1993 August, and early September, LBL spearheaded the effort to perform a tracer test at Raymond. The test was manned by personnel from both LBL and the USGS. Chloride and bromide ions, deuterium, and fluorescent microspheres were introduced into well SW3, after well 0-0 had been pumped for several days to establish a quasi steady-state flow pattern. Pressures were monitored by pressure transducers in wells 0-0, SW1, SW2, and SW3 during this convergent tracer test. Real-time monitoring of the arrival of the tracer at the pumped well was accomplished by running the pumped water past chloride- and bromide-ion-specific probes and relaying the resulting signal to the computerized data acquisition system. Results of the test will be analyzed and presented at the 1994 May High-Level Radioactive Waste Management Conference to be held in Las Vegas, NV. Background on the AECL project, details on the data acquisition system developed by LBL, and description of the setup for the tracer test will be presented in 1993 October at the Geological Society of America Meeting in Boston by LBL.

2. Report of AECL Activities at Canada's URL

2.1 Introduction

The primary objective of AECL's Transport Properties in Highly Fractured Rock Experiment (HFR Experiment) is to develop and demonstrate methods for determining the solute transport properties of zones of highly fractured rock. The specific objectives are to:

- determine the permeability, porosity and compressibility of highly fractured zones of plutonic rock; and
- determine the transport porosity and dispersivity of major fracture zones and establish whether these parameters are scale- or direction-dependent.

The groundwater tracer tests are being performed in a relatively uniform region of high-permeability within Fracture Zone 2 (FZ2) at the URL, where there are numerous boreholes available for testing. These boreholes provide a network to examine the scale- and direction-dependent properties of the fracture zone.

During 1990 November to 1992 October, six tracer tests (TT1, TT2, TT3, TT4, TT5 and TT6) ranging in scale from about 17 to 100 m were performed: TT1, TT2 and TT4 at scales ranging from 17 m to 29 m; TT3 at a scale of 77 m; and TT5 and TT6 at scales of about 100 m. During this reporting period, TT7 was conducted over a distance of about 200 m within FZ2. This test is the final tracer test planned in this region of FZ2 and it overlaps the areas tested within the fracture zone during TT5 and TT6 (Figure 1).

FIGURE 1: LOCATION OF TT7

2.2 Groundwater Tracer Tests

A summary of the test results for Tracer Test No. 7, including testing-well information, tracer injection data and tracer breakthrough data, is presented in Table 1.

Tracer Test No. 7

Tracer Test No. 7 (TT7) was conducted over a distance of about 200 m between boreholes HC29 (injection well - collared on the 240 Level of the URL facility) and M1A (withdrawal well - collared at surface) as shown in Figure 1. TT7 was performed to investigate the solute transport properties of the fracture zone at a larger scale of testing than previous tracer tests. TT7 overlaps the areas tested during TT5 and TT6.

TT7 was initiated on 1992 November 2 and was completed on 1993 June 14. TT7 was performed as a continuous recirculating withdrawal/injection test at a constant flow rate of 36 L/min. The test was started with a pulse injection of iodide (I^-) tracer solution (11772 L at a concentration of approximately 954 mg/L) in borehole HC29.

Tracer breakthrough was monitored at the withdrawal well borehole M1A and at HG4, a borehole located approximately midway between the withdrawal and injection wells (Figure 1). The results obtained from TT7 show good tracer breakthrough at both of these locations.

Transport within the fracture zone between boreholes HC29 and HG4 is characterized by a single, well-dispersed tracer breakthrough curve (Figure 2). An initial I^- breakthrough was observed approximately 3 days after the start of the tracer injection. After the initial breakthrough the tracer concentration rose steadily, reaching a peak concentration of 3.33 mg/L. The I^- concentration slowly decreased to a value of about 0.54 mg/L after 224 days of tracer recirculation. The arrival and peak concentration times of the tracer breakthrough observed at HG4 during TT7 are quite similar to those observed previously during TT5 (HC29 to HG4 tracer test) as shown in Figure 3.

Transport within the region of the fracture zone between boreholes HC29 and M1A is also characterized by a well-dispersed tracer breakthrough curve. However, the tracer breakthrough at borehole M1A is much more dispersed than that observed at HG4 and several well-defined secondary concentration peaks occurred at M1A (Figure 4). These secondary peaks were not observed in the tracer breakthrough data from the previous test performed between boreholes HG4 and M1A (TT6). An initial I^- breakthrough was observed at borehole M1A approximately 16 days after the start of the tracer injection at HC29. After the initial breakthrough the tracer concentration rose steadily, reaching a peak concentration of 0.44 mg/L. The I^- concentration slowly decreased to a value of about 0.33 mg/L after 224 days of tracer recirculation. Secondary tracer breakthrough peaks were observed at times of approximately 18, 71, 100, 121, 148, 170 and 192 days after the start of the tracer injection.

