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FLUID SAMPLING AND CHEMICAL MODELING OF
GEOPRESSURED BRINES CONTAINING METHANE

FINAL REPORT

(March 1980 to February 1981)

Prepared by

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GRI Contract Manager
Leo A. Rogers
Geopressured Methane

July 1982

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4. The fourth part of the document discusses the implications of the findings. It suggests that the results have significant implications for the field of study and may lead to further research in this area.

5. The fifth part of the document concludes the study. It summarizes the key findings and provides a final statement on the importance of the research.

Title	Fluid Sampling and Chemical Modeling of Geopressured Brines Containing Methane
Contractor	Lawrence Berkeley Laboratory University of California Berkeley, California 94720
Principal Investigators	B. Dudak, R. Galbraith, L. Hansen, D. Sverjensky, O. Weres
Report Period	March 1980-February 1981 Final Report
Objective	To design, fabricate, and test a remote sampler capable of returning fluid samples from geopressured wells for subsequent analysis, without leakage and with minimum sample disturbance or alteration. In addition, to review the state of knowledge of geopressured brine chemistry, with special attention to evaluation of computer codes used to model such systems.
Technical Perspective	If the energy available in several forms in the fluids from geopressured formations is to be developed commercially, accurate knowledge of the nature of the fluids is essential to understanding the size of the resource, the effect of production on the resource, and the environmental effects of production and re-injection. The careful analysis needed and the subsequent geochemical modeling and predictions required presuppose a sample that truly reflects the composition of the reservoir fluid, with minimum modification by the sampling itself. Only a remote sampler can return this type of sample with a high confidence level. Later work may allow deduction of this composition from analysis of wellhead samples, but only remote samples will allow one to determine the compositional relationships for a new well. Once such a sample is available, sophisticated geochemical techniques should be used to interpret its chemistry and origin, and to predict the chemical consequences of resource utilization. This requires careful selection and evaluation of geochemical modeling codes and their thermodynamic data bases.
Results	A flowthrough remote sampler for geopressured fluids has been designed, fabricated, and tested. Constructed entirely of the alloy MP35N, it will return to the surface, without leakage and with minimal alteration by the container, about one liter of fluid from any geopressured well where the pressure is below 20,000 psi and the temperature is below 450°F. It has been laboratory and field tested, the latter in a geothermal well at The Geysers, California. The sampler has performed entirely satisfactorily.

A separate review of available information on brine chemistry concludes that selected existing computer codes for modeling brine-rock interaction can be applied to geopressured problems with reasonable modifications, principally by properly extending their thermodynamic data bases. These codes should allow adequate interpretation of in situ brine chemistry, and the prediction of the behavior of geopressured reservoirs under production conditions with acceptable accuracy.

Technical Approach

The sampler design had to take into account conditions of salinity, temperature, and pressure somewhat more severe than oil field brines, where much previous experience in remote sampling has been obtained. It was decided early to avoid sliding seals where possible and a flowthrough sampler was chosen as the best choice for geopressured application. The sampler size was set by the volume of fluid desired (about one liter) and the pressure. To prevent corrosion by the hot brine, the multiphase alloy MP35N was chosen (in spite of its poor machinability) because of generally good experience with it in corrosive environments. To eliminate electrolytic corrosion, all parts in contact with the fluid are of this same alloy, except the O-ring seals (viton). To avoid uncertainty in the time of closure, and to supply adequate sealing force to prevent O-ring extrusion, the valves are closed with energy stored in springs which are set manually at the surface and held open by an electromagnet energized from the surface through the wireline conductor. Reducing this current initiates closure, which breaks the electrical circuit, providing positive evidence of closure at the surface.

Actual field testing was performed in a geothermal well at a depth of about 7400 feet and at a temperature of about 260°F. Laboratory tests at higher temperatures and pressures indicate that the sampler will perform properly in any geopressured well.

Review of the literature of geopressured systems indicates that geopressured fluids are within the range of compositions that should be tractable with present geochemical modeling techniques, although requiring some extrapolation in temperature and pressure. Existing computer codes are capable, with appropriate additions to their data bases to cover the high temperatures and pressures, of predicting the properties of geopressured brines under reservoir conditions. It would be of considerable value to modify one of the existing codes to incorporate the Pitzer theory of electrolyte solutions, which would enable the chemistry of the brine to be modeled accurately under production conditions.

