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BOREHOLE CEMENT AND ROCK PROPERTIES STUDIES
Progress Report

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The Materials Research Laboratory
The Pennsylvania State University

August 10, 1976

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CARBIDE

OFFICE OF WASTE ISOLATION
OAK RIDGE, TENNESSEE

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BOREHOLE CEMENT AND ROCK PROPERTIES STUDIES

Progress Report

to

**Office of Waste Isolation
Union Carbide Corporation
Nuclear Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830**

Subcontract No. 4091

**for the period
up to 1 August 1976**

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August 10, 1976

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I. CEMENT FOR RADIOACTIVE WASTE ISOLATION

1. 1 Introduction: The Role of Cement in Radioactive Waste Management

Several major problems must be considered in assessing the role of cements and their potential utilization in the whole Radioactive Waste Isolation program. At least four categories are of major concern, and are listed below, of which we have addressed certain aspects of A) concerning thermal properties measurement; and of C) concerning physical properties measurements such as permeability and the preparation of stable dense cements, during this period. Other aspects of A, B, and C will be addressed in proposed work for FY '77.

A. Thermal Stability of Cements. Conventional hydrated portland cements have been considered to be applicable almost solely for room temperature/normal ambient conditions. For prediction of behavior and assessment of suitability for use either in borehole plugging or in other radioactive waste management areas it is necessary to study their thermal stability under a wide variety of conditions, including atmospheric and elevated pressure, and the resultant mechanical, physical and chemical properties.

B. Adsorption of RW ions Under Realistic Conditions. It is necessary to determine the relative adsorption of RW ions on hydrated cements and cement components such as hydrated calcium silicates and calcium aluminate species formed both at room temperature and elevated temperatures. This kind of information is necessary for assessment of long-range feasibility for use of cements as either plug material or for otherwise isolating radioactive waste species.

C. Optimization of Properties of Cements for Specific Radioactive Waste Management Needs. Optimized cements for borehole plugging include those which will be stable not only thermally but also chemically and mechanically throughout the extended time framework required properties such as low per-

meability are of course of high importance. Methods and mechanisms for obtaining maximum densification and a means for assuring at least an approach to thermodynamic stability under the anticipated environmental conditions will be a part of future considerations.

D. Special Cements and Cementing Mechanisms for Compatibility with Radioactive Waste. Conventional portland cements are not necessarily those which may be optimal for long term stability when incorporating, or adjacent to high concentrations of certain radioactive waste species. The studies would involve investigating a broader range of chemistry to achieve greater stability and compatibility; and thorough chemical characterization of cements and composites. Thermal and mechanical stability of such materials as a function of specific history would be investigated. Important are the studies of mechanisms of solidification, as well as stability with respect to leaching and transport properties, as well as potential radiation damage.

1.2 Preparation and Characterization of Dense Low Permeability Cements

1.2.1 Physical Properties Measurements: Permeability

An important physical property of any material envisioned as a container or repository for radioactive wastes is its permeability to gases and liquids. As a consequence of this we have constructed two cells capable of measuring permeabilities of set cements, concretes and "typical" borehole rock types. One cell is reserved for permeability measurements using gases (N_2 , air, He) while the other is reserved for liquids (H_2O only has been used to date). The two apparatus and an enlargement of the pressure cell are pictured schematically in Fig. 1.

The two apparatus are basically of similar design. They both employ a commercial gas cylinder and regulator as a source of stable pressure which can be varied between 0-60 psi. Each set-up also has an auxiliary pressure gauge between the tank regulator and pressure cell. This gauge is of finer

Figure 1. Schematic diagrams of the gas and water permeability apparatus. Stippled areas represent water in system.

calibration and pressure can easily be read to within ± 0.1 psi. In the gas permeability apparatus the gas passes directly through the sample contained in the brass sample cell. The liquid permeability equipment has an aluminum vessel intermediate to the gas cylinder and cell in which water is pressurized and forced through the sample. The sample cell is made from 2" diameter brass, is internally threaded (1-1/4" x 12) to accept the pictured brass screws which are fitted with silastic o-rings. Once the gas or liquid has passed through the sample it is measured by displacing water or by rising in a calibrated buret, respectively.

