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FUNDAMENTAL GEOSCIENCES PROGRAM

ANNUAL REPORT 1977

MASTER



**EARTH SCIENCES DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA**

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FUNDAMENTAL GEOSCIENCES PROGRAM ANNUAL REPORT 1977

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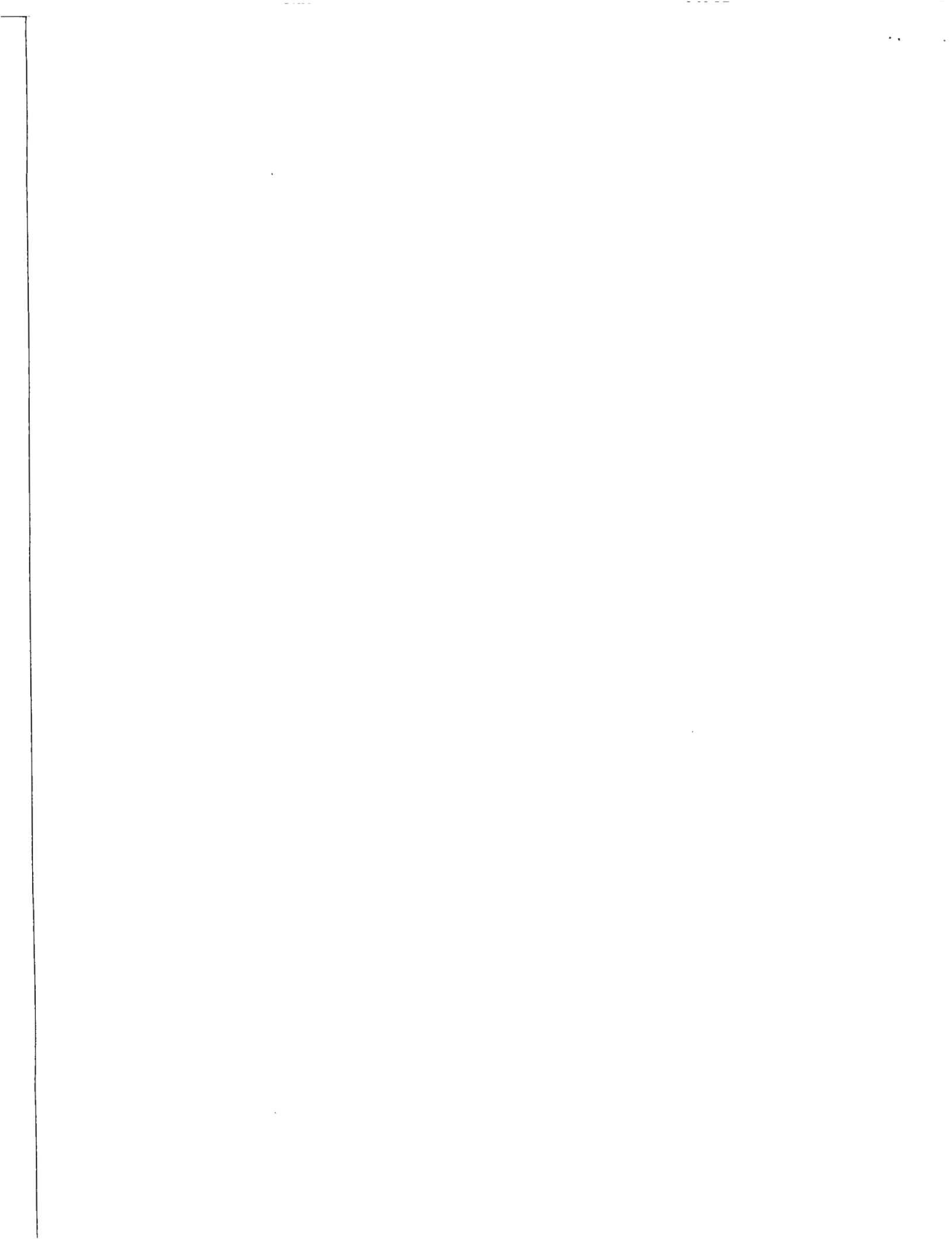
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This report is a reprint of the Fundamental Geosciences section of the Lawrence Berkeley Laboratory's Earth Sciences Division Annual Report 1977 (LBL 7028). The organization of the Fundamental Geosciences Program, its funding sources, and the papers submitted by each group are shown in the table below.

Project title/Principal investigator	Report title/Author
FUNDAMENTAL GEOSCIENCES - FUNDING BY DIVISION OF BASIC ENERGY SCIENCES (DOE)	
Geosciences relating to geothermal energy. P.A. WITHERSPOON	
Reservoir dynamics. C.F. TSANG	On some fundamental aspects of reservoir dynamics. T.N. NARASIMHAN, M.J. LIPPMANN, and P.A. WITHERSPOON
	Thermal energy storage in aquifers. C.F. TSANG and M.J. LIPPMANN
Properties and behavior of rock-fluid systems at high temperatures and pressures. W.H. SOMERTON	Properties and behavior of rock-fluid systems at high temperatures and pressures. W.H. SOMERTON
Thermodynamics of high temperature brines. K.S. PITZER	Thermodynamics of high temperature brines. K.S. PITZER, L.F. SILVESTER, P.Z. ROGERS, and J.R. PETERSON
Geochemistry and mass transfer in geothermal systems. J.A. APPS	Selected albites as candidates for hydrothermal solubility measurements. J.A. APPS and J.M. NEIL.
Thermodynamic properties of silicate materials. I.S.E. CARMICHAEL	Thermodynamic properties of silicate materials. I.S.E. CARMICHAEL, S.A. NELSON, and L. MORET
Magmatic materials: high precision neutron activation analysis. F. ASARO	Studies of magmatic materials. F. ASARO and H.V. MICHEL
In situ stress measurements: seismic wave velocity. T.V. McEVILLY and J. WANG	In situ stress measurements. T.V. McEVILLY and J. WANG
National geothermal information resource (GRID). S.L. PHILLIPS	Viscosity of aqueous sodium chloride solutions from 0°C to 150°C. H. OZBEK and S.L. PHILLIPS

(continued)

Project title/Principal investigator

Report title/Author

FUNDAMENTAL GEOSCIENCES - FUNDING BY DIRECTOR'S DEVELOPMENT FUNDS

In situ leaching of uranium ore.
J.W. EVANS

In situ leaching of uranium ores. J.W. EVANS

Properties of magmas. I.S.E. CARMICHAEL

Methods for determining the equilibration temperatures of magmatic crystalline assemblages: trace metal distributions. H.R. BOWMAN, I.S.E. CARMICHAEL, and S.A. NELSON

Surface and electrochemical characterization of pyrite sulfur in relation to the removal of pyrite from coal.
D.W. FUERSTENAU

Electrochemical studies on the dissolution and flotation behavior of ore-pyrite and coal-pyrite. D.W. FUERSTENAU

In situ properties of soils and soft rocks and their stability. J.K. MITCHELL

Determination of the properties of soils and soft rocks by in situ measurements. J.K. MITCHELL and W.C.B. VILLET

High resolution mass spectrometry.
M.C. MICHEL

High precision mass spectrometry. M.C. MICHEL

Radon in subsurface waters as an earthquake predictor, Central California studies.
A.R. SMITH and H.A. WOLLENBERG

Stress flow behavior of fractured rock systems. R.L. TAYLOR

Stress flow behavior of fractured rock systems. R.L. TAYLOR, P.A. WITHERSPOON, H.M. HILBER, and J. VAN GREUNEN

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FUNDAMENTAL GEOSCIENCES

INTRODUCTION

Progress is reported on *which are part*
 Fundamentally geoscience studies, within the
 Earth Sciences Division of the Lawrence Berkeley
 Laboratory consist of three major programs:

geosciences relating to geothermal energy, the development of techniques for precise measurement of physical and chemical properties of geological materials in order to understand geological phenomena, and a developmental program that includes new and promising geoscience studies with a variety of applications in energy resource development.

The geoscience program relating to geothermal energy consists of four projects. In the project on reservoir dynamics, sophisticated codes have been written to simulate the dynamics of heat flow in geothermal reservoir systems. These codes have also been applied to the investigations of natural aquifers as a storage system for thermal energy. In the second project, core samples are studied to determine the high temperature and high pressure behavior of aquifers in the presence of saturating fluids. The third project covers the systematic evaluation of the thermodynamic properties of electrolytes in order to interpret the behavior of geothermal fluids. The fourth project involves hydrothermal solubility measurements of various minerals to elucidate the chemistry and mass transfer in geothermal systems.

The second major program includes four projects which involve precise measurements and analysis of physical and chemical properties of geologic materials. These include measurements of the thermodynamic properties (viscosity, density and heat capacity) of silicate materials to help understand magma genesis and evolution, high-precision neutron activation analysis of rare and trace elements in magmatic materials, and the precise measurement of seismic wave velocities near geological faults, in order to determine the build-up of stress in the earth's crust. Support is also provided for the National Geothermal Information Resource (GRID) project, in which the current literature is searched for experimental data of relevance to the geothermal energy industry. Reports are published periodically summarizing and critically reviewing the data.

Third, the development program in fundamental geosciences includes six innovative projects providing techniques applicable to energy resource development. These projects include research in the in situ leaching of uranium ore, properties of magmas, removal of pyrite from coal, properties of soils and soft rocks, stress flow behavior of fractured rock systems, and high-precision mass spectrometry.

ON SOME FUNDAMENTAL ASPECTS OF RESERVOIR DYNAMICS

T. N. Narasimhan, M. J. Lippmann, and P. A. Witherspoon

This report summarizes the research activities of the authors during fiscal 1977 on some fundamental aspects of reservoir dynamics. The research work touched upon the following: constitutive laws; chemical transport; land subsidence; flow in fractured media; and numerical modeling of the non-linear diffusion equation.

Although (1) has generally been satisfactory for saturated systems, its extension to unsaturated or two-phase systems has been questionable. It is customary in the soil physics literature to neglect the possibility of matrix deformation in the unsaturated zone and effectively set $\sigma' = \sigma$. On the other hand, extensive work in the deformation of unsaturated soils has given rise to the modified constitutive law:

CONSTITUTIVE LAWS

It is now well recognized that the release of stored fluids from most hydrogeological systems is dominated by a reduction in the pore volume of the reservoir. While fluid flow is governed by pore-pressure changes, the skeletal deformation is caused by the stress changes on the matrix. For modeling fluid flow in deforming media, a fundamental necessity is therefore a constitutive relation between pore-pressure change and the effective stress (skeletal stress) change. For saturated systems it is customary to use

$$\sigma' = \sigma - \psi \rho_w g \tag{1}$$

where σ' is the effective stress, σ is the total stress, ψ is the pore-pressure head, ρ_w is the density of water, and g is the gravitational constant.

$$\sigma' = \sigma - \chi \rho_w g \psi \tag{2}$$

where $0 \leq \chi \leq 1$ and $\chi = \chi(\psi)$ in the unsaturated zone. Or, in a generalized fashion,

$$\sigma'_{ij} = \sigma_{ij} - \chi \rho_w g \psi \delta_{ij} \tag{3}$$

where δ_{ij} is the Kronecker delta.

A constitutive law of the form (2) or (3) is essential, not only for properly unifying flows in the saturated and the unsaturated domains, but also for understanding such field phenomena as ground fissuring in heavily dewatered aquifers in arid zones and the subsidence associated with organic soils.

The aforesaid concepts were discussed in a presentation entitled, "The Significance of the

Storage Parameter in Saturated-Unsaturated Flow" presented before the American Geophysical Union.²

CHEMICAL TRANSPORT

The transport of reactive or non-reactive species in flowing groundwater is of fundamental interest in many branches of earth sciences (e.g., radioactive waste disposal and geothermal reinjection). Mathematically the mechanism of chemical transport is customarily simulated by the convective-diffusion equation of the form

$$\nabla \cdot D \nabla C + v \cdot \nabla C = \frac{\partial C}{\partial t} \quad (4)$$

where D is a diffusion coefficient, v is the pore-velocity of the fluid and C is concentration. While the numerical simulation of (4) is generally satisfactory when D is large (i.e., diffusion dominates convection), the solutions are affected significantly by numerical dispersion when D is relatively small (convection-dominated systems). Recent field investigations seem to suggest that many field situations may be characterized by low diffusion. Therefore, ability to successfully handle convective-dominated diffusion problems is of considerable practical interest.

A study of the formulation of the convective diffusion equation suggested that reformulating the problem directly in an integral form and re-examining the solution procedure will greatly help minimize the problem of numerical dispersion. Accordingly, work was commenced during the summer of 1977 to solve the one-dimensional convective diffusion equation by integral methods. By the end of summer, the preliminary calculational model was developed and favorable comparisons achieved with analytical solutions of low diffusion problems.

LAND SUBSIDENCE

Numerical models for simulating reservoir compaction in isothermal³ as well as non-isothermal⁴ systems have already been developed at LBL. These models, however, do not include the propagation of reservoir deformation to the land surface through the overburden, especially when the reservoir is buried at a great depth. If we recognize that reservoir deformation is primarily caused by the internal loading process of pore-pressure withdrawal and that the overburden deforms are the boundary displacements imposed at the reservoir-overburden boundary, it becomes apparent that an efficient and economic way of modeling land subsidence is to employ a dual model using the existing models^{3,4} (which have been found so very well suited for reservoir deformation) for simulating the reservoir and use the more general (and expensive) non-linear finite element models for simulating the overburden deformation. Accordingly, work was initiated during the second half of the year on a very general pseudo-elastic finite element model for overburden deformation. By the end of the year, this model, developed by W.N. Houston and A.G. Kasim of the Department of Civil Engineering, University of California at Berkeley, was being used for parametric studies on a two-layered system. The results are slated to be presented in

the Engineering Research Conferences of the American Society of Civil Engineers, Pensacola, Florida, January, 1978.

FLOW IN FRACTURED POROUS MEDIA

It is known from field experience that many geothermal wells and deep waste disposal wells may be intersected by natural or artificial fractures. Although, in general, the reservoir could be idealized as a porous medium, the fractures may so dominate the flow near the well that due consideration will have to be given in modeling the pressure transient behavior of such wells. In the literature, analytic techniques (e.g. the Green's functions⁵) as well as semi-analytic techniques⁶ have been used to study flow to fractured wells. However, these techniques are limited by the constraints imposed on analytic solutions. In order to be able to handle arbitrarily complex problems, the numerical model developed earlier by Narasimhan and Witherspoon^{7,8} was applied to the study of near-well flow phenomena in wells intercepted by finite conductivity vertical fractures. The validity of the model was successfully verified by comparison with known analytic and semi-analytic solutions. The ability of the model to handle well-bore storage and deformable fractures was also verified.

NUMERICAL MODELING OF THE NON-LINEAR DIFFUSION EQUATION

The mathematical simulation of groundwater systems leads to the consideration of a non-linear, parabolic differential equation of the form

$$\nabla \cdot K(\phi) \nabla \phi = S(\phi) \frac{\partial \phi}{\partial t} \quad (5)$$

where K is permeability, ϕ is potential and S is the storage coefficient. It is well known that equation (5) could be numerically solved using the method of finite differences, integrated finite differences, or finite elements. It was shown⁹ by Narasimhan et al. that one could maximize the advantages of the integrated finite differences and the finite elements by combining them into a single algorithm in which the conductance matrix is formed using the finite element approach, and the solution process is carried out using the mixed explicit-implicit strategy used in the integrated finite difference scheme. During fiscal 1977, the applicability of the new approach to subsurface hydrology problems was demonstrated.¹⁰ In addition work was initiated in the summer to prepare a users' guide (with examples) for the new algorithms (called FLUMP); this work was continuing at the end of the year.

PLANNED ACTIVITIES

During 1978, the users' guide for FLUMP is expected to be completed. Research work on all the other aspects referred to above will be continued.

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THERMAL ENERGY STORAGE IN AQUIFERS

C. F. Tsang and M. J. Lippmann

INTRODUCTION

The development of practical and low-cost methods for storing large amounts of thermal energy is of fundamental importance for the utilization of solar energy as well as the implementation of total energy systems. The basic function of a storage system is to act as a buffer between time-varying energy inputs and thermal and/or power demands. The purpose of the present project is to study the feasibility of storing hot water in natural aquifers underground. The purpose is to understand the hydrodynamic and thermal behavior of an aquifer, to estimate the efficiency of thermal storage and retrieval, and to suggest optimal arrangements for implementation.

Aquifers are geologic formations that contain and conduct water. They are found at depths ranging from a few meters to several kilometers. Confined aquifers are those bounded above and below by impermeable layers and saturated with water under pressure. For many years such aquifers have been used for liquid waste disposal and for storing fresh water, oil products, and gas. However, their use for hot water storage is a relatively new concept suggested by Robbimov et al.,¹ Kazmann,² and Meyer and Todd³ in the early 1970's.