During TT7 periodic measurements of electrical conductance were made on intermittent groundwater samples withdrawn from borehole HG4. Periodic

TABLE 1
SUMMARY OF TRACER TEST TT7

TRACER TEST WELL INFORMATION

Tracer Test No.	Withdrawal Well	Injection Well	Well Separation (m)	Test Date Start	Test Date Finish	Test Duration (d)	Recirculating Flow Rate (L/min)	Groundwater Tracer
TT7	M1A	HC29	209	1992 Nov. 2	1993 June 14	224	36	I-1

TRACER INJECTION AND BREAKTHROUGH DATA

Tracer Test No.	Groundwater Tracer	Tracer Volume (L)	Injection Concentration (mg/L)	Tracer Mass (Kg)	Tracer Sampling Well	Well Separation (m)	Tracer Breakthrough Time	Peak Tracer Concentration Time	Peak Tracer Concentration (mg/L)
TT7	I-	11772	954	11.230	HG4	102	3 days	14 days	3.33
					M1A	209	16 days	119 days	0.443

TT7 : HC29 TO M1A TRACER TEST HG4 Iodide Breakthrough

FIGURE 2: TT7 - TRACER BREAKTHROUGH AT BOREHOLE HG4

HFR EXPERIMENT - TT5 and TT7 HG4 Tracer Breakthrough Curves

FIGURE 3: COMPARISON OF TT5 AND TT7 TRACER BREAKTHROUGH AT BOREHOLE HG4

TT7 : HC29 TO M1A TRACER TEST M1A Iodide Breakthrough

FIGURE 4: TT7 - TRACER BREAKTHROUGH AT BOREHOLE M1A

measurements of pH and electrical conductance were also made on the groundwater withdrawn from borehole M1A before it was recirculated and injected back down into borehole HC29. The electrical conductance of the groundwater at HG4 slowly increased from about 490 uS/cm at the start of the tracer test to about 530 uS/cm at the termination of the test whereas at M1A it slowly increased from about 495 uS/cm at the start of the tracer test to about 560 uS/cm at the termination of the test. The field pH of the recirculated groundwater at M1A slowly increased from a value of about 8.5 pH units at the start of the tracer test to a value of about 8.6 pH units at the termination of the test.

Following completion of TT7, groundwater was purged from boreholes intersecting the high permeability region of FZ2 in the area surrounding Room 211 of the 240 Level and from boreholes HG4 and URL8. Samples were collected during these purging activities to determine the spatial distribution of the tracer in the fracture zone at the end of the tracer test.

Other Observations

The results of hydraulic pressure monitoring in FZ2 indicated that the hydraulic pressure conditions within the region of the fracture zone at borehole M1A changed gradually during the long time period of TT7. The changes show that the permeability of the fracture zone gradually decreased at the withdrawal well M1A. The decrease in permeability did not affect the rate of groundwater recirculation between boreholes HC29 and M1A during TT7 as the flow was periodically adjusted to maintain a constant rate of 36 L/min. Investigations have been completed since the termination of TT7 which indicate that the decrease in permeability at the withdrawal well was caused by fracture plugging due to iron bacteria growth and/or iron precipitation.

2.3 Modeling

Numerical modeling of the tracer tests using the MOTIF finite-element code is continuing.

The suitability of simple 1-D channel models to simulate the tracer tests has been investigated. Three types of models were considered: a single 1-D path; two distinct 1-D paths; and two interconnected 1-D paths. None of these models appear to be suitable. While the sharp tracer breakthrough peak of Tracer Test 1 is likely a result of a distinct channel, in general the transport appears to be multidimensional.

A study of the impact of transverse dispersion on tracer breakthrough simulations has shown that it can have more effect than previously believed and may have to be specifically considered in model calibration.

As a routine precautionary check, a comparison has been made between MOTIF predictions and those using analytical and approximate-analytical solutions for flow and transport. The differences are higher than initially expected but have been satisfactorily explained.

A new finite-element mesh for simulating all seven tracer tests has been completed. Checks of the numerical accuracy of the calculations are being made prior to detailed model calibration. A suitable discretization has been found for the groundwater flow simulations but additional refinements maybe required for the solute transport simulations.

4. Future Work

A final report on the complete series of seven tracer tests and their analysis is scheduled to be completed by 1993 December 31.