Both cells are constructed to accept a 1" diameter test specimen consisting of a central 11/16" portion of rock or cement paste surrounded by a plastic ring. A sample cylinder (11/16" x 1/4" high) is cored from a suitable sample and mounted in an epoxy or polyester ring forming a cylindrical donut having a final 1" diameter. Once cored the plastic-sample combination is mounted in a lathe where it is faced with a carbide tool producing smooth

parallel surfaces on both ends of the sample cylinders. Once prepared the sample's permeability can be determined in either apparatus (gas or liquid) since the pressure cells are identical.

Darcy's law for horizontal laminar flow of liquids ($k^* = \frac{\mu q h}{A(\Delta P)}$) is also valid for gases if the flow rate, q , is measured at the mean pressure of the exit gas ($\frac{P_1 + P_2}{2}$). These considerations have been taken into account and have been applied to the determination of permeability.

We have determined the gas permeability of a number of samples using both nitrogen and helium. These data are presented diagrammatically in Fig. 2 and also in tabular form in Table 1. The comparison of permeability coefficients obtained using He and N₂ is quite good. Since experience has shown us that both gases are comparable, the use of nitrogen is preferred, due to its lower cost. The type I (high alkali cement) has a higher permeability (2.6×10^{-5} Darcys) than the low alkali (type V) cement (7.4×10^{-6} Darcys). A natural sandy shale sample had the lowest permeability, 2.5×10^{-6} Darcys.

Based upon preliminary experiments using a type V cement, we found a definite change in permeability as a function of drying conditions. This change was approximately 2 orders of magnitude (7.4×10^{-6} , by standing in air at room temperature; 2.5×10^{-4} , dried at 105°C). The increase in permeability might be due to the expulsion of water or to the propagation of microfractures. More work of this type is proposed, since changes of this type, whatever the cause may be, must be understood and counteracted if necessary.

* k = permeability coefficient, Darcys.

μ = viscosity of fluid, centipoise.

q = flow rate, cc/sec.

h = height, cm.

A = cross sectional area of sample cylinders, cm².

ΔP = pressure differential, atmosphere.

Figure 2. k versus $1/\Delta P$ for various cement and rock samples. Broken lines are He determinations. Solid lines represent N₂ determinations. The lower-half of the figure represents the changes in permeability observed as the water content of a type V cement was varied.

Table 1
Permeability Data for Rock and Cement Samples.

Sample	Gas Used	k, Darcys
Oak Ridge Cement #04.43	He	4.3×10^{-5}
Oak Ridge Cement #04.43	N ₂	2.6×10^{-5}
Type I Cement	N ₂	2.6×10^{-5}
Local Sandy Shale	N ₂	2.5×10^{-6}
Type V Cement - water saturated	N ₂	2.2×10^{-6}
Type V Cement - dried at 25°C	N ₂	7.4×10^{-6}
Type V Cement - dried at 105°C	N ₂	2.5×10^{-4}

1.2.2 Thermal Properties

1.2.2.1 Thermal Conductivity. Experience has been gained with thermal conductivity measurements of hardened cement pastes at room temperature. Comparisons have been made with those made by Oak Ridge personnel. These are reported in Section 3.2 along with the description of instrumentation.

1.2.2.2 Thermal Expansion. Apparatus for thermal expansion measurements has been put into operation, as described in Section 3.1; cement paste samples will be studied after the current series of standard samples and rock samples measurements is completed. The method is described in Section 3.2.

1.3 Reactivity of Rock with Cement

Preliminary work on rock aggregates has proceeded to the point of making and curing suitable cement-aggregate (graded fine aggregate) samples containing cement and reactive opal as well as cement plus shale. These samples will be measured for length changes, compressive strengths determined,

samples mounted on slides to make thin section investigations and finally, fracture surfaces will be investigated with the SEM.