The physical basis of the concept of storing hot or cold water in aquifers lies in: (1) the low thermal conductivities of caprock and bedrock materials, (2) the large volumes of many aquifers (of the order of 10^7 m^3), and (3) the capability of storing water under high pressures. To estimate

the feasibility and efficiency of such a storage system, the behavior during injection and withdrawal cycles must be understood, such as: (1) thermal behavior of and heat loss from the system during successive cycles of operation; (2) pressure distribution in the aquifer during the process; and (3) rock-water chemical reactions and the resulting change in aquifer permeability.

It is only recently that sophisticated computer models have been developed to study these questions using the proper physical conditions and parameters, and to make realistic predictions of the energy recovery efficiency of aquifer storage systems. Furthermore, physical models and field experiments^{4,5} have been initiated to test this concept. These will not only provide data to verify numerical models, but also give an indication of the feasibility and possible problems that may be encountered during the implementation of the aquifer storage concept.

THIS YEAR'S ACTIVITIES

In this project, which was started December 1976, we made use of a numerical model developed at the LBL to investigate hot and chilled water storage. The numerical model employed is called "CCC" which stands for "Conduction, Convection, and Compaction."^{6,7} It is based on the so-called integrated-finite-difference method.⁸ The model computes heat and mass flow in three-dimensional water-saturated porous systems. Concurrent with the mass and energy flow, the vertical deformation of the aquifer system is simulated using the one-dimensional consolidation theory of Terzaghi.⁹

Thus the following physical effects can be included simultaneously in the same calculations.

- Flow of hot and cold water with large viscosity and density differences
- Effects of temperature on rock and fluid properties (e.g., heat capacity, viscosity, and density)
- Heat convection and conduction in the aquifer, caprock and bedrock
- Effects of gravity on fluid flow
- Effects of regional groundwater flow
- Combined effects of many injection and withdrawal cycles
- Spatial variations in aquifer properties.
- Possible compaction and the associated land subsidence due to pressure changed during the injection-withdrawal history

Five different cases have been studied:

1. Hot water daily storage: hot water is injected for 12 hr during daytime and produced for 12 hr during nighttime.
2. Hot water seasonal storage, semiannual cycle: hot water is stored in spring for 90 days, pumped to use for air-conditioning in summer for 90 days, then hot water is again stored in autumn for 90 days and finally pumped out to use for heating in winter for 90 days.
3. Hot water seasonal storage, annual cycle: hot water is stored in summer for 90 days and used for 90 days in winter for heating. There is no injection or production during spring or fall.
4. Chilled water seasonal storage: chilled water (at 4°C) is stored in winter for 90 days and produced for 90 days in summer to be used for air-conditioning. There is no injection or production during spring or fall.
5. A two-well (doublet) system: during storage period, water is produced from well, heated and then injected into the other one; during the utilization period, hot water is retrieved from the latter and the cooled, used water is injected back into the former.

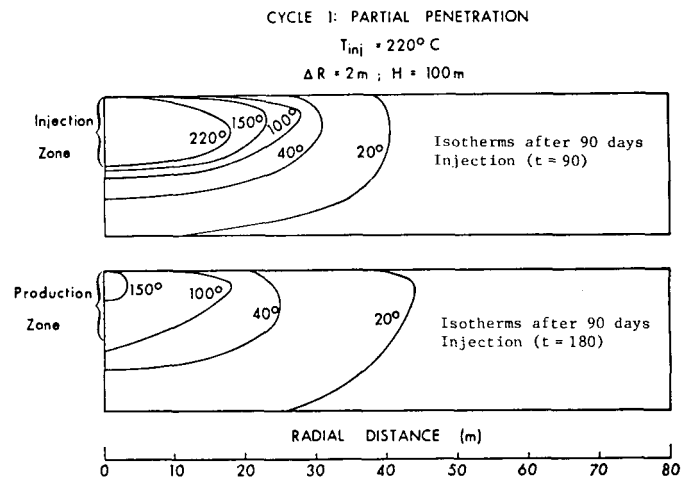
The rates of injection and production are kept the same, equal to 10^6 kg/day.

The initial temperature of the aquifer in all cases is assumed to be 20°C. For Cases 1 through 3 we have performed calculations with injection temperature T_i assumed to be 120°C, 220°C, and 320°C. It appears that the temperature of the produced water for different injection temperatures approximately scales according to the factor

$(T_i - T_0)$. For Case (4), only one injection temperature, 4°C, has been used. Some typical results are shown below.¹⁰

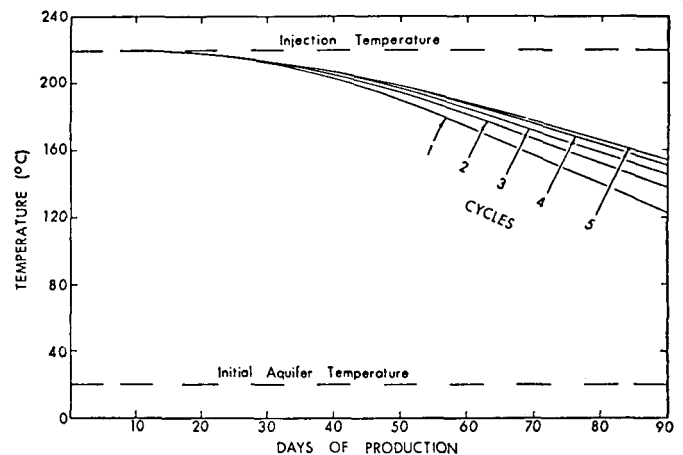
For Case 2, seasonal storage, semiannual cycle, we have performed calculations not only for a well fully penetrating the aquifer (thickness 100 m) but also for a well partially penetrating the aquifer for 50 m. Figure 1 displays the temperature contours within the aquifer for the partial penetration case (1) at the end of the injection period of the first cycle and (2) at the end of the production period of the same cycle. The thermal front is not sharp due to heat conduction within the aquifer and within the confining beds.

Figure 2 represents the production temperature at the well during the production period for



XBL 777-9715

Figure 1. Temperature contours in the aquifer after 90 days of injection and after 90 days of production in Cycle 1, for the case of semiannual cycle, seasonal storage. The well penetrates the upper 50 m of the aquifer. Numbers labeling the contours are in degrees Celsius.



XBL 777-9714

Figure 2. Temperature at the well versus production time for each cycle. The case shown is for seasonal storage with semiannual cycle; well fully penetrates the aquifer.

Table 1. Summary of results: semiannual cycles with full penetration.

	CYCLE				
	1	2	3	4	5
Energy injected, joules	5.71×10^{13}	5.71×10^{13}	5.7×10^{13}	5.71×10^{13}	5.71×10^{13}
Energy recovered, joules	4.96×10^{13}	5.092×10^{13}	5.144×10^{13}	5.18×10^{13}	5.2×10^{13}
Energy loss from aquifer, joules	5.34×10^{11}	6.81×10^{11}	7.7×10^{11}	8.41×10^{11}	9.1×10^{11}
Energy diffused to heat up aquifer, joules	7.10×10^{12}	5.5×10^{12}	4.9×10^{12}	4.46×10^{12}	4.2×10^{12}
Percentage of energy recovered	86.8	89.2	90.0	90.7	91.1
Production temperature at end of cycle, °C	124	139	147	151	155

Full penetration: 1 Cycle = 180 days, $T_i = 220^\circ\text{C}$, $T_o = 20^\circ\text{C}$, $Q = 1 \times 10^6$ kg/day, $H = 100$ m, $\Delta R = 2$ m, no. of layers = 4.

successive cycles for the case of semiannual cycle with full penetration. The recovery temperature is increased for each successive cycle as the aquifer is heated up, making it a more efficient hot water storage system. The process will reach quasi-equilibrium when later cycles do not change the temperature appreciably.

The results for semiannual cycles with full penetration are summarized in Table 1. It can be seen that the energy recovered (which may be calculated from the integral of temperature over time in Fig. 2) improves with each successive cycle. The heat lost is also shown and is two orders of magnitude smaller than the energy recovered. The difference between energy injected and recovered is the energy diffused to heat up the aquifer, making it a better storage system for the following cycle. The last line gives the minimum recovery temperature during production. This corresponds to the lowest temperature found at the end of each production period, as shown in Figure 2.

For Cases 1 through 3 the percentage of energy recovered (i.e., recovered energy divided by total injected energy) during each cycle is plotted against cycle number in Figure 3; the values shown in Figure 3 are surprisingly high (>80%).

For Case 4, where chilled water is stored, the temperature of production during the summer is shown in Figure 4, and the highest temperature during production (at the end of the production period) versus cycle number is shown in Figure 5.

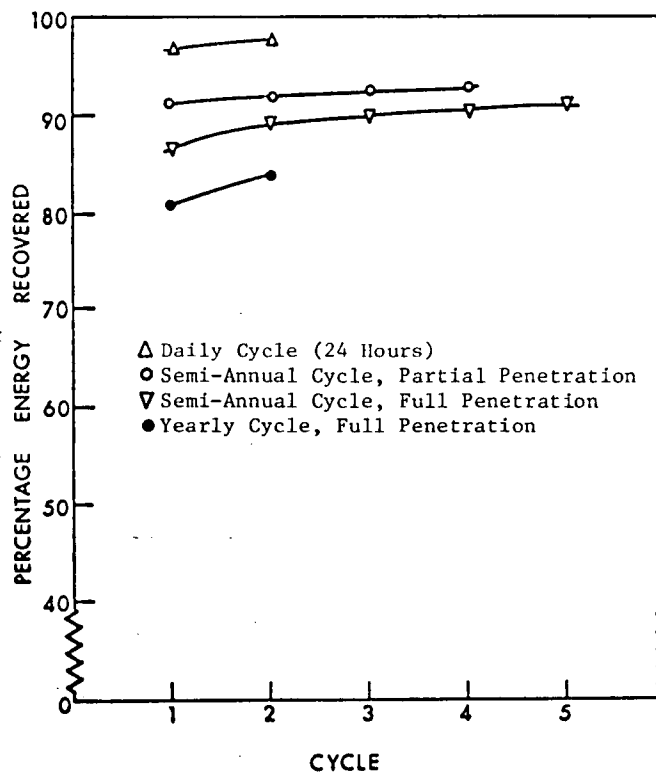


Figure 3. Percentage of energy recovered over energy injected versus cycle number.

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Thus after three cycles, the temperature during production is expected to stay below 10°C during the whole production period.

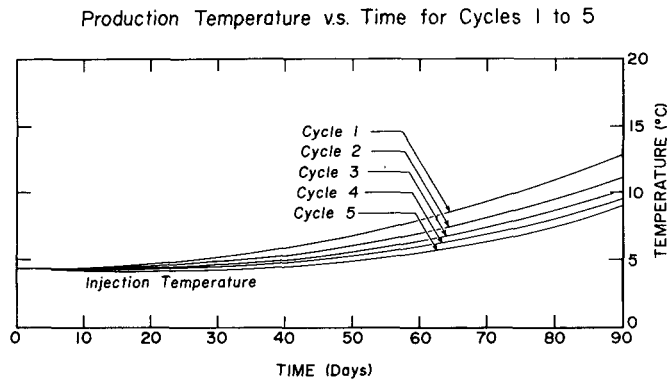


Figure 4. Chilled water storage: temperature at the well versus production time for each of the Cycles 1 to 5.

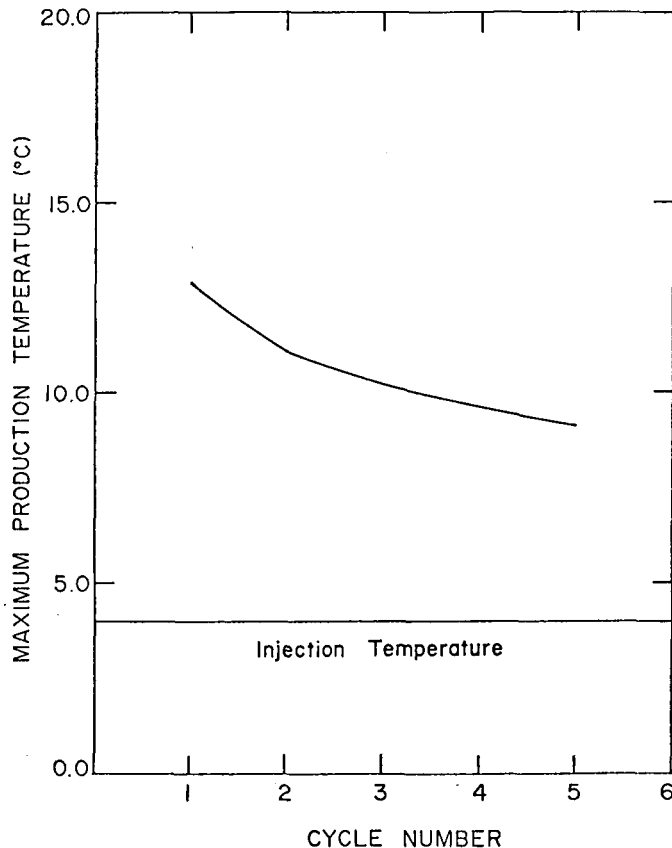


Figure 5. Chilled water storage: temperature at the end of each production period (maximum production temperature) versus cycle number.

FUTURE ACTIVITIES

During the next fiscal year, the following tasks will be addressed.

1. Further calculations will be done for a "typical" aquifer system, exploring the effects of variations in parameters, such as thickness, permeability, flow rates, and boundary conditions.
2. Further calculations will be made for multiple-well systems with the goal of identifying optimal arrangements for heat storage and retrieval.
3. Collection and evaluation of field data collected from thermal storage field experiments (e.g., those of Auburn University). Suggestions may be made to the experimenters for new or additional measurements. We will draw from the LBL expertise in geophysical studies and well-test analysis.
4. Modeling of these field cases will be made using our numerical model. This will (1) validate our model, (2) possibly suggest new crucial experiments that should be done, and (3) possibly indicate optimal implementation procedures for the hot water storage concept.

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PROPERTIES AND BEHAVIOR OF ROCK-FLUID SYSTEMS AT HIGH TEMPERATURES AND PRESSURES

W. H. Somerton

INTRODUCTION

The objectives of this project are to determine the physical properties and behavior of rock-fluid systems under environmental conditions encountered in geothermal reservoirs or in other subsurface thermal operations. Because these properties are difficult to measure and require a great deal of time for each measurement, a second objective is to develop models and correlations which will permit estimation of properties and behavior from other more easily determined characteristics of the system. These relations should then be useful in modeling subsurface reservoir behavior.

This project provides rock properties data for other Earth Science Division projects. In particular, thermal data have been provided for several geothermal and similar projects. Data are also available on flow and storage capacity of rocks at high temperatures and other properties of rocks related to borehole stability, subsidence prediction, and interpretation of well-log and geophysical data.

In earlier work, a good deal of equipment and techniques for measuring rock properties has been developed. Several models and correlations of rock behavior have been developed; they are being improved as new data are obtained.

THIS YEAR'S ACTIVITIES

Principal emphasis in this year's work has been on the thermal properties and behavior of a large range of rock types. These include volcanics, basalts, limestones, and a wide range of sandstones, siltstones, and shales. Some work has also been done on unconsolidated sands (including tar sands) and drill cuttings. These data are being cataloged and tested against previously developed models and correlations. Work is continuing on an improved 3D model of heat flow through multi-fluid saturated porous media to aid in the correlation work. The computer program for calculating specific heats from oxide analysis has been revised and updated so that thermal diffusivity data can be provided for the above rock-fluids systems.

Work was completed on the study of P and S wave velocities at elevated temperatures.¹ The apparatus for measuring these properties simultaneously on fluid-saturated rocks was tested and found to perform satisfactorily. From data generated for several sandstones, it was possible to calculate dynamic elastic properties useful in borehole stability and fracturing studies. The ratios of S-to-P wave velocities were found to correlate well with the degree of liquid saturation, leading to the possibility of detecting vapor-liquid boundaries from borehole velocity measurements. Because the ratio of the velocities squared is directly proportional to Poisson's ratio, this modulus also shows a direct correlation with degree of liquid saturation.

Measurements of fluid flow capacities of rocks at high temperatures are continuing to show a larger than expected effect. Liquid permeabilities are found to decrease by factors of 4 to 5 when the temperature is increased to 200°C. No permanent structural damage appears to occur; air permeability tests before and after heating show no significant change in permeability. The system is being redesigned so that pressure drops will be measured directly across the core rather than with external measurements which require system pressure loss corrections. Further tests will be made to evaluate the brine sensitivity of cores at elevated temperatures.

A new apparatus was designed and constructed for the measurement of both bulk and pore compressibilities at elevated temperatures. From this apparatus, the effects of temperature and pore pressure on rock storage capacity can be determined. This same apparatus may also be used to determine pore and bulk thermal expansions of liquid saturated rocks.