Experiments will be repeated using elevated temperature curing, which has as its goal both studying accelerated reaction as a means of investigating samples in a higher state of maturity, as well as detecting possible problems due to deleterious creation. Such samples will be similarly characterized as above.

1.4 Other Effort

During the early part of the present period concluding experimental work was carried out on hydrothermal cements for borehole plugging, following the earlier Feasibility Study. Most of this research was described in Report ORNL-Sub-4091-3 dated February 28, 1976. In addition, Mr. S. O. Oyefesobi completed his Ph. D. thesis, in which some of this work was elaborated (Oyefesobi, 1976). In addition, a paper was presented at the annual American Ceramic Society Meeting, May 1976, describing some of the results (Roy, et al., 1976). The general experimental conclusions are given below.

Calcium silicate - and aluminosilicate - compositions based on mixtures of fine grained quartz with various cements of calcium silicate compounds have been investigated under hydrothermal conditions in the temperature range 110-250°C and pressure range 1000-10,000 psi (6.8 - 68 MPa), pressures which are always in excess of that required to maintain liquid H₂O, and approximate the confining pressures which might be anticipated in deep boreholes.

All silicate cement combinations investigated [(a) Type V, (b) expansive cement, (c) a commercial "hydrothermal" cement containing β -Ca₂SiO₄, and (d) a laboratory-synthesized β -Ca₂SiO₄] produce materials having adequate strength after reaction times of 1 day or longer. The calcium aluminate ce-

ment used was also adequate with respect to strength but would need to be investigated more extensively for overall properties because of its highly reactive chemistry.

Reaction kinetics were investigated, and it was found that the most rapid reactions were obtained with the laboratory-prepared β - C_2SiO_4 plus quartz, while the expansive cement was the most sluggish. The commercial β - C_2SiO_4 -containing cement was also slow reacting and somewhat erratic in behavior from sample to sample. Using the same type I cement with quartz added in different ratios, a large excess of quartz appeared to inhibit the reaction.

Porosity generally (though not always) was found to decrease with reaction time. Unfortunately, experimental difficulties prevented an accurate assessment of permeability. SEM observations indicate generally increased density of the microstructures with increasing reaction time.

Mineralogically, the products consisted of mixtures of poorly crystalline calcium silicate hydrate, CSH(I) and tobermorite plus residues of quartz and, in case of shorter experiments, anhydrous cement compounds. No calcium silicate hydrate compounds richer in silica than tobermorite were observed. Tobermorite, the thermodynamically stable phase under the range of p-T conditions investigated, and from compositions having a 5:6 $\text{CaO}:\text{SiO}_2$ ratio is obviously the desirable reaction product from the standpoint of stability. However, some excess quartz in the products (most compositions were designed to have at least a light excess of quartz) would not produce a mechanically unstable material, if, after a very long time, tobermorite + quartz should react to produce some gyrolite, reyerite, or truscottite (the high silica phases), since all these crystalline phases have relatively low densities.

The mini-rock cylinder-cement plug hydrothermal experiments in both limestone and sandstone resulted in reasonable magnitudes of bonding strength. This is, of course, only a first step at approaching hydrothermal borehole

cementing conditions, as obviously the thermal conductivity of the surrounding rock would produce temperature gradients, rather than the static conditions used in the current experiments. The experiments do suggest, however, that such cements would be suitable for either rock type. The shear strengths were adequate, yet the extruded cement plug had sufficient integrity for it to have a quite high compressive strength. The typical shear strength of a hydrothermally treated cement-sandstone plug is 7 MPa (1030 psi), and the compressive strength of the extruded cement plug is 65 MPa (9550 psi).

II. SHALE/CLAY STUDIES: EFFECT OF THERMAL TREATMENT OF CLAYS AND SHALES ON THEIR CATION EXCHANGE CAPACITIES AND RELATIVE SORPTIONS OF CATIONS

2.1 Introduction

It is well known that cations in solution can be sorbed by clays and shales and that when mixtures of cations are involved certain sorption preferences are found. When radioactive waste is buried, the possibility of its dispersal by solution in ground water is an important consideration. The highly soluble monovalent and divalent fission products produced by the Oklo nuclear reaction, notably Cs, Rb, Sr, Ba, and possibly Cd, have for the most part disappeared from the immediate locality. Before the potential usefulness of clays and shales for confining such ions can be assessed, it is clearly necessary to consider how their sorption and fixation properties may be affected by the temperatures generated by buried radioactive waste materials.

The present studies represent the first steps towards supplying quantitative data on the effect of high temperatures on the sorption and fixation properties of clays and shales.

2.2 Design of the Experiments

Shales normally contain a variety of minerals, mainly quartz, various layer silicates such as micas, and a variety of ultra-fine grained clay minerals which also are mainly layer silicates. Therefore to understand the behavior and properties of shales, it is necessary to consider some representative minerals that are commonly present. Quartz contributes little or nothing to the total sorption properties. Coarse and fine-grained micas are important. We have considered muscovite, biotite and phlogopite as representative coarse-grained micas and illites as fine-grained micas. Among the clays, montmorillonite and vermiculite are potentially important because of their high cation exchange capacities and very large specific surface areas. Mont-

morillonite is important also in that montmorillonite layers are commonly interlayered with mica layers in the fine-grained illites.

Secondly, we have considered the thermal effects by heating the selected minerals to 300°, 500°, and 750°C in air for 24 hrs. In future experiments it will be important also to consider hydrothermal heating because such conditions are likely to arise from deep burial of radioactive waste.

Thirdly, we have considered how the relative sorptions of two kinds of cations may be influenced by the thermal treatment. It is known, for example, that if a Na-saturated clay is exposed to a solution containing equal equivalent amounts of two cations, such as K^+ and Ca^{2+} ions, the divalent ions will be more strongly sorbed than the monovalent. The preference for one kind of cation over the other can be expressed by the ratio $R(K/Ca) = (K^+ \text{ equivalents sorbed}) / (Ca^{2+} \text{ equivalents sorbed})$ when K^+/Ca^{2+} is 1:1 in the external solution. A value of $R(K/Ca) > 1$ will indicate a preference for K^+ as compared with Ca^{2+} , and $R < 1$ the opposite preference. In the present context we wish to know how such ratios will be affected by thermal treatment of minerals.

So far, our experiments have been limited to considerations of K^+ and Ca^{2+} ions. Their relevance to the main problem is that Cs^+ and Rb^+ ions can be expected to behave like K^+ ions (all are large cations, monovalent, and with low hydration energies). The Ca^{2+} ions can be regarded as those likely to be present in percolating ground waters.

2.3 Experimental Methods

The methods used are those conventionally employed in studying cation exchange reactions. The various clays were initially Na-saturated by using 0.5 N pH 7 sodium acetate solutions. The samples were then given 5 centrifuge washings with a 1:1 mixed solution of 0.005 N $CaCl_2$ and 0.005 N KCl. The Ca^{2+} and K^+ ions taken up by the minerals were then displaced by 5 centrifuge washings with 0.1 N $MgCl_2$ solution and the amounts of Ca^{2+} and K^+ dis-

placed were determined by atomic absorption analysis. It can be expected that all Ca^{2+} and K^+ taken up will, in fact, be displaced by Mg^{2+} ions.

From these measurements, the total cation exchange capacity of the minerals will be obtained, and also the ratio $R(\text{K}^+/\text{Ca}^{2+})$, with both ions expressed in equivalents. In addition, the results will show how these data are affected by the thermal treatments.

2.4 Results

The results of Table 2 show (i) the total milliequivalents of $(\text{K}^+ + \text{Ca}^{2+})$ exchanged per 100g of material, and (ii) the ratio $R(\text{K}^+/\text{Ca}^{2+})$.

2.5 Discussion

2.5.1. Exchange Capacities and Effects of Thermal Treatments

The exchange capacities are those normally found for the minerals studied, viz., low values for micas, high values for montmorillonites and vermiculites and rather variable values of illites; the illite values probably vary according to the proportion of expandable layers.