Construction of the new high temperature rock properties apparatus was not started because of the uncertainties of private sector funding. Grant requests were made to three oil companies who had expressed positive interest in supporting this work. These requests were made late in the year and at this writing, no response has yet been received.

ACTIVITIES PLANNED FOR NEXT YEAR

All work described above, with the possible exception of velocity measurements, will be continued in the coming year. Principal emphasis again will be on thermal measurements and correlations with the goal of preparing and publishing a manual on thermal properties and behavior of rock-fluid systems. Continued efforts will be made to improve fluid flow capacity measurements and to gain an understanding of the seemingly excessive temperature effects on permeability. The new apparatus for study of storage capacities will be tested, and by midyear data will be taken and analyzed for the effects of temperature and pore pressure on this property. It is to be hoped that

funding for the new rock-properties apparatus will be complete so that construction may be started early in the year.

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THERMODYNAMICS OF HIGH TEMPERATURE BRINES

K. S. Pitzer, L. F. Silvester, P. Z. Rogers, and J. R. Peterson

INTRODUCTION

An understanding of brines is essential for the technical utilization of many geothermal resources. Consequently, a study of the solution thermodynamics of brine systems, both simple and complex, weak and strong, covering a wide temperature and pressure range, and combining both modeling and experimental work began in 1975.

The initial work involved analysis of existing thermodynamic data on simple electrolyte systems using equations developed by Pitzer and co-workers.¹⁻⁴ The goal of the modeling was to provide a compact set of equations capable of reproducing at various temperatures and pressures the existing data within experimental error up to practical concentrations (~6M) in terms of parameters having physical significance. The modeling equations for NaCl(aq) solutions were integrated into GEOTHERM, an LBL computer program for modeling geothermal power plants.⁵

The program to measure heat capacities arose because of inadequate literature data on electrolyte systems. The experimental program has two goals: (1) to supply data on simple and complex electrolyte systems previously unreported, plus extending existing data to higher temperatures and pressures both along and away from the liquid-vapor saturation curve; and (2) to provide a data base for checking and refining various models.

Although the modeling and experimental work relate directly to electrolyte systems common to geothermal brines, the results are applicable to such areas as biological fluids, battery electrolytes in aqueous and nonaqueous solvents, plating baths, waste effluents, materials corrosion from electrolyte systems, and marine chemistry.

PROGRAM IN 1977

During the period of this report the modeling calculations emphasized sulfuric acid and the rare

earth salts which are the subjects of separate sections below. In addition the work on sodium chloride, reported last year,⁶ was extended to deal with the solubility of solid NaCl and was prepared for journal publication,⁷

A national chemical engineering conference requested K.S. Pitzer to prepare a paper on the origin of the acentric factor and its use in modeling normal fluid properties. This paper⁸ was presented as the opening lecture at the Conference on Estimation and Correlation of Phase Equilibria and Fluid Properties in the Chemical Industry, January 1977. In addition to the history and original rationale of the acentric factor, a brief review was given of recent developments in this area.

The development and testing of a high temperature flow calorimeter continued during this period. Various problems in control and measurement were overcome but at a rate limited by the personnel time available. Further improvements are required before satisfactory measurements will be possible but we believe these are feasible.

Sulfuric Acid

In contrast to a strong acid, such as hydrochloric, only the first dissociation of sulfuric acid is complete. For our modeling calculations, the equations for the partial dissociation of the bisulfate ion HSO_4^- were added to the regular set of equations for the ions present. The primary data set included results for three electrochemical cells over the temperature range 0°-60°C together with water vapor pressure and heat of dilution data for 25°C. Our analysis covered the composition range from 0 to 6 molal. In each of the cells, the H^+ activity was measured with a hydrogen electrode; that of SO_4^{2-} was determined by lead, lead sulfate; mercury, mercurous sulfate; or lead dioxide, lead sulfate electrodes, respectively.

There is no difficulty in obtaining concordant results for the range above 0.1 M but conflicts between data arise for the very dilute solutions. In this range, results were considered also for a fourth electromechanical cell which measured mixed H_2SO_4 -HCl solutions and used the silver, silver chloride electrode. While the conflicts remain and alternative parameters were reported, the preponderant evidence favors the parameter set including a dissociation constant of 0.0105 for HSO_4^- at 25°C. Either set of parameters reproduce satisfactorily all data above 0.1 M; hence, there is no real uncertainty for many practical applications.

The numerous equations and parameters are now published⁹ along with the results of several secondary calculations made possible with this treatment. Rabindra N. Roy, a visiting scientist in the summer of 1976, participated in the work on sulfuric acid.

Rare Earth Chlorides, Nitrates, and Perchlorates

In a very extensive series of papers Spedding and associates have presented various thermodynamic data for the nitrates, chlorides, and perchlorates of most of the rare earths. While excellent comparative treatments of the results for any one series are given in these papers, it seemed to us to be of some interest to fit a general array of these data to a single type of equation. We have considered the osmotic coefficient, the heat of dilution, and the volumetric data for all of the chlorides, perchlorates, and nitrates. Thus, in effect, we consider the Gibbs energy and its temperature and pressure derivatives. The parameters obtained are useful for various thermodynamic calculations and will be especially valuable for mixtures where the other components have been treated in the same system.

The equations for activity and osmotic coefficients and for enthalpies have been published.⁷ For the volumetric properties the derivation is similar to that for enthalpy, but the measured property is the density rather than the heat of dilution, and this yields the absolute rather than the relative apparent molal volume. The additional term, the partial molal volume of the solute at infinite dilution V^0 , must be evaluated. One has, then,

$$\phi V = \bar{V}^0 + v|z_M z_X| (A_V/3b) \ln(1+bl^{1/2}) - 2v_M v_X RT(mB_{MX}^V + m^2 C_{MX}^V) \quad (1)$$

where

$$B_{MX}^V = (\partial \beta_{MX}^{(0)}/\partial P)_{I,T} + (\partial \beta_{MX}^{(1)}/\partial P)_{I,T} \times (2/\alpha^2/1) [1 - (1+\alpha)^{1/2} \exp(-\alpha)^{1/2}] \quad (2)$$

$$C_{MX}^V = 1/2 (v_M v_X)^{1/2} (\partial C_{MX}^0/\partial P)_{I,T} \quad (3)$$

The density is related to the apparent molal volume by the expression

$$d = \frac{1000 + M_2 m}{(1000/d_0) + \phi V m}$$

where d_0 is the density of the pure solvent and M_2 the molecular weight of the solute. The Debye-Hückel parameter for volume is

$$A_V = -3A_\phi RT[3(\partial \ln D/\partial P)_T + (\partial \ln V_w/\partial P)_T] \quad (5)$$

where the last term is the negative of compressibility of the solvent. The equations for the volume and the dielectric constant for water which were adopted earlier were used to calculate A_V . The value of A_V is 2.626 cc $kg^{1/2}$ mole $^{-1/2}$ for water at 25°C.

The specific parameters for each rare earth salt were evaluated by least squares from the original data of Spedding et al.¹⁰ together with any other published data¹¹ which was judged to be of comparable accuracy. For the chlorides good fits were obtained up to the highest concentrations, frequently saturation. For the perchlorates and especially for the nitrates, it was possible to get good fits only up to about 2 M and the final calculations were based only on data up to this maximum molality for these salts.

The details of this evaluation process and the resulting tables of parameters are available in LBL Report 6399 and will be published soon.

It is interesting to note the magnitude of the temperature and pressure derivatives in relation to the parent functions. For the important parameter $3/2 \beta^{(0)}$, which is of the order of unity, the temperature derivative is less than 0.0004 K $^{-1}$. Consequently, a 25°C change in temperature causes less than 1% change in $\beta^{(0)}$ or 2% change in γ at 1 M. The pressure derivative is less than 0.00006 atm $^{-1}$; hence a 160 atm change causes less than 1% change in $\beta^{(0)}$. The Debye-Hückel coefficient is somewhat more sensitive to temperature, with 25°C causing a 4% change, but is even less sensitive to pressure. Thus, the properties of these solutions do not change rapidly with temperature or pressure, and the dominant effect is the change of Debye-Hückel parameter with temperature.

In the full report (LBL-6399) and in our MMRD progress report the conclusions of interest to chemical theory at the molecular level are discussed. This research was supported, in part, also by the MMRD program at LBL.

PLANS FOR 1978

In the modeling work for next year our first attention will be given to estimates from the limited data now available for the effects on brine properties of the secondary constituents in typical geothermal brines. We hope also to complete work on sodium chloride at pressures in excess of the saturation curve and to develop a model for NaCl on a constant volume basis. This would be very useful as a basis for extrapolation to even higher temperatures and pressures.

The experimental program will give first priority to the development of the flow calorimeter into a successfully operating unit and to the measurement of heat capacities of brine components and thereafter of typical brines.

As time allows we expect to extend our program into problems in equilibria of solids with aqueous phases. Examples of geochemical interest will be chosen.

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SELECTED ALBITES AS CANDIDATES FOR HYDROTHERMAL SOLUBILITY MEASUREMENTS

J. A. Apps and J. M. Neil

INTRODUCTION

Ground waters contain many dissolved chemical components that result from reactions between mineral phases and the aqueous phase. In spite of the large effort which has gone into the study of these reactions little is yet known of either the equilibrium thermodynamic relations or the reaction kinetics between water and even the most common rock-forming minerals. Such information is required in order to interpret the physical and chemical changes that can take place in aquifers during ground water migration. In particular the problems of exploiting geothermal energy from liquid dominated reservoirs, ground water migration in formations adjacent to nuclear waste storage repositories, and chemical reactions involving the leaching or precipitation of toxic metals from solution all require an understanding of the thermodynamics and the kinetics of rock-water interactions.

The first part of our study will involve the measurement of the equilibrium solubility of albite, $\text{NaAlSi}_3\text{O}_8$, between 25°C and 400°C in sodium chloride solutions of varying ionic strength. Albite is a common rock forming mineral that is found in a wide range of geological environments. However, albites vary both in composition and in the degree of order in their aluminum silicate lattices. The compositional and structural variability result in significant changes in the thermodynamic properties; so the albite chosen for this study should be well characterized in terms of its chemical composition and structural state. Ideally, the sample should be chemically pure and well ordered.

This report describes our efforts to identify a well ordered low albite which would be obtainable in sufficient quantities for our experimental program.

SAMPLE DESCRIPTION AND CHARACTERIZATION

Six different albites were purchased from three mineral supply houses, and one albite was collected from the Franciscan formation in northern California. The sample descriptions are summarized in Table 1.

Moonstone is defined as a semitransparent, opaline lustered, adularia; however, the term is also used for opalescent plagioclase (especially albite). For this reason, sample AB-006 was purchased for analysis.

A potential, local source of high purity material is the vein albite from the Franciscan exposure at Tiburon. However, these veins are not widespread or persistent enough to make it feasible to collect sufficient material for our experimental program. Following a suggestion by R. Coleman, USGS, a large sample of albite was collected from veins in a monolith of glaucophane schist located near Cazadero, California.

Clean and mineralogically pure fragments of albite from each of these samples were prepared for chemical analysis using the procedure described by Hebert and Street.¹ Special care was taken to avoid sodium and potassium loss during the fusion stage. The analyses were made with a non-dispersive x-ray fluorescence spectrometer especially designed for light element measurements. The data

Table 1. Source and description of possible albite starting material.

Sample number	Description	Sample source and supplier
AB-001	Albite, variety Cleavelandite	Bob Ingersoll Mine, Keystone, South Dakota, Minerals Unlimited
AB-002	Albite with biotite	Dungannon Township, Ontario, Canada, Minerals Unlimited
AB-003	Albite	Custer, South Dakota, David New - Minerals
AB-004	Albite	Near Keystone, South Dakota Wards Natural Science Establishment
AB-005	Albite	50 miles SE of Virginia City, Madison County, Montana, Minerals Unlimited
AB-006	Moonstone	India, David New - Minerals
AB-007	Albite, veins from tectonic blocks in the Franciscan Formation	Cazadero, California, collected from location

from 2-minute runs were reduced by a computer code which made absorption and background corrections. The results are reported in Table 2. The samples were compared with a standard made from a mixture of the USGS standards, APG, and PCC, and against USGS standard G2. Errors are reported as the simple root-mean square deviation.

Table 3 shows the results listed in Table 2 recalculated as the number of atoms in a feldspar molecule with 32 oxygen atoms. All elements that are reported in Table 2 as being below a limit of accurate determination are not used in the calculations. The iron is assumed to be in the +2 state and to substitute for Ca in the M site,

Table 2. Provisional chemical analyses for albite (reported as weight percent oxide).

	Sample number ^a						
	AB-001	AB-002	AB-003	AB-004	AB-005	AB-006	AB-007
Na ₂ O	10.6±0.4	11.4±0.3	11.0±0.2	11.3±0.2	10.3±0.2	3.4±0.2	9.7±0.2
MgO	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Al ₂ O ₃	19.7±0.2	24.5±0.2	19.6±0.2	19.8±0.2	19.5±0.2	19.1±0.2	18.7±0.2
SiO ₂	66.8±0.4	58.1±0.4	68.1±0.4	67.9±0.4	67.2±0.3	62.6±0.4	62.8±0.4
K ₂ O	0.28±0.02	1.94±0.04	0.05±0.01	0.15±0.04	0.79±0.02	10.8±0.2	<0.03
CaO	0.43±0.02	1.78±0.03	0.29±0.01	0.20±0.03	0.85±0.03	0.38±0.03	1.11±0.03
TiO ₂	<0.02	<0.04	<0.03	<0.02	<0.01	0.74±0.06	<0.02
Cr ₂ O ₃	<0.02	<0.02	±0.01	<0.01	<0.01	<0.01	<0.01
MnO	<0.02	<0.02	±0.02	<0.02	<0.01	<0.02	<0.02
FeO	0.11±0.03	0.07±0.02	0.07±0.01	.02±0.01	0.48±0.02	0.03±0.02	0.03±0.02
Total	97.92	97.79	99.11	99.37	99.12	97.05	92.34

^a Samples are described in Table 1.

Table 3. Number of atoms in a feldspar molecule on the basis of 32 oxygen atoms $[\text{Na,K,Ca(Fe)}](\text{Al}_4\text{Si(Ti)}_{12})\text{O}_{32}$.

	Ab-001	Ab-002	Ab-003	Ab-004	Ab-005	Ab-006	Ab-007	Amelia albite ^a
Na	3.665	4.070	3.428	3.851	3.544	1.235	3.555	3.963
Mg	-	-	-	-	-	-	-	-
Al	4.141	5.317	4.085	4.100	4.078	4.213	4.164	3.996
Si	11.914	10.701	12.044	11.935	11.926	11.716	11.872	11.989
K	0.062	0.454	0.011	0.032	0.179	2.577	-	0.096
Ca	0.081	0.351	0.054	0.056	0.162	0.076	0.219	-
Ti	-	-	-	-	-	0.130	-	-
Cr	-	-	-	-	-	-	-	-
Mn	-	-	-	-	-	-	-	-
Fe	0.016	0.010	0.010	0.002	0.008	0.005	0.005	-
X	3.824	4.885	3.503	3.941	3.893	3.893	3.779	4.06
Z	16.055	16.018	16.129	16.035	16.004	16.059	16.035	15.99
mole % Ab	95.84	83.32	97.86	97.72	91.04	31.72	94.07	97.6
Mole % An	2.54	7.39	1.83	0.81	4.37	66.20	5.93	-
mole % Or	1.62	9.29	0.31	1.47	4.60	2.08	-	2.4

^a Analysis from Deer, Howie and Zussman.⁴

while the titanium is assumed to substitute for the silicon in one of the T sites. One of the analyses reported by Deer, Howie, and Zussman² for the Amelia Court albite is included for comparison. According to Deer, Howie, and Zussman, a criterion of analytical accuracy is that the sum of the atoms in the M site should be 4 ± 0.1 , and the sum of the atoms in the T site should be 16 ± 0.1 .

STRUCTURAL STUDIES

X-ray powder patterns of the albite samples were obtained using a 114.6-mm Debye-Scherrer diffraction camera with silicon metal as an internal standard. The films were read on a standard light table, and the least-squares refinement code by C.W. Burnham was used to refine the data. Table 4 lists the refined values of both the direct and reciprocal lattice constants as well as the various structural parameters which can be determined

from cell constants. The cell parameters used by Borg and Smith³ to generate a theoretical powder pattern are also included for a comparison.

CONCLUSIONS

Three of the five albites examined (Ab-001, Ab-003 and Ab-004) appear to possess the required degree of purity for our hydrothermal solubility measurements. Ab-002 and Ab-007 have unacceptably high concentrations of calcium and potassium. However, the calcium in Ab-007 may be due to zoisite contamination. Final choice of a suitable sample will be made after further optical and transmission electron microscope studies. An x-ray structure determination will be made on the selected albite to verify that it is ordered, and therefore a low albite.

Table 4. Crystallographic parameters of albites.

	Ab-001	Ab-002	Ab-003	Ab-004	Ab-005	Ab-006 ^a	Ab-007	Ab Standard ^b	maximum microcline ^b
A* (Å ⁻¹)	0.1374	0.1373	0.1377	0.1377	0.1373	0.1301	0.1375	0.1374	0.1299
B*	0.0786	0.0785	0.0784	0.0781	0.0783	0.0772	0.0783	0.0784	0.0772
C*	0.1565	0.1566	0.1567	0.1566	0.1568	0.1534	0.1566	0.1566	0.1539
α* (deg)	86.2986	86.4026	86.4100	86.3047	86.3878	90.3926	86.2817	86.3326	90.441
β*	63.5604	63.5573	63.4877	63.4501	63.5070	64.1537	63.4641	63.5227	64.170
γ*	90.6050	90.4403	90.5799	90.3544	90.4162	92.0488	90.4269	90.4646	92.262
A (Å)	8.1371	8.1417	8.1249	8.1268	8.1463	8.5494	8.1345	8.138	8.560
B	12.7603	12.7816	12.7929	12.8372	12.8069	12.9700	12.0872	12.789	12.964
C	7.1558	7.1493	7.1536	7.1603	7.1452	7.2205	7.1586	7.156	7.215
α (deg)	94.4364	94.2380	94.3027	94.3092	94.2447	90.5564	94.3707	94.33	90.605
β	116.5444	116.5307	116.6106	116.6357	116.5799	115.8491	116.6280	116.570	115.833
γ	87.4789	87.7151	87.5567	87.7534	87.7306	87.9136	87.6617	87.65	87.70
volume cubic cell (Å ³)	662.6456	663.7989	662.8836	665.8311	664.8216	720.0475	664.7321		

^a Ab-006 indexed on maximum microcline.

^b Data from Borg and Smith.

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THERMODYNAMIC PROPERTIES OF SILICATE MATERIALS

I. S. E. Carmichael, S. A. Nelson, and L. Moret

INTRODUCTION

The crust of the earth, in particular that under the oceans, is made up of basaltic lavas, which before crystallizing or congealing, were silicate liquids of rather variable and complex composition. Generally speaking, they are made up of eight major oxide components-- SiO_2 , TiO_2 , Al_2O_3 , FeO , MgO , CaO , Na_2O and K_2O --so that any experimental investigation of the properties of silicate liquids of relevance to nature must be designed to measure the partial molar quantities. Despite the very great importance of natural silicate liquids to many phenomena in the earth (volcanoes, geothermal localities, ore-bodies of certain types), there is surprisingly little experimental data available on their properties, presumably because of the high temperatures involved ($1000^\circ - 1500^\circ\text{C}$). Last year an essential start was made on measuring the heat capacities (C_p) of silicate liquids in the temperature range $1200^\circ - 1650^\circ\text{K}$ and their derived partial molar quantities, which are independent of temperature within experimental error. This study also considered the ascent of basaltic magma, for in many cases what we observe on the surface has been determined as much by the ascent pattern as by the conditions of the source region in the earth's mantle.

ACTIVITIES IN 1977

An apparatus, comprising an electronic balance and vertical furnace, has been constructed to measure the density of a variety of silicate liquids using the Archimedes principle. After thorough testing of thermal stability, operational ease, and calibration, the first measurements are at hand on one silicate liquid. The apparatus will be used to determine density, and its temperature dependence, of a wide variety of silicate liquids, so that the partial molar volumes and expansivities can be obtained; this will allow the data to be extended to natural silicate liquids of all types.

Many silicate liquids, when cooled quickly, form a glass, metastable with respect to crystals, but each with its own reproducible and unique properties. In solids, Al undergoes a change in co-ordination with oxygen at high pressure, for in $\text{NaAlSi}_3\text{O}_8$ crystals it is tetrahedrally co-ordinated, but in high pressure $\text{NaAlSi}_2\text{O}_6$, it is octahedrally co-ordinated. The same effect should be present in liquid $\text{NaAlSi}_3\text{O}_8$, and a number of samples were quenched to a glass from 1500°C and in the pressure range 1-60 kbars. One way in which this co-ordination change could be manifested is in the heat capacity at moderate temperatures (to

avoid annealing), for the heat capacity of Al_2O_3 in sixfold co-ordination is greater than in fourfold co-ordination. Our preliminary results so far show that change in C_p with pressure decreases up to 40-50 kbars, but that the 60-kbar sample has a larger C_p than the 1-bar sample.

The common mineral quartz, SiO_2 , undergoes a transformation near 848°K with an enthalpy change of approximately 290 cal/mole. It has been known for 20 years that the inversion temperature varies with the temperatures of growth, but no data were available at that time on the latter. We have collected quartz crystals from a wide range of known temperatures of growth, both natural and synthetic, and it appears that the α - β inversion temperature is indeed inversely proportional to the growth temperature; this is probably due to solid solution of Na, etc. We have found that there is a very good correlation between the inversion temperature, the volume of the unit-cell (which decreases slightly with increase in foreign ions in solution), and the growth temperature. It appears that easily measurable properties of quartz, particularly that grown above 848°K , may be used as a geothermometer.

PLANNED ACTIVITIES FOR 1978

In addition to continuing the density measurements, an apparatus has been designed and partially built to determine the sound wave velocity in silicate liquids. The intention is to determine the adiabatic compressibility of silicate liquids, and its temperature dependence, on the same compositions as have been used for density measurements. Eventually we hope to obtain partial molar compressibilities (isothermal), their temperature dependence, which together with the volume data should allow a complete description, apart from co-ordination change effects, of the volume of all varieties of natural silicate liquids in the P-T field in which they occur. As a successor to the study of heat capacities, we intend to study other compositions in order to obtain partial molar heat contents in the liquid state. It is anticipated that about 20 compositions will be analyzed by neutron activation to determine the major components in order to check the effect of foreign ions on the properties of natural quartz.

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STUDIES OF MAGMATIC MATERIALS

F. Asaro and H. V. Michel

INTRODUCTION

The purpose of this study is the adaptation of high precision techniques of chemical measurement to problems in geochemistry, geothermal studies, and problems relevant to storage of nuclear wastes. It should permit more accurate determinations of the thermodynamic quantities such as distribution coefficients of elements between lava melts and crystals and also offer new ways of measuring temperatures of lava chambers.

The project started on a rather small scale in 1973 and has undergone considerable modification since then.

In the prior years many lavas and crystal inclusions had been measured by neutron activation analysis for about 30 trace, minor, and major elements. Although lava measurements were reliable, crystallized material from the lava and specific minerals separated from the lavas or nodules in them appeared to contain extraneous inclusions or impurities.

1977 ACTIVITIES

In this last year, separation techniques in use on the U.C. Berkeley campus have resulted in purer samples of crystals and mineral separates. Measurement techniques of neutron activation analysis along with better sample preparation techniques improved to the extent that differences in chemical abundances due to fractionation of minerals within a sample bottle are obvious.

In the neutron activation process material of unknown composition is placed in a neutron flux, and the neutrons cause stable isotopes of the various elements in the unknown to transform to excited or radioactive species. Many of these species or their radioactive daughter products will have characteristic radiations, usually gamma rays, which can be measured subsequent to the irradiation. The amounts of the different elements are determined by comparison with amounts of characteristic radiations emitted by standards of known composition. The precision and accuracy of measurement depend on the care with which irradiation conditions are controlled and calibrated. They also particularly depend on the care with which the gamma ray spectral measurements are made. Generally precise determinations necessitate: irradiation and measurement of standards and unknowns in the same configuration; selection of appropriate gamma rays for study and removal of spectral interferences with these gamma rays; and determination of losses of data in counting equipment as a function of counting rate. In addition, if a small part of a sample is removed for analysis, then the sample must be more homogeneous in the abundances of the elements of interest than their precision of measurement. Otherwise the precision is wasted.

Table 1 shows the abundances of four of the most precisely measured elements in a basalt analyzed by neutron activation methods described above. Also shown are measurements by x-ray fluorescence and wet chemical methods. Included in the table are the estimated (1 standard deviation) errors. The agreement is consistent with the errors. Thus the uncertainties in the neutron activation measurements are about 1% or less for elements shown. In addition, three different techniques give the same answer when the work is carefully done. This neutron activation analysis is part of a measurement system in which about 50 elements are searched for by INAA, about 40 are usually detected in materials with compositions similar to the earth's crust, and about 30 are measured with good precision.

Table 1. Basalt abundances as measured by different techniques.

Element	Basalt abundances, %		
	Neutron activation analysis	Wet chemistry ^a	X-ray fluorescence ^b
Na	2.34 ± 0.015		2.35 ± 0.04
Fe	9.67 ± 0.08	9.69 ± 0.06	9.76 ± 0.12
Al	7.16 ± 0.08		7.27 ± 0.04
Ti	1.65 ± 0.02	1.64 ± 0.02	1.57 ± 0.05

^a I.S.E. Carmichael

^b H.R. Bowman and R.D. Giauque

The precision of trace element measurement can be evaluated by comparison of neutron activation results from different laboratories on nearly identical samples. Table 2 shows a comparison of the measurements by the Hebrew University of Jerusalem and the Lawrence Berkeley Laboratory. The abundances of three elements - Eu, Sc, and Ta - in samples of a fired clay and rhyolite (a siliceous material erupted in the later stages of volcanism) are tested in Table 3. The agreement is excellent from one point of view as the two laboratories agree within about 3% on elements with abundances of the order of 1 ppm.

From another point of view the agreement is not perfect. The errors due to counting radioactivity (1 standard deviation values) are also included in Table 2, and the two values for scandium differ by nearly 6 standard deviations for the rhyolite. Although this might be due to actual differences in composition between different

Table 2. Trace element abundances as measured at different laboratories by neutron activation analysis.

Element	Abundances, ppm		
	Fired Clay	Rhyolite	Laboratory
Eu	1.468 ± 0.022	0.045 ± 0.007	H.U. ^a
	1.498 ± 0.013	0.047 ± 0.005	LBL ^b
Sc	20.08 ± 0.04	3.049 ± 0.012	H.U. ^a
	20.10 ± 0.06	2.954 ± 0.013	LBL ^b
Ta	1.336 ± 0.024	2.055 ± 0.033	H.U. ^a
	1.33 ± 0.01	2.01 ± 0.01	LBL ^b

^a Hebrew University (see Ref. 1)

^b Lawrence Berkeley Laboratory (see Ref. 1)

Table 3. Precision of neutron activation analysis from six nearly identical samples.

	RMSD, %	Standard deviation	Procedural
		of counting error, %	uncertainty, %
Sm	0.23	0.14	0.18
	0.27	0.09	0.26
Sc	0.30	0.20	0.22
	0.26	0.20	0.17
Mn	0.33	0.29	0.16
Ce	0.51	0.33	0.39
Fe	0.58	0.43	0.39
	0.57	0.37	0.43
Eu	0.49	0.43	0.23
Ta	0.56	0.49	0.27
Average	0.41		0.27

splits of the rhyolite, it seems more probable that one or both institutions are making a small error in their scandium measurements. Table 3 shows a limit on the precision of measurements made at our laboratory. The root-mean-square deviations for the 10 most precisely measured radiations in six samples is 0.41%. If the standard deviations due to uncertainties in counting gamma rays are removed, the average remaining uncertainty is 0.27%. Although this may be due in part to actual variations in abundances in the six samples, it seems most likely to be due to unknown problems in the Berkeley measurement system. By cross-checking measurements with other techniques and laboratories we hope to approach 0.27% as our actual precision for the best measured elements.

It is worth noting that unless care is exercised in the selection and preparation of samples, one portion of a roughly ground rock sample may have a much different abundance for some elements than an adjacent portion.

Next, applications of neutron activation analysis to problems in geology will be considered. In the northwest United States in the region of the Columbia River Plateau, basalt flows have been ejected periodically over many millions of years. They have formed layers that total several thousand feet in depth; each layer is somewhat homogeneous chemically. Such basalts are considered as possible repositories for commercial radioactive wastes.² In studies aimed at determining the feasibility of each storage, the ability to make a positive identification of a sample (of a drill core) with a specific flow is useful. The major elements have been used with some success for this purpose. Even the inclusion of a few trace elements, however, makes the assignments more definitive as will be shown next.

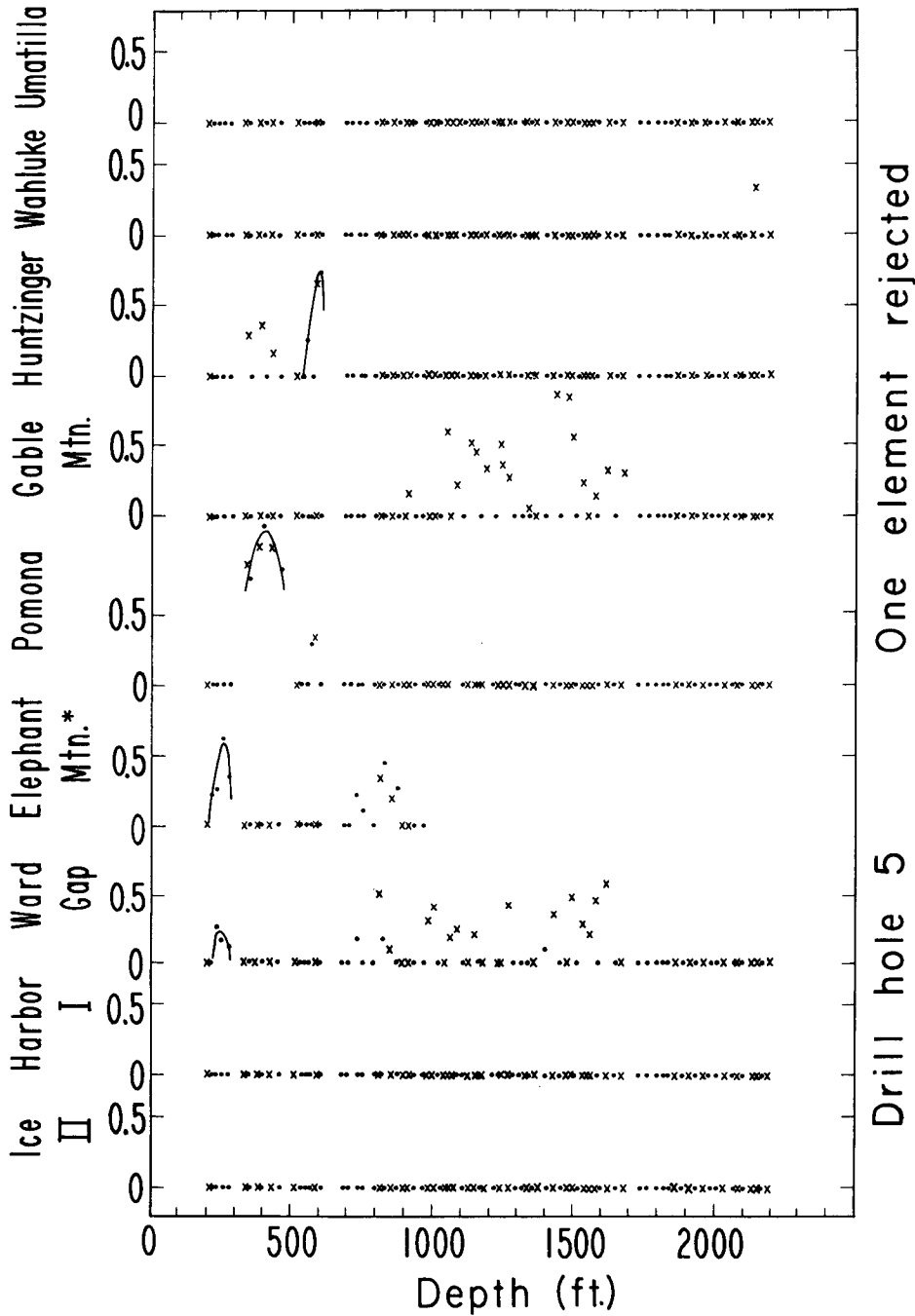
The Atlantic Richfield Hanford Company (ARHCO), which has now become Rockwell Hanford Operations, sampled the Columbia River Plateau basalts in a number of reference areas.² The samples were chemically analyzed by atomic absorption and usually by neutron activation. These data were used to form reference groups of known flows. Each flow was designated by a mean value and a standard deviation for each element considered. ARHCO had in addition drilled several boreholes into the Plateau basalts and sampled the cores about every 20 or 30 ft. The core samples were analyzed in the same way as the reference samples but fewer neutron activation analyses were made.