The thermal effect is generally a decrease due to exchange sites becoming unavailable as a result of a collapse of the layers. This reduction is particularly noticeable for the swelling minerals, montmorillonite and vermiculite. In the present context, these decreases are probably not too important, because under the natural conditions for radioactive waste burial we can assume large surrounding masses of clay and shale.

However, the major component of many shales is the micaceous mineral illite, or a mixed-layer illite-montmorillonite. For these minerals, the diminution of the exchange capacity is less dramatic than for montmorillonite. The Na-vermiculite which alone shows an increase is a highly special case which scarcely affects the general considerations.

Table 2
Effect of Temperature on Cation Exchange Capacity and Cation Exchange Ratio.

Minerals* studied	Cation exchange capacity (CEC), meq/100 g				Cation exchange ratio, R(K ⁺ /Ca ²⁺)			
	Un-heated	Heated** to 300°C	Heated** to 500°C	Heated** to 750°C	Un-heated	Heated** to 300°C	Heated** to 500°C	Heated** to 750°C
<u>Micas</u>								
Biellite, Ontario, < 50 μm	5.3	4.6	2.0	1.0	3.03	2.35	0.67	1.02
Phlogopite, Ontario, 0.2-20 μm	2.8	2.4	2.0	1.1	1.55	1.46	0.94	0.82
Muscovite, Norway, < 177 μm	1.1	1.0	1.8	0.8	1.67	1.13	1.52	1.36
Micromica, a fine ground muscovite	2.4	2.2	1.7	1.9	1.67	1.44	1.43	1.11
<u>Montmorillonites</u>								
Na-montmorillonite, TX	80.5	75.2	32.1	6.5	0.12	0.11	0.17	0.27
Na-montmorillonite, WY	79.5	66.9	41.8	8.3	0.09	0.09	0.12	0.11
Ca-montmorillonite, AZ	120.4	108.9	17.2	4.3	0.21	0.18	0.30	0.19
<u>Illites</u>								
Na-Beavers Bend illite, < 1 μm	11.3	9.4	nd	8.4	0.77	0.65	nd	0.65
Illite, Ouachita #13, 0.2-2 μm	7.2	5.6	6.7	5.2	1.06	0.75	0.97	0.86
Fishian illite, < 4 μm	13.9	14.8	18.5	10.9	0.35	0.35	0.45	0.54
Illite #9, < 0.2 μm	24.6	22.6	24.6	15.0	0.42	0.36	0.46	0.58
Illite #10, 0.2-2 μm	17.9	17.2	16.5	8.0	0.57	0.54	0.60	0.63
<u>Micaceous vermiculites</u>								
Na-vermiculite, S. Africa, < 20 μm	144.0	144.1	173.9	160.9	0.22	0.23	0.81	1.16
Micaceous vermiculite, S. Africa, 20-125 μm	94.7	98.0	92.7	7.7	0.41	0.38	0.51	0.93
Vermiculitic phlogopite, KS, > 500 μm	28.4	16.6	8.3	4.9	0.32	0.30	0.73	0.75
<u>Shale</u>								
McAvoy shale, pulverized	11.0	9.4	8.4	5.0	0.38	0.40	0.56	0.67

*Minerals with natural saturation unless otherwise indicated.

**All the heat treatments are for 24 hours in air.

2.5.2. Cation Sorption Ratio. $R(K^+/Ca^{2+})$; Effect of Thermal Treatment

Generally the ratio R is less than unity which means that Ca^{2+} ions are sorbed preferentially to K^+ ions. This is a very well-known result. Among the unheated samples, only the micas give values of $R > 1$, which means that micas exhibit a preference for K^+ ions. This also is well known and is a result of the low hydration of K^+ ions which permits K^+ ions to enter "wedge" sites where the layers are somewhat open near the edges in preference to the effectively larger hydrated Ca^{2+} ions ($Ca^{2+} \cdot 6H_2O$).

Among the illites, two have high values of R , namely 0.77 and 1.06, while three have low values, namely 0.35, 0.42 and 0.57. The first two illites are probably close to mica in their sorption properties, and the three latter illites with the higher exchange capacities are probably mixed-layer illite-montmorillonites.