The correlations of about 80 samples from one of these boreholes (DH-5)³ are shown in Figure 1 with each of the nine reference flows. The abscissa is the depth from which the samples were taken and the nine ordinates are the correlation values. These values equal $1.5 - \sqrt{\chi^2/(n-2)}$ where χ^2 has its conventional meaning and is summed over $n-1$ elements. The element whose abundance agrees the poorest is rejected. The lowest value of the correlation is taken as 0. In Figure 1, data which include neutron activation analysis for four trace elements as well as atomic absorption measurements on nine major and minor elements are represented by dots. Atomic absorption data alone are represented by x's. There are three prominent correlations in the top 600 ft but also a few ambiguities. Many of the correlations below 700 ft would probably be reduced with high precision trace element analyses on both reference and borehole samples.

The effect of trace element measurements on a much greater proportion of the samples is indicated in Figure 2 which shows data from another borehole, DDH-3. There were no ambiguities in these data for the first 1100 ft. In fact, all of that data can be compressed into one graph. As seen in Figure 2, there are four distinct flows with no overlap. The probability of an error in assignment to one of the flows (Pomona) was calculated to be less than 1 in 10¹⁰ with certain restrictive

assumptions. Lower flows, even with four trace elements measured, have many ambiguities as seen in Figure 3. It is possible that these data could

be correlated much more definitively if a much larger number of trace elements were used in the analysis.



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Figure 1. Correlation diagrams for rock samples from upper part of borehole DH - 5. Data points indicated by "x" - eight major elements and one minor element (Ba) included in the correlation. Data points indicated by "•" - an additional four trace elements (Cr, Eu, Sc, and Co) included in the correlation.

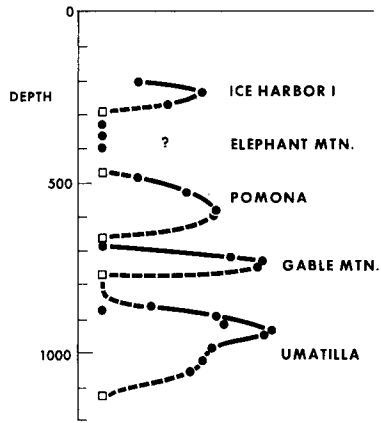


Figure 2. Correlation diagram for rock samples from upper part of borehole DDH - 3. Data points indicated by "●" - 13 major, minor, and trace elements included in the correlation. Data points indicated by "□" - correlations are so small samples are not basalts.

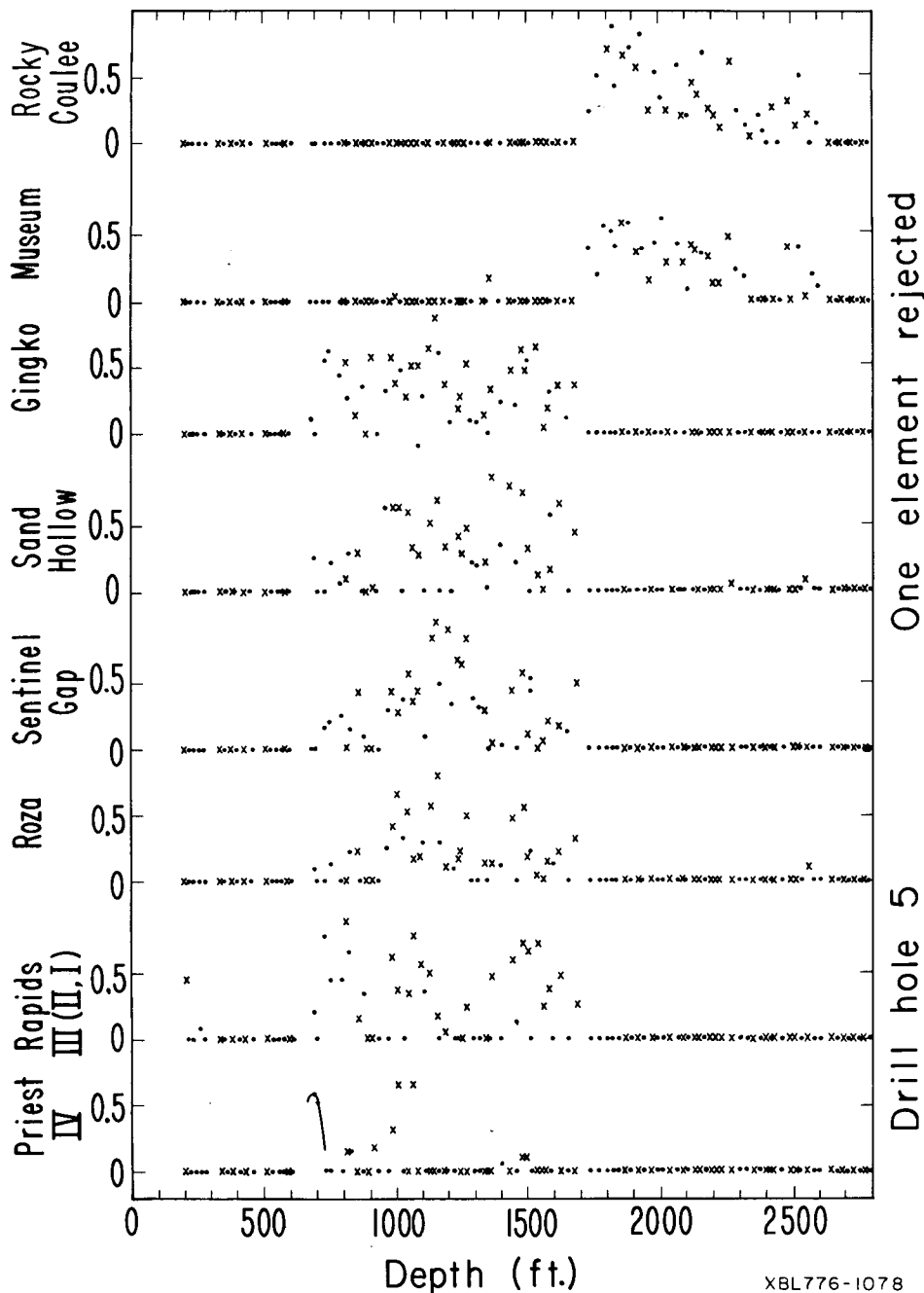


Figure 3. Correlation diagrams for rock samples from middle part of borehole DH - 5. The meaning of the symbols is the same as in Figure 1.

The measurement methods studied here apply to fossil fuel studies (raw and spent oil shales and oily waters), studies of distribution of trace elements in aquifer systems, and fingerprinting of rhyolites for stratigraphic dating (in collaboration with the U.S.G.S.).

Next year the effect of sample fractionation between sampling and measurement will be studied. High precision measurement techniques will be applied to fingerprinting of basalts to determine if different flows can be better distinguished by these methods.

IN-SITU STRESS MEASUREMENTS

T. V. McEvilly and J. Wang

INTRODUCTION

In laboratory experiments, changes in the state of stress of rocks typical of crustal composition produce measurable changes in elastic properties. It follows that a technique for precise measurement, in situ, of changes in elastic properties of crustal rocks would have potential in monitoring subsurface stress changes. Clearly, applications exist in the areas of geothermal reservoir changes, underground waste disposal effects, dam-induced seismicity, earthquake risk at critical facility sites, and in other less spectacular subsurface processes. By 1974, using seismic waves from earthquakes and explosions, seismologists had demonstrated a capability to detect changes greater than about 10^{-2} in average velocity along a "path of convenience," that is, a source-to-receiver path of undetermined geometry. However, the available precision was insufficient for detecting changes in average velocity over a small zone at depth despite attempts to do so by changing source and receiver locations.

It was clear that precision and stability of measurement had to be improved by 1 to 2 orders of magnitude, and that the best possible system would be based on current seismic reflection technology developed for petroleum prospecting. With support from Continental Oil Company (Conoco), the U.S. Geological Survey, and LBL, a special purpose

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VIBROSEIS (tradename, Conoco) programmable seismic wave source and recording system was fabricated to test the feasibility of precise velocity monitoring using travel-time of reflections from deep discontinuities within the earth's crust. Initial tests in 1976 were very encouraging.

1977 RESULTS

System stability better than 10^{-4} was verified and indications were obtained that tidal stresses (<0.1 bar), as well as shallow stress changes (<1 bar) accompanying creep events on the San Andreas fault, produced detectable changes in velocities. Considerable time was spent in studies of instability sources and methods to eliminate them, so that a long-term accuracy of 10^{-4} can be maintained. The concept as well as the special two-man field system have proved very successful.

PLANS FOR 1978

Research will continue in 1978, but the program support will come from the U.S. Geological Survey, under the Earthquake Prediction Program, directly to the Seismographic Station, Department of Geology and Geophysics, University of California, Berkeley. Routine measurements are being planned to measure and study velocity changes in regard to earthquake prediction.

VISCOSITY OF AQUEOUS SODIUM CHLORIDE SOLUTIONS FROM 0°C TO 150°C

H. Ozbek and S. L. Phillips

INTRODUCTION

The purpose of the National Geothermal Information Resource (GRID) is mainly to compile and evaluate basic data on geothermal energy for electrical and nonelectrical uses. While the larger work covers a number of areas, this report is limited to a critical evaluation of data on the viscosity of sodium chloride solutions at elevated temperatures, pressures, and saturation concentrations. The objective is establishing a databank of published data on basic energy properties of aqueous NaCl solutions covering the ranges of geothermal interest: temperatures to 350°C, pressures to 50 MPa (500 bars), and concentrations to saturation. The present work gives the results of a survey and evaluations of a subset of this databank: that dealing with the viscosity of sodium chloride solutions.

The literature screened in compiling the viscosity data covers the period from 1929 to 1977; data obtained prior to 1929 are contained in the International Critical Tables for NaCl solutions at atmospheric pressure over the temperature range 0°C to 100°C, and concentrations from 0 molal to 5 molal. From 1929 to 1977, researchers generated viscosity data for temperatures to 150°C, pressures to 30 MPa, and concentrations to saturation.

ACCOMPLISHMENTS IN FISCAL YEAR 1977: EVALUATION AND CORRELATION

A comprehensive search of the published literature for NaCl viscosity data was made, and all available copies of the original publications were assembled using the following main sources for literature references: (1) the Department of Energy Technical Information Center's RECON System, which includes the Energy Data Base and Water Resources Abstracts; (2) the International Critical Tables; and (3) relevant journals and reports.

The data selected for correlation are reported experimental values, and do not include either smoothed or calculated data.² All data in this table have been converted where necessary to the ¹²C scale of atomic weights, to the g/cm³ basis for density, to centipoise for viscosity, from molar to molal concentrations, and from relative to absolute viscosity values. The needed water viscosity data were taken from the results of the Eighth International Conference on the Properties of Steam.

The following statistical equation was developed from the experimental data:

$$\eta = c_1 + c_2 \exp(\alpha_1 T) + c_3 \exp(\alpha_2 m) + c_4 \exp[\alpha_3(0.01T + m)] + c_5 \exp[\alpha_4(0.01T - m)] \quad (1)$$

where

$$\eta = \text{viscosity, cp}$$

T = temperature, °C

m = concentration, molality

$$c_1 = 0.1256735 \quad \alpha_1 = -0.04296718$$

$$c_2 = 1.265347 \quad \alpha_2 = 0.3710073$$

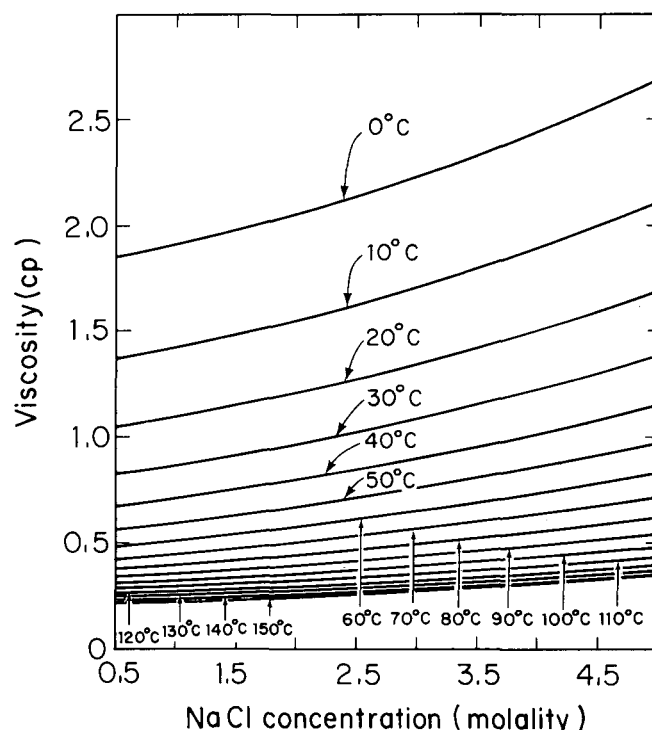
$$c_3 = -1.105369 \quad \alpha_3 = 0.4230889$$

$$c_4 = 0.2044679 \quad \alpha_4 = -0.3259828$$

$$c_5 = 1.308779$$

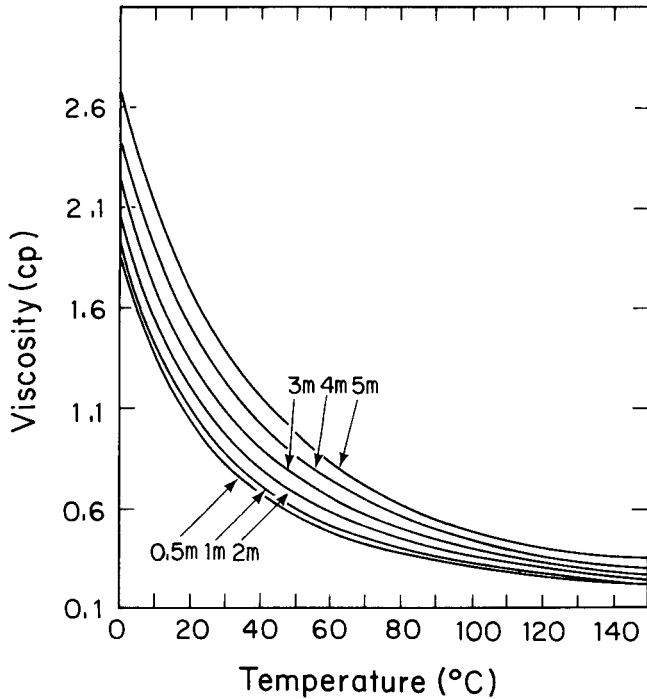
Equation (1) is valid only to pressures of 30 MPa and at temperatures to 150°C.

Figure 1 shows viscosity versus concentration, from Eq. (1), for selected temperatures between 0°C and 150°C. Figure 2 is a plot, based on Eq. (1), of viscosity versus temperature. Data may be interpolated with Eq. (1) to a standard deviation of 1.5% over the entire temperature, pressure, and concentration range (see Fig. 3). Table 1 contains smooth values of viscosity, calculated from Equation (1).



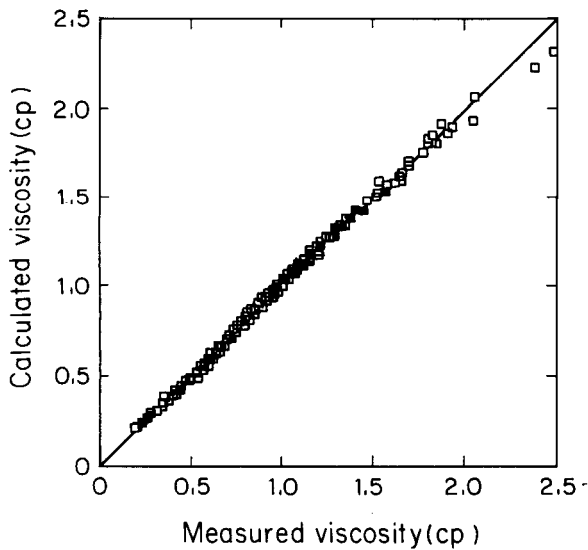
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Figure 1. Viscosity of NaCl solutions versus concentration using Eq. (1).



XBL 783-518

Figure 2. Viscosity of NaCl solutions versus temperature using Eq. (1).



XBL 783-422

Figure 3. Comparison of calculated NaCl viscosity using Eq. (1) with measured values. Deviation for all values is 1.5%.