The thermal treatment drastically diminishes the R values of the micas, but for the montmorillonites R is mainly increased slightly. For the illites, the first two (the mica-like ones) show a diminution of R but the three latter show mainly an increase of R .

The thermal effect, then, is such that the R values are not drastically changed except for the coarser grained micas. Therefore, when we consider that K^+ ions probably behave in the same way as would Cs^+ and Rb^+ ions, we can feel reasonably confident that heating clays and shales will not diminish their capability of taking up these monovalent ions when they are present in percolating waters containing Ca^{2+} ions.

We still have to consider large divalent ions, notably Sr^{2+} and Ba^{2+} . Their behavior vis-a-vis Ca^{2+} ions will be governed mainly by their hydration characteristics and at this stage of the investigation it is pointless to guess their behavior.

2.6 Further Studies

It is relevant to remark that the measurements discussed in this report have been undertaken wholly in the 3-month period, May-July 1976. The following experiments are obviously necessary: (i) A consideration of hydrothermal heating in addition to heating in ambient conditions, (ii) Experiments specifically involving Cs^+ , Rb^+ , Sr^{2+} , and Ba^{2+} ions, (iii) Experiments relating to fixation as distinct from sorption. Part of this work is under way, and other continuations of the present work are discussed in the Proposal for Continued Support of the Research Program.

III. THERMAL PROPERTIES INSTRUMENTATION, MEASUREMENT, MODELING OF CEMENT AND SHALE

3.1 Instrumentation

3.1.1 Atmospheric Pressure

The instrumentation for thermal properties measurement at atmospheric pressure is essentially complete, although some of the apparatus now being developed will be used for atmospheric pressure measurements as well. Measurements of thermal conductivity and thermal expansion are made fairly routinely at atmospheric pressure. New differential thermal analysis and thermogravimetric analysis equipment are being added to the overall laboratory facilities.

3.1.2 Elevated Pressures

A method has been designed for experimental heat flow studies in shales and cement, to give evidence concerning the effect of the critical point of water on the thermal properties. A heated chamber embedded in a homogeneous porous medium will be effectively isolated from surrounding water.

The method involves studying the temperature distribution inside a shale sample 25 cm in diameter by 25 cm long using a cylindrical electrical resistance heating source at the center. The heating source will be controlled in an oscillatory thermal cycle and the temperature field sampled by numerous thermocouples embedded in the sample. The heat source and the data acquisition are to be under micro-computer control. The data will be processed in the IBM computer on campus and telephone lines will be used to dump the data from one computer to the other.

Preliminary studies will be made on hydrated cement or mortar samples at atmospheric pressure. When the characteristics of the apparatus are better understood the sample will be tested in the chamber. After some experience

with cement, we will then be ready to study the shale. The pressure vessel has been built and the control and computation facilities designed.

3.2 Thermal Properties Measurements at Atmospheric Pressure

3.2.1 Thermal Conductivity

Thermal conductivity is being measured with a Colora Thermoconductometer, based upon a method devised by J. Schroeder (1959). Schroeder's article (1963) gives considerable detail of the apparatus. Dynatech Corporation is sole distributor in the United States for the instrument.

The instrument requires time measurements only and does not involve any calorimetric measurements. A cylindrical sample (16 - 18 mm diameter) of test material is brought into contact with two boiling liquids having a suitable boiling point difference (10° - 20°C). Trichloroethylene/water are the two liquids being used. The mean of their boiling temperature is 93.5°C. Therefore, the " λ ", values obtained represent the thermal conductivity of the test materials at this temperature. The time is measured for a given quantity of heat, determined by the volume of liquid which evaporates from the "cold" side of the sample to flow through the sample. Figure 3 represents the measurement principle for the unit.

A calibrated sample with known thermal conductivity was measured (time) with the above liquid pair. From these data, a calibration diagram was obtained, Fig. 4. The thermal resistance values of subsequent samples are read directly from this diagram, once the time has been measured to collect one ml of condensate.

The specific thermal conductivity, λ , of the material under test is obtained by the equation

$$\lambda = \frac{h}{R \cdot F} \text{ (cal/cm s } ^\circ\text{C)}$$

Figure 3
Measurement Principle

Figure 4. Calibration curve for the liquid pair water/trichloroethylene.

Materials mixed thoroughly and placed in glass vials (22 x 50 mm length) - six vials per sample. Vials filled in thirds, with material packed 25 times with glass rod after addition of each segment.

Continued thermal conductivity testing of rocks and cements is planned. In addition, rock samples will be heat treated at pre-determined temperatures and new thermal conductivity values obtained. These values will be compared with the values obtained prior to heat treatment.

3.2.2 Thermal Expansion

Initial thermal expansion tests are being performed on an Orton Automatic Recording Dilatometer, manufactured by the Edward Orton Jr. Ceramic Foundation, Columbus, Ohio.

The unit is designed to plot automatically the percentage linear thermal expansion versus temperature. Sample length must be two inches and up to 3/4 inches in diameter. Length changes are transmitted through an alumina pushrod to the plunger of the linear variable differential transformer. The output of the LVDT is changed by movement of the plunger. A transducer exciter-demodulator supplies an alternating current to the primary of the LVDT and converts the transducer output to a dc millivoltage which is proportional to movement of the transducer plunger.

Figures 5-7 represent thermal expansion curves of the following: Fig. 5, a calibration curve of aluminum oxide ceramic; Fig. 6, sample number PSU-36 (UElm-Eleana, cross section slice from 152.928 m end); Fig. 7, a sandy shale. Testing of rock samples, as received, will continue along with the testing of various cement samples. Expansion of samples will be examined and compared from room temperature to 800° - 1000°C.

Correlation among rock samples from room temperature to 100°C should give valuable information for comparison of properties of various rock types. It is recognized that textural and porosity effects have a substantial in-

Figure 5. Thermal expansion curve for Al₂O₃ standard.

Figure 6. Thermal expansion curve for Sample No. PSU-36.

Figure 6. Thermal expansion curve for sandy shale from the Oswego.

fluence on thermal expansion measurements at one atmosphere pressure and at elevated temperatures and will differ from the expansion of rocks buried in the earth. However, porosity and permeability measurements will also be made on the same rock samples for which the expansion data up to the 800° - 1000°C are obtained.

3.2.3 DTA and Thermogravimetric Analysis

DTA is, of course, routinely used for rock characterization, and for study of dynamic thermal effects in cements. The new thermogravimetric analysis apparatus expected soon in the laboratory will make the latter types of studies more convenient.

3.3 Thermal Analysis of Buried Radioactive Waste

The objective of this research is to model the thermal response of geologic materials, particularly water saturated shales, which are used as a deep storage and isolation medium for high level radioactive wastes, and of hy-

drated cements used in conjunction. The temperatures and fluid pressures surrounding a deep borehole containing the waste will be calculated, using the finite difference technique for numerically solving the appropriate equations.

A fluid free zone may be generated by heating immediately around the waste which would have the positive effect of isolating it from any circulating water for a certain period, but would also lead to a decrease in the thermal conductivity of the rock, resulting in the generation of possibly unacceptably high temperatures.

A mathematical model may be derived to describe heat and mass transfer in a porous medium, based on balance equations for the conservation of mass, momentum, and energy, and constitutive relationships concerning pressures, temperatures, saturations, and thermodynamic properties of water. With certain necessary simplifying assumptions, the system can finally be described by two nonlinear second order partial differential equations posed in two unknowns, or calculated parameters: density and viscosity of rock, fluid, and vapor; permeability of rock to fluid and vapor; porosity and thermal conductivity of rock; mass and energy source terms; gravitational acceleration; spatial coordinates; and time. All physical properties of rock and water may be assumed constant, or may be considered as variables in space or time.