Table 1. Smooth values of the viscosity of NaCl solutions calculated from Eq. (1).

m NaCl °C	Viscosity, cp					
	0.5	1.0	2.0	3.0	4.0	5.0
0	1.853	1.914	2.058	2.234	2.448	2.701
10.0	1.373	1.428	1.556	1.712	1.899	2.118
20.0	1.049	1.098	1.212	1.349	1.512	1.699
30.0	.827	.871	.972	1.092	1.232	1.391
40.0	.673	.712	.800	.905	1.024	1.158
50.0	.564	.598	.675	.765	.866	.978
60.0	.484	.513	.580	.657	.743	.835
70.0	.423	.449	.507	.572	.644	.719
80.0	.377	.399	.449	.504	.564	.626
90.0	.340	.359	.401	.448	.498	.549
100.0	.310	.326	.362	.401	.443	.487
110.0	.285	.299	.329	.363	.399	.439
120.0	.264	.276	.302	.331	.363	.402
130.0	.246	.256	.279	.305	.336	.376
140.0	.231	.240	.261	.285	.316	.361
150.0	.218	.227	.246	.270	.304	.357

SUMMARY AND CONCLUSIONS

The currently available experimental data on the viscosity of NaCl solutions is sparse and covers mainly pressures from atmospheric to 30 MPa (300 bars), concentrations to saturation, and temperatures to 150°C. A correlation equation was developed which reproduces the experimental data by 1.5% over the temperature range 0°C to 150°C. Additional laboratory measurements on the viscosity of NaCl solutions to 350°C and 500 bars are needed.

PLANNED ACTIVITIES FOR FISCAL YEAR 1978

Thermal conductivity data for aqueous sodium chloride solutions will be compiled and disseminated. Enthalpy data on sodium chloride solutions are expected to be critically evaluated, a correlation expression developed, and the result of this work disseminated as an LBL report. Other basic properties (e.g., free energy) would be compiled in the remainder of fiscal year 1978.

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IN-SITU LEACHING OF URANIUM ORES

J. W. Evans

A major portion of the effort expended on this topic was aimed at defining a suitable research program, submitting a request to ERDA for substantial funding, and completing the design of a prototype experimental rig for use in the investigation.

In situ leaching of uranium ore is now being practiced at approximately a dozen sites in south Texas, Wyoming, and Colorado. A leaching solution (usually ammonium carbonate/bicarbonate solutions plus hydrogen peroxide) is pumped into the underground ore body through several injection wells. The leaching solution passes through the ore body (typically a permeable sandstone deposit) oxidizing the uranium to the hexavalent form and thereby enabling it to pass into solution. The solution is pumped out of the ore body through recovery wells and treated on the surface (usually by ion exchange) to recover the uranium values.

Discussions were held with research and operating personnel of four companies (Intercontinental Energy Company, Anaconda, Mobil Oil, and Atlantic Richfield) involved in in situ leaching, as well as with U.S. Bureau of Mines and ERDA personnel most closely involved in this technology. A visit was paid to an operating mine (Pawnee Mine, ICE) and two conferences on this topic were attended (American Nuclear Congress, Golden, Colo., April 1977; and American Institute of Mining Metallurgical and Petroleum Engineers, Corpus Christi, Texas, September 1977).

A clearly defined problem encountered in the leaching operation is changes in permeability of

the ore body which occur during leaching. Under some circumstances loss of permeability occurs and results in reduced productivity and/or higher pumping costs. The ore body must be "restored" after leaching. This entails removing residual leaching reagents remaining in the ore body by flushing with water or chemical solutions. Permeability loss prior to or during restoration would make this environmentally important step more difficult.

The circumstances under which permeability loss occurs are poorly understood, as is the reason for permeability loss. Hypotheses that have been put forward include blinding of pores by either evolved oxygen bubbles or transported fines, swelling of clay particles within the ores and alternative solution, then precipitation, of various species.

The research program that we are developing at Berkeley is aimed at determining under what conditions such permeability loss occurs and the cause of permeability loss. Similar work is being performed by Westinghouse research laboratories under contract to the U.S. Bureau of Mines. Our proposed experimental approach is similar except that it entails using smaller (and therefore more versatile) equipment. The emphasis will be on the fundamental causes of permeability loss while the Westinghouse contract places no obligation on their investigators to study the causes of the effects they observe.

A sketch of the prototype permeability rig is shown in Figure 1. Ore is to be crushed and

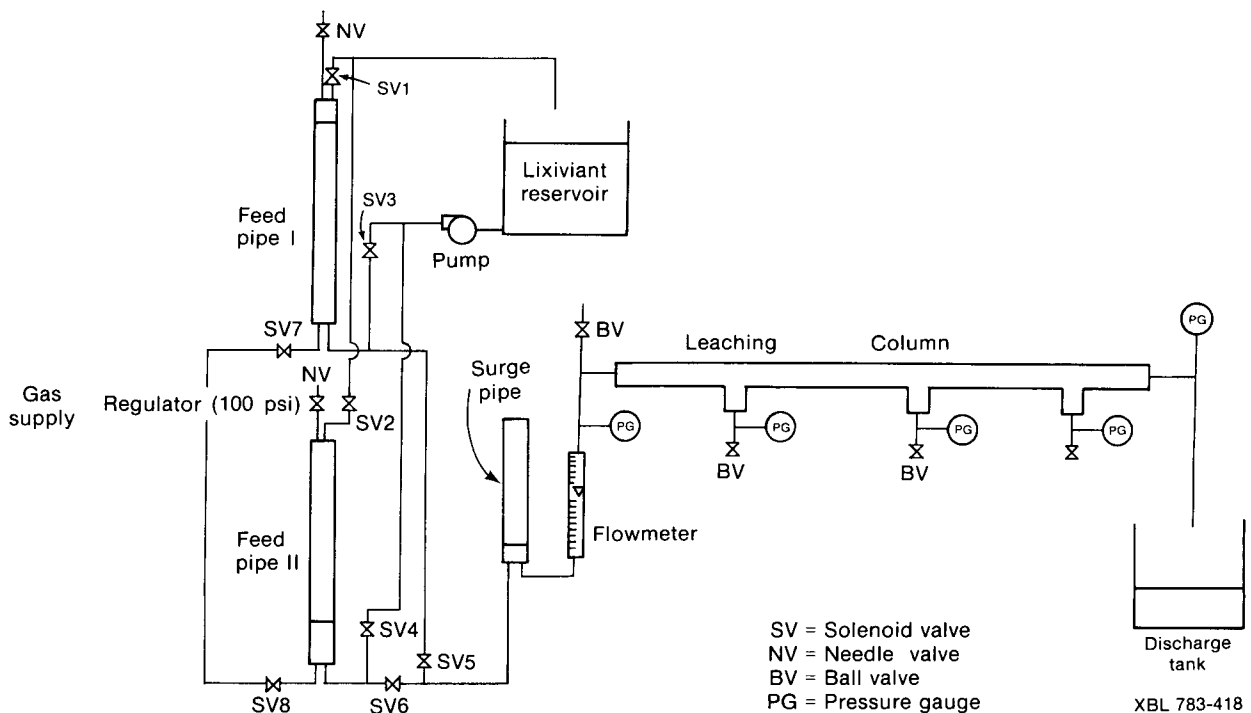


Figure 1. Permeability apparatus for in situ leaching investigation.

packed into Pyrex columns that are 2 in. in diameter and 12 ft long. Solutions will be driven by gas pressure through these columns from one of two 1-in. diameter pipes. A system of solenoid valves (SV) operated by a time switch enables one of the 1-in. columns to be filled by a pump from a reservoir tank while the other column is discharging. Pressure gauges at both ends and along the length of the ore column enable determination of the pressure profile along the column; together with measurement of the flow rate this enables determination of the permeability as a function of time.

A battery of tests (particle size determination, scanning microscopy, BET surface area measurement, etc.) can be used to examine the ore before and after permeability loss in an effort to determine the cause of the loss.

It is hoped that funding will be provided through the Grand Junction Office of the Department of Energy sometime in fiscal year 1978. In the meantime it is planned to build the prototype experimental permeability rig using Program Development Funds.

METHODS FOR DETERMINING THE EQUILIBRATION TEMPERATURES OF MAGMATIC CRYSTALLINE ASSEMBLAGES: TRACE METAL DISTRIBUTIONS

H. R. Bowman, I. S. E. Carmichael, and S. A. Nelson

INTRODUCTION

One of the more difficult tasks in geology is to estimate the temperature at which any crystals grew in a natural liquid, as in a rock, particularly if the crystal growth occurred in the range 750^o-1300^oC. Unfortunately, magmas show a compositional range, so that those which typically inhabit the 800^oC range are quite different in composition from those which crystallize at higher temperatures. Therefore, there are two effects to be isolated, one due to the change in composition of the solid-solutions, and the other due to temperature.

1977 ACTIVITIES

We decided to make a preliminary investigation of the distribution of the rare-earth elements, as determined by neutron activation, between various crystals in lavas which crystallized over a wide temperature range. In Figure 1 the concentration of the elements in the solid phase divided

by that in the liquid is shown for a number of rare-earth elements found in a variety of co-existing solid-solutions.

Clearly, the magnitude of the distribution coefficient, plotted on a logarithmic scale, increases with decreasing temperature, and indeed the pattern, or shape, of these curves also changes. By formulating these results as exchange equilibria, taken in conjunction with experimentally determined values of the equilibrium constant, it is possible to decipher the compositional dependence of the distribution of elements between crystals as the major components in the crystals change. This is of great importance in any attempt to unravel the equilibration temperatures of minerals in mantle fragments brought to the surface by volcanoes. Only in this way will it be possible to map the isotherms at depths up to 150 km, the region that has the greatest effect on the earth's surface and on those parts of the crust which are of economic and social importance.

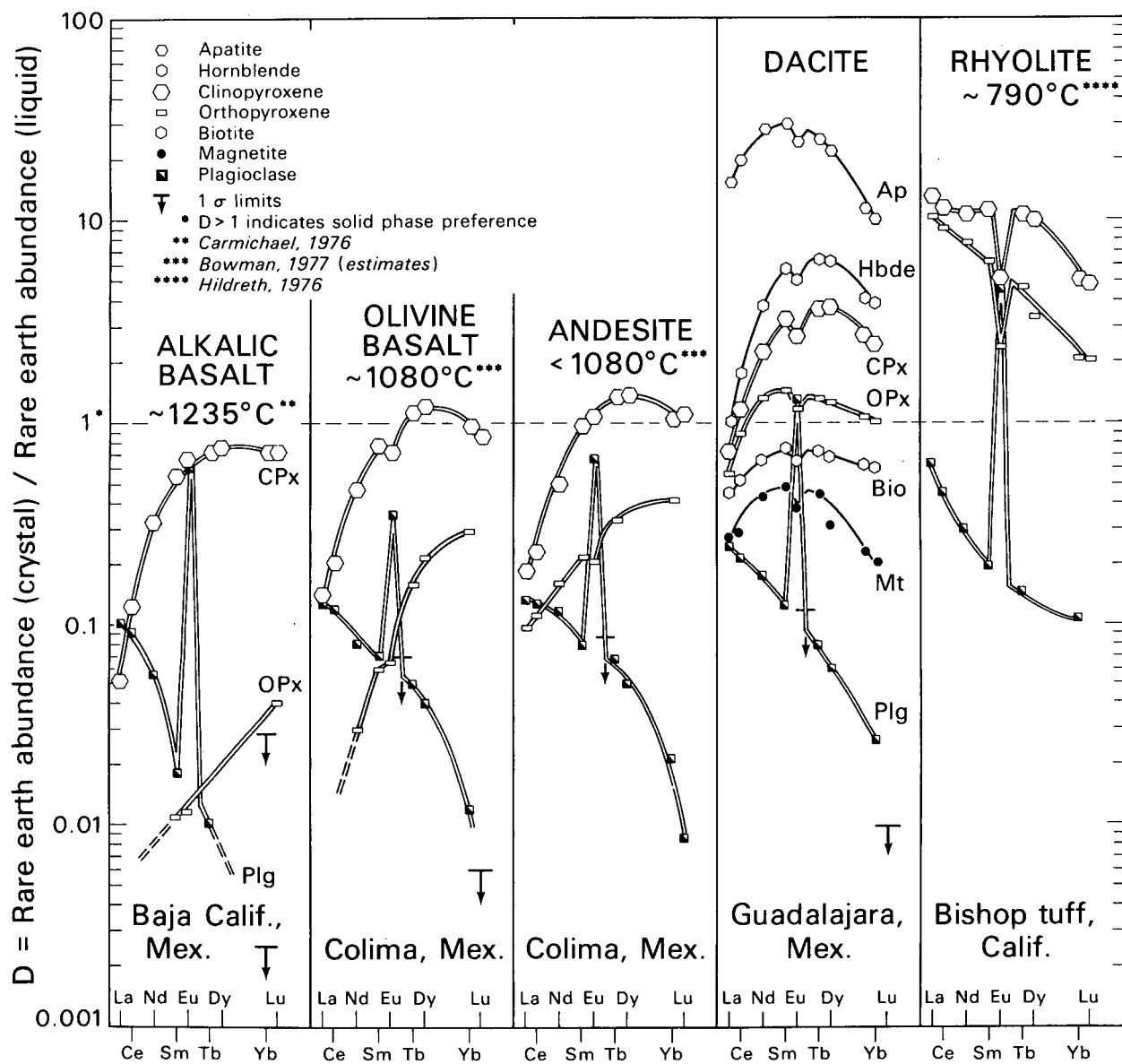


Figure 1. Neutron activation analysis: rare earth element distribution (D) between crystals and liquids for various lavas. Lava temperatures decrease from left to right.

ELECTROCHEMICAL STUDIES ON THE DISSOLUTION AND FLOTATION BEHAVIOR OF ORE-PYRITE AND COAL-PYRITE

D. W. Fuerstenau

INTRODUCTION

The necessity for the increased use of coal for energy has increased the interest in research on the desulfurization of coal as well. Thus far, the two most common methods used to deal with the problem of sulfur in coal are (1) flue gas desulfurization after combustion and (2) physical mineral beneficiation processes for separating mineral matter (ash and pyritic sulfur) from coal before combustion. The first method has the disadvantage that it creates the problem of disposal of spent sulfate slurries at the power plant site; in addition, there are other operational problems, such as corrosion and clogging of scrubbing towers. Sulfur removal at the mine site is interesting but the process is limited not only by the degree of liberation that can be obtained between coal and mineral phases by comminution, but also because the relatively fine particles produced cannot be readily handled. However, recent increased interest is being directed toward the desulfurization of coal by flotation or by leaching methods, and some of the new processes have been tried on a pilot plant scale. A study of the mineral/solution interface and the surface-chemical reactions taking place at this interface is important to further development of both leaching and flotation processes.

First of all, it is known that the mineral pyrite (the main inorganic sulfur-bearer in coal) is a semiconductor and hence some of the reactions occurring at the pyrite/aqueous interface are of an electrochemical nature. Therefore, investigation of the electrochemical nature of pyrite in aqueous systems of interest to the leaching and flotation of coal were undertaken. Some studies on the flotation of pyrite from coal have suggested that coal-pyrite behaves differently from ore-pyrite. Hence, in this brief research program, the electrochemical technique of linear-sweep voltammetry (LSV) was used to attempt to discern any difference between coal-pyrite and ore-pyrite.

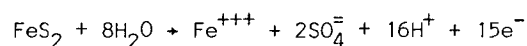
EXPERIMENTAL METHODS AND MATERIALS

A single crystal of ore-pyrite and a hand-picked pyrite sample occurring near a coal seam were used for the study. The coal-pyrite has coal particles well interspersed within it, as observed by optical and scanning electron microscopy. The crystal structure of both samples was analyzed by x-ray diffraction methods and was confirmed to be that of pyrite. "Energy dispersion analysis by x-ray" (EDAX), and "electron microprobe analysis" both showed the chemical composition to be close to that of pyrite, at least within experimental limitations of these two analytical techniques. The three-electrode system used for LSV studies had saturated calomel and platinum electrodes as the reference and auxiliary electrode, respectively. The studies included polarization experiments in aqueous solutions used in leaching and flotation processes.

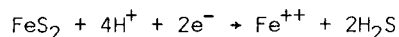
RESULTS AND DISCUSSION

The rest potential (the open-circuit potential) of both types of pyrite electrodes change from a high of about +800 mV to a low of about +20 mV as the pH is changed from 1 to 13. A higher positive potential indicates noble behavior of the mineral at low (as well as neutral) pH's compared to other sulfide minerals, although at higher pH's pyrite tends to be more active. The voltammograms for both coal-pyrite and ore-pyrite in all of the aqueous inorganic systems studied have similar characteristics in terms of occurrences of current peaks at different applied potentials. This suggests that probably in aqueous inorganic solutions there is little difference in the behavior of ore-pyrite and coal-pyrite, and the small differences in our case may have resulted merely from the polycrystallinity of coal-pyrite and/or the presence of the coal phase in it.

In 0.1 N sulfuric acid solution, a cathodic peak at about -0.3 V and an anodic peak at about +0.9 V was observed in the voltammogram. An anodic attack at a low pH may occur by the following reaction:



and cathodic attack, which leads to the production of ferrous ions and hydrogen sulfide gas, by the reaction:



The evolution of hydrogen sulfide was observed in our experiments in a qualitative way (identified by the smell of the gas).

Sulfide minerals, including pyrite, can be leached at low pH's by the addition of Fe^{3+} ions, which provide a highly oxidizing medium. We carried out LSV studies in 0.1 M ferric chloride adjusted to pH 1.8 by the addition of hydrochloric acid, and the results are similar to those in the sulfuric acid studies, except that the peak currents are considerably higher. This indicates high reaction rates. Also, one cathodic and one anodic peak were observed at -0.4 V and +0.4 V, respectively -- peaks which were absent in the experiments with sulfuric acid. These peaks are probably due to the redox couple $\text{Fe}^{2+}/\text{Fe}^{3+}$.

For studies in alkaline medium, 1 N and 0.1 N sodium hydroxide solutions were used. The results were similar for both cases, except that the rest potentials of electrodes were higher and currents lower for the dilute solutions. The voltammogram for 0.1 N sodium hydroxide is shifted to more anodic potentials compared to the 1 N solution; that is, it required higher anodic over-potential to carry out the reactions at lower concentrations of NaOH. No distinctive peaks were observed in the voltammograms and the potential scan range which could be used was very short, mainly because of

the active nature of pyrite at higher pH values. The reaction products of alkaline dissolution of pyrite have been suggested to be sulfate and ferric oxide. We were not able to confirm this through our experiments.

Comparison of voltammograms obtained for pyrite electrode in the presence and absence of potassium ethyl xanthate (a pyrite flotation collector) in 0.025 M borate solution indicates that dixanthogen is probably formed at the electrode surface.

As mentioned earlier, we have attempted to understand the leaching and flotation behavior of

pyrite in various aqueous media from the point of view of studying the electrochemical reactions. Specifically, we compared the behavior of ore-pyrite and coal-pyrite under similar experimental conditions to ascertain whether the two types of pyrite involve different electrochemical reactions at the mineral-aqueous interface. Our studies have indicated that electrochemically speaking there is no significant difference in the leaching and flotation behavior of ore-pyrite and coal-pyrite. We feel that the difference in the flotation behavior observed by some researchers for coal-pyrite and ore-pyrite was probably due to the presence of some coal particles, attached to the coal-pyrite particles, in the sample used for their studies.

DETERMINATION OF THE PROPERTIES OF SOILS AND SOFT ROCKS BY IN-SITU MEASUREMENTS

J. K. Mitchell and W. C. B. Villet

INTRODUCTION

Accurate identification and characterization of subsurface conditions are essential for the economy and success of construction both in and on the earth. Reliable information on subsurface conditions in general, and specific geotechnical parameters in particular, is needed for the analysis of problems related to the utilization of underground space, subsidence, energy storage and extraction from the ground, and groundwater pollution owing to extraction or injection of fluids into the ground.

Traditionally, the required data have been obtained through sampling and testing of so-called "undisturbed" samples. There exist severe limitations to this approach, however, arising from such associated problems as sample disturbance, changes in sample properties due to unloading and exposure, and the difficulties attached to preventing or re-establishing in the laboratory the in situ state of stress as well as temperature, chemical, and biological environments. These limitations have become particularly evident as the volume of underground and offshore construction has increased. The need for reliable and improved techniques for site characterization and for the in situ determination of engineering properties of soil and soft rock has emerged as one of the most important geotechnical problems.

This research project, which was initiated in spring 1976, is concerned with the identification, development and implementation of new and promising approaches for site characterization and in situ measurement of soil and soft rock properties. A closely related objective is the evaluation of presently available techniques.

ACCOMPLISHMENTS IN FISCAL YEAR 1977

Emphasis in the research project thus far has been on the evaluation of existing techniques and

on the development of a new approach based on the acoustic response of the ground during penetration at a constant rate.

Planned activities for 1977 were as follows:

1. Completion and publication of a state-of-the-art report on in situ measurement of soil properties
2. Further study and evaluation of the suitability and potential of remote and geophysical measurements to provide data from which quantitative measures of the mechanical properties of soil and rock may be deduced
3. Further study of acoustical measurements during quasi-static cone penetration tests as a basis for determining soil type and properties

Presently used in situ methods for the determination of soil and soft rock properties include:

1. Permeability tests by pump-in, pump-out and piezometer methods, employing both transient and steady state techniques
2. The Standard Penetration Test
3. Cone penetration tests of various types, including both static and dynamic methods
4. The Vane Shear Test
5. The Iowa borehole shear test
6. Pressuremeter tests
7. Plate bearing tests
8. Screw plate tests

9. Hydraulic fracturing tests
10. Down hole and cross hole seismic methods

A report has been completed and is in press. It presents a description of the various testing techniques, the evaluation theories or correlations for obtaining geotechnical parameters, an assessment of the suitability of each method for the determination of specific geotechnical parameters and their potential for future development. Extensive references are listed, and the report should serve as a definitive starting point for anyone interested in the subject.

Several less direct techniques for the in situ determination of site characteristics and soil properties are currently being studied. These predominantly involve applications of geophysical methods and include:

1. Seismic methods, including refraction, reflection, cross hole, and down hole techniques
2. Resistivity surveys including focused probes
3. Gravimetric methods
4. Magnetic methods
5. Nuclear methods - surface and subsurface
6. Radar methods
7. Spontaneous or self potential methods
8. Electro-magnetic methods
9. Thermometric methods
10. Remote sensing techniques such as GEOSAT

As a result of these studies a report is being drafted which will present the theory of each technique briefly, describe testing methods and evaluation theory, assess the current suitability of each technique for determining specific geotechnical parameters, and assess their potential for future development. It is intended that this report will serve as both a guide to what is currently feasible and as a stimulus to future research.

A penetrometer has been designed which measures the acoustic response of soils during quasi-static penetration tests. Permanent records are

obtained using a tape recorder. The influence of soil properties and penetration procedure on frequency, amplitude, variability in both frequency and amplitude, and the distribution of acoustic energy over the frequency range of the generated signals are being studied.

Emphasis in the acoustic cone research is on:

1. Evaluation of the manner in which soil properties and testing procedures influence the acoustic signal generated during a quasi-static cone penetration test
2. Development of bases for the recognition of soil type, and the deduction of soil properties, from acoustic response spectra
3. Development of means for locating and evaluating very thin seams, which may have a large influence on ground stability, included between or within thicker zones.

It is believed that analysis of the sound generated during penetration may form the basis of an improved method for in situ soil "recognition," profile definition, and property characterization.

Support for a greatly expanded level of research on the acoustic response characteristics of soils during penetration has now been received from the National Science Foundation.

It may therefore be seen that the research project progressed very much as planned for 1977. The delay in publication of the state-of-the-art report on in situ measurement of soil properties has resulted from the time needed for extensive revision, editing, and typing of the manuscript. The report should, however, be available soon.

PLANNED ACTIVITIES FOR FISCAL YEAR 1978

It is understood that additional LBL support for this research will be limited and that the study will be phased out during fiscal year 1978. The main objective of the LBL-supported work will be completion and publication of the report on geophysical methods for site characterization and quantitative evaluation of soil properties.

HIGH PRECISION MASS SPECTROMETRY

M. C. Michel

INTRODUCTION

The interest in isotope measurements in geologic and cosmologic research has increased recently through the discovery of remarkable isotopic anomalies in several elements contained in a select group of carbonaceous chondrites, principally the one large meteorite, Allende. No definitive interpretation is possible as yet, but the new data will clearly put much-needed experimental restraints on theories of the origin of the solar system.

A less startling, but perhaps equally significant discovery has been that the earth's mantle shows strong evidence of preserving isotopic inhomogeneities for long periods of time, a fact that opens the possibility of a new technique for the study of mantle processes. Again, the data are difficult to interpret and workers in the field disagree on many details, but we are probably at the beginning of a new episode of research.

Each advance in isotope geochronology seems to increase the emphasis on achieving higher and higher precision in the experimental data, either to improve an existing technique (such as the Rb-Sr system) or to expedite the use of a new and potentially more useful system (such as the ^{147}Sm - ^{143}Nd pair).

Last year we began a project to adapt our 5-ft radius isotope separator to high precision mass spectrometry through the simultaneous collection of several isotopes of the same element. This far from novel method has been standard for light element isotope ratios and would be even more advantageous for the heavier elements, most of which are not gaseous and therefore require ion sources that are inherently less stable in ion output. However, practical considerations have made it difficult to use this method on any but the largest mass spectrometers.

Preliminary work in fiscal year 1976 convinced us that it would be possible to measure isotopic ratios to a precision of one part in 10^5 using essentially commercially available amplifiers and digitizing equipment with relatively straightforward, custom designed auxiliary circuitry. Results in fiscal year 1977 have substantially verified that conviction although some work remains before an operating system can be tested. The remaining problems seem to be tractable.

ACTIVITIES IN FISCAL YEAR 1977

Since we originally intended to be able to apply the results of the mass spectrometric development to specific problems, we also included in our research plans the ability to do contamination-free chemical separations on geological samples, and isotopic dilution chemical analyses of selected elements such as rubidium.

The various activities planned and pursued during the year were as follows.

Ion Source Development

As explained in an earlier report, the ion source needed for the high precision work places rather stringent requirements on materials, design, and ease of fabrication (cost). Proceeding through about three basic design changes, a cavity-type, directly-heated thermal ion source was developed and tested which seems to meet the requirements as well as they can be defined at present. These are ease of loading, emission of ions from a well defined area, relatively constant ion output at constant temperature, high efficiency, and reasonable cost. Testing of the source shown in Figure 1 was done with strontium, but it should be adaptable to many other elements.

Contamination-Free Chemistry

In spite of considerably less than ideal laboratory facilities, a simple HCl eluant ion exchange technique was developed to separate rubidium and strontium from geologic samples, in forms and amounts suitable for isotopic ratio determinations and chemical analysis by isotopic dilution. Introduction of extraneous material of the same elements is well below the levels that would interfere with the measurements. For typical samples of strontium totaling a few micrograms, the strontium blanks are below 10^{-10} g.

Isotopic Dilution Analysis

Using another smaller mass spectrometer, a method of chemical analysis by isotopic dilution was developed and tested; the method allows analysis to a precision (but not necessarily accuracy) of about 0.2%. Testing was done with rubidium; other elements may deviate slightly in precision.

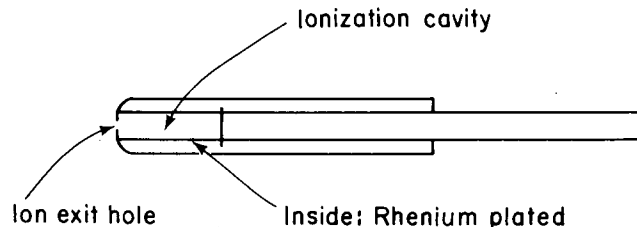


Figure 1. Cavity type thermal ion source. Material is tantalum except as noted.

Design of Four-Channel Data Readout for Isotope Separator

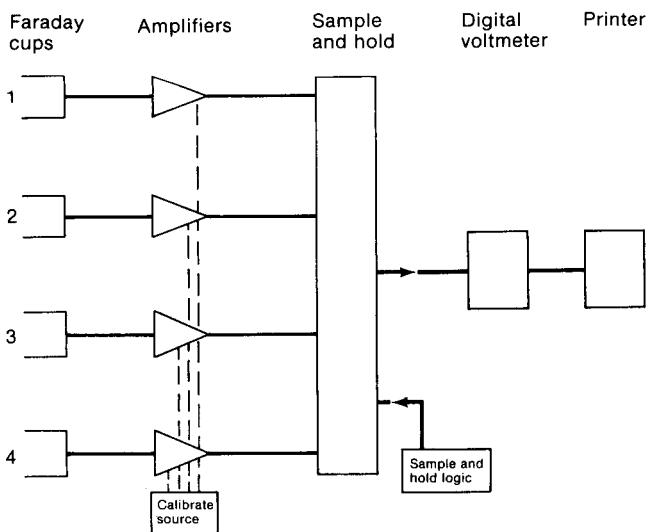
The greatest effort has gone into the design of a four-channel readout system that should have the ability to measure simultaneously four isotope beams to a precision of one part in 10^5 or better. Figure 2 shows a block diagram of this basically simple system. It is for the moment assumed that the input signals to each Faraday cup are properly representative of the relative abundance of each isotope (this may not be true for several experimental reasons which we will ignore at present).

Each Faraday cup signal is amplified by a separate amplifier which is essentially an impedance matching device, producing a low impedance voltage output proportional to the input current at very high impedance. Each channel could now be measured simultaneously by four voltmeters and the appropriate ratios calculated. For convenience the voltmeters are usually fast reading digital voltmeters which are easily arranged to read simultaneously.

It is obvious that several critical properties of this system determine the precision with which the isotopic ratios can be measured. These properties are: (1) the reproducibility, linearity, and time and temperature dependence of the amplifier gains and zero offsets (output with no input signal); (2) the linearity and short-term stability of the voltmeters; and (3) our ability to make all four amplifiers and voltmeters respond identically for reasonable times to arbitrary identical inputs.

It became apparent that at least two commercially available small solid-state amplifiers would be suitable for this work. Extensive tests of their stability, time drift, and response to overload and noise sources showed that, given proper care, they have acceptable properties. They must also, as shown in the block diagram, be capable of calibration to identical gains by switching the same constant current source quickly among the four amplifiers and adjusting the gain to give identical outputs (note that knowledge of absolute signal sizes and gains is not necessary). This last requirement is clearly possible, and once calibrated, the stability is sufficient to make repeated measurements before recalibration is necessary. However, the best switching procedure has not yet been determined, it being very easy to generate a few microvolts of e.m.f. by various means common to switches and relays. For example, surface deformation of most metals can generate small signals which decay away slowly enough to present a serious problem in calibration of the amplifiers.

Assuming that the amplifiers are capable of giving an output accurately reflecting the Faraday cup inputs, we still must now measure each output voltage to a high relative precision. Accuracy is fortunately not critical, since no existing digital voltmeters can meet our requirements. However, all such instruments have much better short-term stability than accuracy, so if one is willing to intercalibrate them, it would be possible to make the desired measurements. To avoid this trouble and reduce the cost of the system, we developed a very simple capacitive sample-and-hold circuit which can collect data simultaneously from the four amplifier channels, preserve it and be sequentially read by a single digital voltmeter; this eliminates many problems. This circuit, controlled by a logic system, allows four capacitors to charge to the output of the four respective channel amplifiers. The level of voltage at any one time will be proportional to the average beam intensity input to the Faraday cup for that channel, and if all channels are also disconnected from their respective amplifiers at the same time, the voltage on each capacitor will likewise be proportional to the input beam. If the decay time-constant is long enough (several days) there will be time to measure all four capacitors sequentially with the same voltmeter and record the data on the output printer, or send it directly to a small computer for data processing. The results are a good approximation to a true simultaneous measurement of the four isotope beams. Note that the further integration of the beam currents by the sample-and-hold circuit in no way affects the precision of the isotope ratios; in fact it helps to eliminate the effect of beam fluctuations on the data.



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Figure 2. Block diagram of four-channel data system.

Table 1 shows the noise levels or statistical uncertainties associated with the various parts of the system, as determined by a variety of test measurements on mock-ups of parts of the system. As is shown, a precision of 6 or 7 parts in 10^6 is possible. Because the test systems were less compact than the final design, and had many other disadvantages, we can expect a little improvement in the complete system, although there may be a

Table 1. Summary of noise and/or measurement uncertainties in a multiple channel readout system, based on individual component tests with simulated signals. Nominal signal = 1 V.

Source	Level, μV
1 Amplifier noise	2.5
2 Calibrate signal noise	2.5
3 Sum of 1 and 2	3.5
4 Collector noise/leakage	2.8
5 Sum of 3 and 4	4.5
6 Sample and hold error	< 1
7 Digital voltmeter error	< 1
8 Residual temperature coeff. error	< 1
9 Total	4.8
10 Error in ratio	6.8
11 Error after correction for fractionation	7.6

small absolute error that we cannot predict. Since recognized isotopic standards are already used to eliminate possible absolute biases between different laboratories, this will be disappointing but not a serious problem, even if it develops.

RADON IN SUBSURFACE WATERS AS AN EARTHQUAKE PREDICTOR, CENTRAL CALIFORNIA STUDIES A. R. Smith and H. A. Wollenberg

We have investigated whether variations in the Rn-222 content of subsurface water can be a useful earthquake prediction parameter in California. Using NaI(Tl) crystal γ -ray spectrometry, high sensitivity high-precision measurement techniques and instrumentation have been developed for both laboratory analysis of discrete samples and continuous monitoring at field installations. Precision and reproducibility were regular within 1-3% in the laboratory; precision of 1% was achieved from counting periods as short as 10 minutes at field stations.

These techniques were applied to determine the validity of the radon method. A discrete sampling program was conducted in the Oroville, California area for 20 months during the aftershock sequence that followed the August 1975 earthquake of Richter magnitude ~ 6 . Through use of a local volunteer organization, we maintained a daily sampling schedule at several wells throughout the study period, and obtained approximately 3000 samples. Since July 1976, a continuous monitoring

As soon as the requirements were firmly recognized, several commonly available digital voltmeters were tested in our laboratory with the same test systems used to determine the noise characteristics; one was selected for purchase.