To assess the validity of numerical results as they are obtained, a laboratory study has been undertaken to examine heat and mass transport in heated and pressurized saturated cement and shale samples. A large pressure cell has been built, which will contain a large cylindrical hydrated cement, mortar, or shale specimen approximately 12 cm in radius by 25 cm long, having a heat source placed in an axial hole, with thermocouples emplaced to measure temperature at various points throughout. It will be placed in a sealed stainless steel cell, and the temperature field generated by different heat inputs measured. These temperatures could be compared to those obtained

numerically from a finite difference model of the system. The interactive use of experimental data with the predicted numbers from the computer analysis, should build confidence in the results and interpretation of the phenomena.

Four large sandy shale samples have been obtained, but only one has satisfactorily withstood the cutting process. (The Pennsylvania State Department of Transportation core drilling equipment was used to cut the shales for us.)

Currently, cement mixed with fine quartz filler is being prepared in the same dimension cylinders as for the shale. After the thermal analysis of the hydrated cement/mortar is well under way more experience will be available for study of the shale specimens.

IV. ROCK PROPERTIES MEASUREMENT/CHARACTERIZATION/ANALYSIS

4.1 Shale-Siltstones

Different series of rocks were studied from the NTS, including the Series ES-S-1 to ES-S-18; ES-S-8A and ES-S-8A'; UEIL Series cores: ES-S-19, A, B, C stream and trench samples; and a large UEIm core. A separate report on these analyses was submitted on June 11. The majority of rocks examined from the NTS were found to be siltstones, varying from coarse into the very fine siltstone range, and containing $> 60\%$ quartz, usually much higher. Samples of the UEIL series of cores, in contrast, had a large clay mineral fraction, as well as some carbonate present. A few were intermediate silty claystones or argillites. Studies are also being made of shales to be used for thermal analysis.

4.2 Evaporites

Similar studies including petrographic analysis of evaporite rocks and formations were performed, which are reported separately. Such analyses can yield valuable information on the quantity and textural relationships between the rock components. Some of the components such as brines, bitumen and hydrocarbons could be of major significance if thermal metamorphism were to cause a concentration and migration of these components towards the location of radioactive waste in an isolation site under the influence of a thermal gradient.

Further modifications of the petrographic and analytical techniques utilized for the present study are continuing and it would be desirable to initiate additional studies of fluid inclusions with the use of a heating and freezing microscope stage. These fluids are of importance as a result of their composition and potential to migrate under thermal gradients and in addition because of their ability when migrating of transferring and concentrating other solid components of the rock.

4.3 Quantitative Petrography with the SEM

The scanning electronmicroscope facility at The Pennsylvania State University has the capability of detecting and characterizing particle size distributions through the utilization of electron back scatter techniques. Coupled with EBS, X-ray fluorescence techniques allow for a seven channel multi-element analysis for each data point. By a prudent selection of elemental constituents, a qualitative mineral analysis, an all-type-particle size distribution analysis, individual-mineral-particle size distribution analysis, sphericity analysis and porosity can be obtained.

Preliminary investigations of a local shale sample are very encouraging. The analysis was primarily aimed at the particle size distribution of quartz. These results were very satisfactory. From the analysis, additional patterns of elemental combinations have developed which allow at least a first approximation to identification of specific mineral assemblages, along with their size distribution and sphericity.

By forming a negative image of the normal EBS signal, an accurate pore size distribution and shape has also been obtained on the shale specimen.

Because of the intrinsic limitations of the X-ray fluorescence techniques, this characterization method cannot stand by itself as a rock characterization tool. However, in conjunction with the other standard characterization techniques described in the reports, a more complete understanding of the physical nature of rock samples can be achieved.

PERSONNEL

The work reported was under the direction of Dr. Della M. Roy. Persons involved at various stages included Dr. H. A. McKinstry, Professor G. W. Brindley, Dr. Barry Voight, Dr. Michael Grutzeck, Dr. S. Komarnehí, Dr. Barry Scheetz, Mr. Gary Iversen, Mr. G. Zimmerman, Mr. George Stephens, Ms. C. Langton, Mr. Norman Suhr and staff of the Mineral Constitution Laboratory, and students F. Rosenzweig and W. Gerber.

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