PLANS FOR FY78

We plan to finish the four-channel system and test it extensively with strontium ion beams for which much data are available on the composition of various isotopic standards. In addition to demonstrating the success of our approach we can use this system to search for beam optical effects on the isotopic ratios to learn how sensitive the data are to minor malfunctions of the mass spectrometer, and therefore how reliable the entire system is over long periods of operation.

We plan to extend the work to the samarium-neodymium system at the first opportunity as well as to investigate the application of this system to lead and other element isotopic measurements.

Finally we will investigate the limitations on precision in the completed system to see what approach might be necessary to improve the precision to an even higher level. If a relatively non-fractionating ion source can be developed, an ultra high precision system would be of use in determining possible natural isotopic variations that are essentially linear with mass (as most physical processes will produce) as opposed to variations resulting from nuclear decay.

station has been in operation at San Juan Bautista in Central California along an active segment of the San Andreas Fault.

The program continued in 1977 at a much reduced level, as dictated by severe funding restrictions. Thus, sampling of wells during the aftershock sequence of the Oroville earthquake was terminated in April 1977. The field program consisted of a monitoring station, located on the San Andreas Fault near San Juan Bautista, operated through assistance from the U.S. Geological Survey National Center for Earthquake Research. The Oroville data show apparent correlation between some radon changes and subsequent seismic activity, but does not yet represent conclusive evidence for validity of the method. The San Juan Bautista data suggest there is correlation between some periodic radon changes and earth tides. In both cases, data interpretation has been complicated by the severe drought conditions.

The major effort of 1977 was to prepare a comprehensive summary report for the study period 1975-1977. Computer codes were written to assist in analysis of data to search for correlations between radon level changes and nearby seismic activity, as at Oroville. These results were reported at the American Geophysical Union 1977 Fall Meeting at San Francisco, December 1977.

STRESS FLOW BEHAVIOR OF FRACTURED ROCK SYSTEMS

R. L. Taylor, P. A. Witherspoon, H. M. Hilber,
and J. van Greunen

INTRODUCTION

The mechanical behavior of fractured rock masses is sensitive to the effects of water flowing through the discontinuities of the system. There is evidence of a connection between seismic activity and the increase in pore pressure within the earth's crust. Low to medium magnitude earthquakes have been reported in connection with the filling of what are called "seismic dams."¹⁻⁴ The possibility that a change in fluid pressure in a fractured system might cause the release of tectonic stresses has been indicated by events at Rocky Mountain Arsenal Well near Denver, Colorado.⁵⁻⁷ More recently, evidence has been gained at the Rangely, Colorado oil field that fluid injection has triggered small earthquakes along a fault.⁸⁻¹⁰ Thus, the concept is now developing that if earthquakes can be caused by injecting fluids into the subsurface, then perhaps the appropriate control of fluid pressures in the fracture system of a fault can lead to a method of earthquake control.

The feasibility of such a concept must be carefully investigated using a combination of analytical-numerical and experimental approaches before it can be developed into a practical model. As a first step, the concept should be tested by numerically and experimentally analyzing the behavior of simple laboratory models. Hence, numerical methods have to be developed such that a broad class of laboratory tests and field situations can be simulated.

Recently several attempts at developing appropriate computational models have been reported.¹²⁻¹⁷ In previous studies a two-dimensional finite element formulation has been developed to simulate quasi-static processes in systems of deformable fractured rock.¹³⁻¹⁵ The dynamic nature of slip mechanisms limits the applicability of the quasi-static model to study of pre-failure conditions. Dietrich developed a dynamic finite element model for a single fault that undergoes slip under the influence of tectonic and predetermined fluid stresses.¹⁸ This model was not designed to incorporate the interactive processes between the fluid pressure, the fracture deformations, and the stresses in the rock.

Since the available computational models seemed to be unnecessarily restricted, an effort

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was made in the present study to develop an improved numerical procedure for simulating transient interactive processes in systems of fractured rock.

The goal of the 1-year study was to continue the development of a finite element method computer program to model the dynamic response of two-dimensional systems of fractured rock subjected to injection and/or withdrawal of fluid from the fractures. The original program development was initiated under NSF contract number GK-42776 by the first two authors at the University of California, Berkeley, and is reported in Ref. 19. A second objective was to perform analyses on some typical problems to illustrate the kind of results which can be obtained using the program.

ACTIVITIES

The activities described in this report commenced on 1 September 1976 and ended on 31 August 1977. A summary of the activities is given below.

The equations governing the behavior of fractured rock systems subjected to fluid injection and/or withdrawal are given by the equations of motion for the fractured rock system and the continuity equation for the fluid flow. After discretization using standard finite element methods the resulting nonlinear ordinary differential equations are

$$\underline{M}_S \ddot{\underline{u}} + \underline{K}_S \underline{u} + \underline{K}_J(\underline{u}) = \underline{R} + \underline{B} \underline{P} \quad (1)$$

for the equation of motion and

$$\underline{B}^T \dot{\underline{u}} + \underline{K}_F(\underline{u}) \underline{P} = \underline{Q} \quad (2)$$

for the continuity equation.^{19,20} In the above equations \underline{M} is the mass matrix; \underline{K}_S is the rock stiffness matrix; \underline{K}_J is the internal force vector in the joints; \underline{u} is the nodal displacement vector; \underline{P} is the nodal pressures due to fluid in joints (fractures); \underline{R} is the external nodal forces on the rock system; \underline{B} is the transformation matrix for pressures and velocities; \underline{K}_F is the flow matrix; \underline{Q} is the vector of nodal flows added or removed; $()^T$ indicates the matrix transpose, and nonlinearities are indicated by an argument on the appropriate term. Finally, the subscripts S, J, and F refer to solid rock, jointed rock, and fluid, respectively. The coupling between fluid pressure

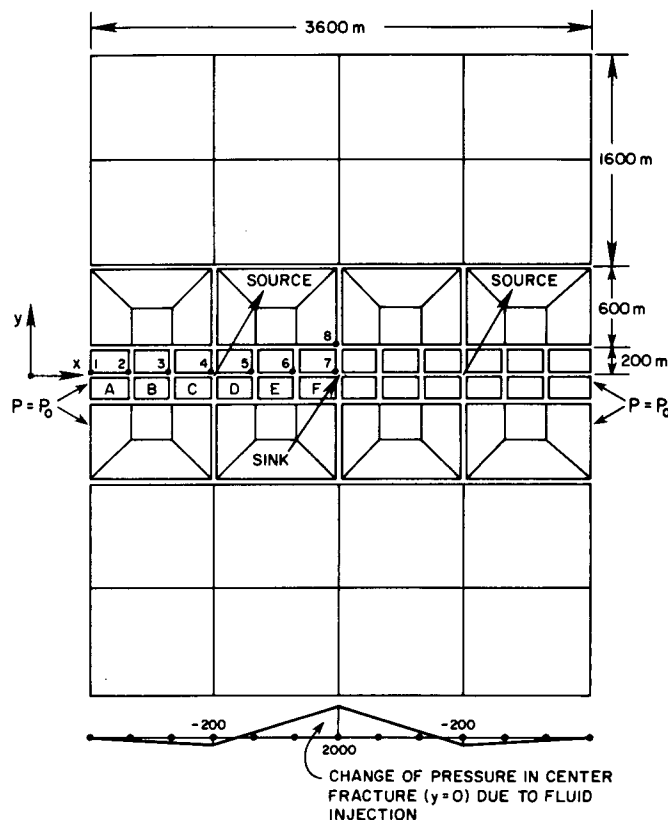
and displacements is clearly seen in the above equations. We solve the above non-linear equations as follows. The time is discretized and derivatives are replaced by the one-step Newmark formulas.²¹ The nodal displacement and fluid pressure at each discrete time are chosen as the primary dependent variables, resulting in a coupled set of non-linear algebraic equations to be solved at each time step. Due to the strong coupling we solve these by first getting the fluid pressures based on the current values of the nodal displacements. Using these pressures we then solve for new estimates to the nodal displacements. The process is then repeated until convergence is achieved, usually in very few cycles through the equations. At each step, stick-slip conditions are checked for each joint; for joints that have shear greater than the dynamic frictional resistance, slip is allowed. The finite element program developed for this analysis is called FAULT and can handle general two-dimensional problems.

One of the difficulties encountered in solving problems was the situations in which joints with extremely small apertures existed. In this case the opening and closing of the joint caused very rapid changes in pressure [this is the $\underline{B}^T \dot{\underline{u}}$ term in (2)] which are unlikely to occur in real situations. In this case a surge (or change in elevation of the fluid surface) will occur with rather small change in pressures. For this case

we merely ignore the $\underline{B}^T \dot{\underline{u}}$ term in (2). In any future work some improvement is necessary, a surge term should be considered. The surge term is a three-dimensional effect and it may be necessary to have a fully three-dimensional model to consider this case. On the other hand, it may be possible to develop equations for the joints which are analogues to the shallow water equations and still retain the two-dimensional modeling for the jointed rock system.

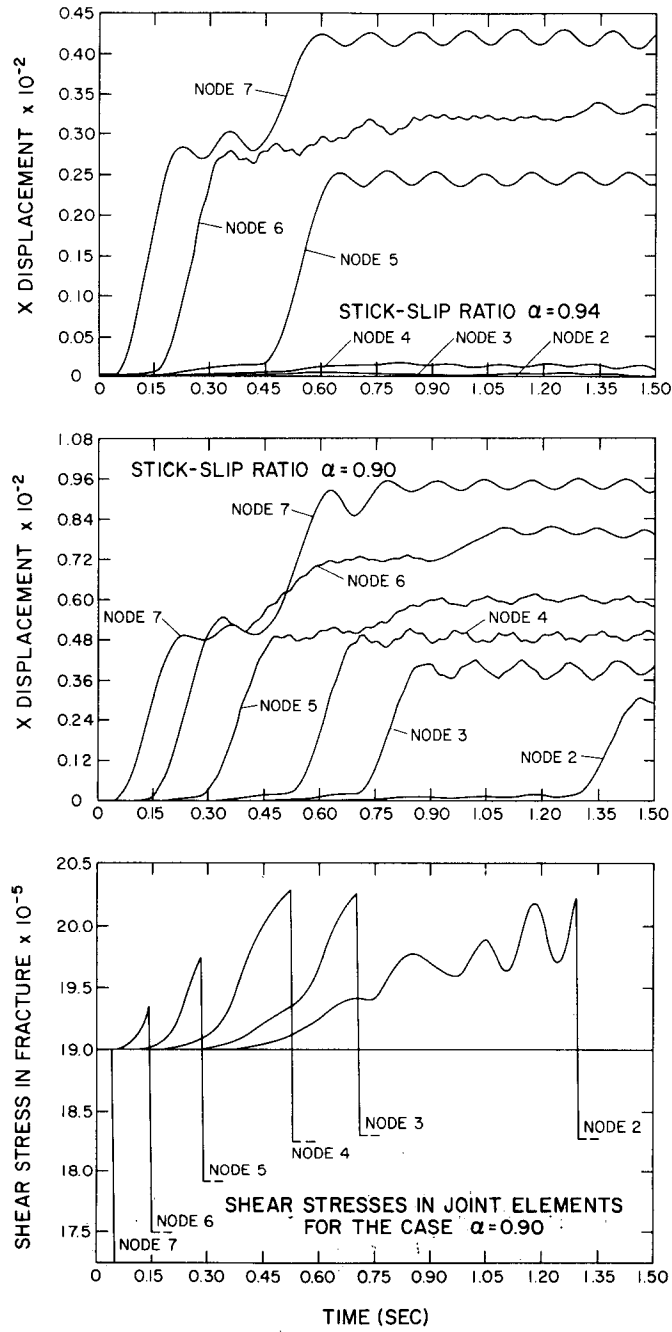
To facilitate use of the program, a graphics package was developed and incorporated into FAULT for use on the LBL system. In addition to mesh plots the package can produce time plots for specified nodal displacements, velocities, accelerations and stresses, as well as fluid pressure and energy quantities.

In Figure 1 we show the mesh of a typical problem considered during the project together with the injection/withdrawal pattern along the principal joint. In Figure 2, the stick-slip characteristics are shown for two static/dynamic friction ratios α . Slip initiates at the static value and continues at the dynamic value until stick again occurs. Figure 3 shows typical displacement velocity and acceleration traces at a node. The resemblance to typical earthquake motions is noted in these traces.



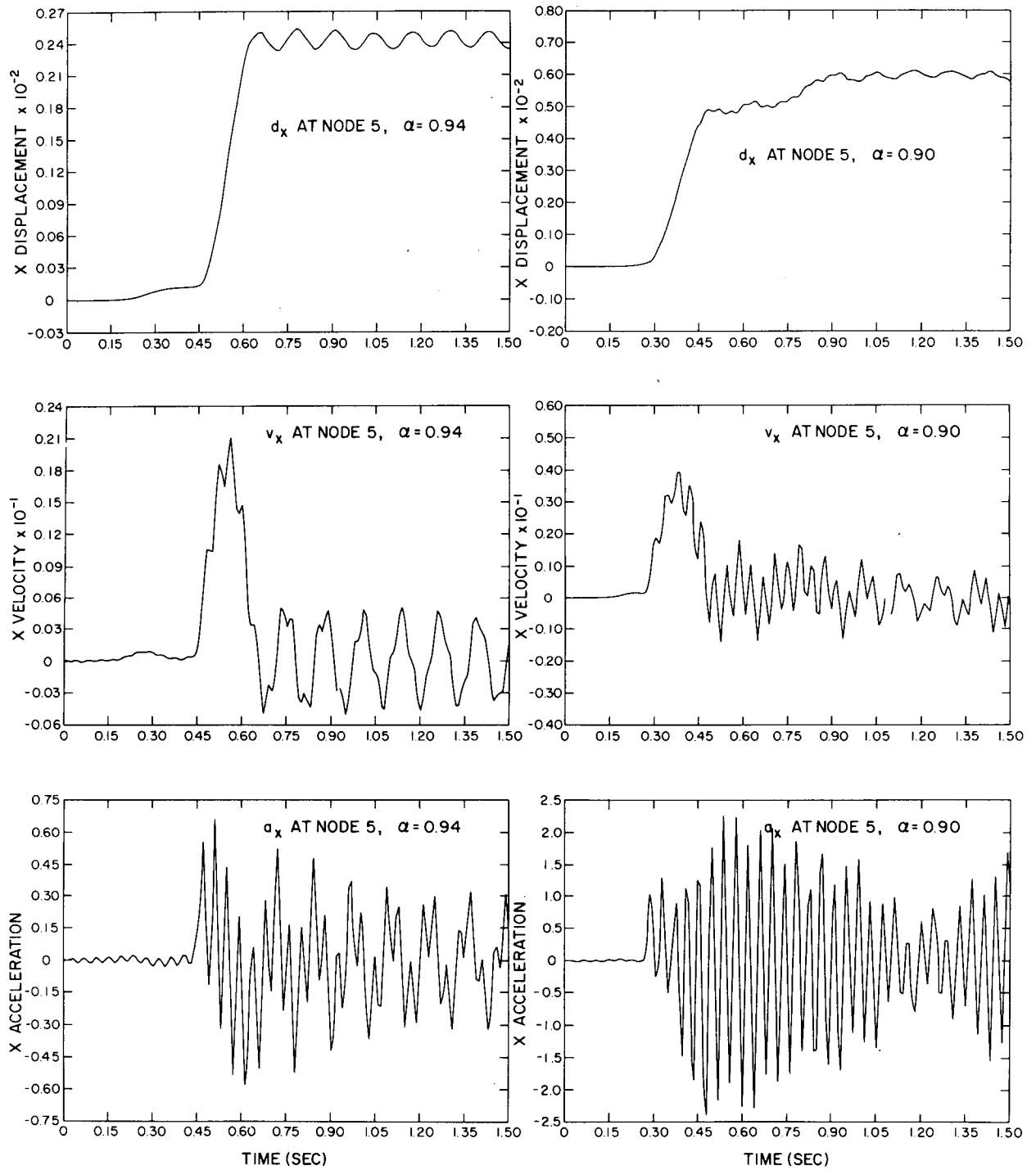
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Figure 1. Finite element mesh of a tectonically stressed straight fault system.



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Figure 2. Displacement histories and shear stress drop at points along central feature.



XBL 779-4812

Figure 3. Displacement velocity and acceleration of node 5 in direction parallel to fault.

In conclusion, we have developed and demonstrated a numerical analysis tool to simulate the dynamic response of two-dimensional fractured rock systems subjected to fluid injection or withdrawal. In addition to demonstrating a possible mechanism for earthquakes, the program can be used to study possible methods for control of earthquakes. Finally the program can be used to generate earthquake records for use in other analysis methods.

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