**Project
Implications**

Although the LBL sampler was completed and tested in an autoclave and a geothermal well the associated sampler retrieval equipment was not completed so the system could be used on a DOE geopressured-geothermal brine well. Completing the sampler system and chemical analysis system for use in wells of interest to the GRI co-production of gas and water will be done in a follow-on contract. Whether a second sampler will be built will depend on evaluations of the completed system and the need for it.

GRI Project Manager
Leo A. Rogers
Manager, Geopressured Methane

4. The fourth part of the document discusses the role of communication and collaboration in achieving the organization's goals. It emphasizes the importance of clear communication and the need for all team members to work together effectively.

5. The fifth part of the document provides a summary of the key findings and conclusions of the study. It reiterates the importance of maintaining accurate records and the need for a systematic approach to data collection and analysis.

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PROJECT SUMMARY

The objective of this project was to provide R&D support to GRI in the development of technology for the recovery of natural gas from geopressured resources. The major effort was directed towards the design and fabrication of a downhole sampler, which will provide data on the amount of methane and other gases present, the chemical composition of the brines, and geopressured reservoir characteristics. Another objective was to define the geochemical characteristics of geopressured brines and reservoirs, and to evaluate the utility of geochemical modeling codes in studying the origin, properties, and utilization of this resource. The project scope for this first contract year consisted of four major tasks, each of which is discussed below.

Support for this project was also provided to LBL by the Division of Geothermal Energy, Department of Energy.

TASK 1

The principal objective for the contract year 1980 was to design, build, and test a flow-through sampler suitable for use in geopressured wells. A backup sampler was to be provided, if feasible. The work plan entailed the conceptual design, detailed design, and subsequent fabrication of the sampler. The work plan also included the implementation of a suitable test plan to validate the sampler for use in geopressured wells.

The following tasks were performed during the contract year. The sampler was completed on January 1, 1981, and the specially required tools were completed two weeks later. Two tests were completed. The magnet assembly was laboratory tested in December 1980 to ensure it operated satisfactorily in air at 388°F (the maximum achievable temperature of the oven that was used).

The completed sampler was laboratory tested in February 1981, which verified the satisfactory mechanical and electrical operation of the sampler when immersed in tap water at ambient temperature. The sampler was successfully field tested at the Geysers (Appendix D).

The sampler specifications are:

Overall length	120.24 in. (not including sinker bars)
Diameter	2.25 in.
Dry weight	112 lbs (not including sinker bars)
Sample volume	980 ml (approximate, pending volumetric test)
	All parts in internal and external contact with brine are machined from MP35N alloy cold work bar stock, and have become partially aged as a result of sampler use.
Recommended cable	MP35N monoconductor cable
Maximum bottomhole pressure	No upper limit
Maximum outward differential pressure	25,000 psi at 450°F (pending hydrostatic proof test)
Maximum inward differential pressure	350 psi at 450°F (i.e., the maximum amount by which the external pressure may exceed the internal pressure before the sampler valves are lifted off their seats, causing the sampler to leak.)
Maximum downhole temperature	450°F (500°F+ may be feasible)

Another, duplicate set of materials and speciality items, including a complete magnet assembly, has been prepared for use in a second backup downhole sampler unit of the same design.

The valves close when a holding current of 40 mA, supplied to the sampler valve action release magnet, is halted or if the current falls below this value. An open circuit indicates successful operation (closure) of the

sampler valves. The required power for holding the magnet at safe holding current is a few hundred milliwatts, depending on the coil temperature.

The operational limitations on the sampler are minimal. Any combination of well-head pressure and bottomhole pressure versus well temperature profile is permissible, given the following conditions: The internal pressure of the sampler must exceed the external pressure at all times during the ascent, the stay in the lubricator, and after removal from the lubricator. However, the internal pressure of the sampler must not exceed the external pressure by more than 25,000 psi at any time during its ascent to the surface. The temperature at any time must be less than 450°F. Once filled with oil, the sampler cable head must be kept upright at all times until the sampler has been removed from the lubricator after sampling.

The major technical problems encountered during this contract year were:

- o Producing a satisfactory conceptual design
- o Converting the concepts into a satisfactory design
- o Resolving material and manufacturing problems
- o Scheduling and funding limitations
- o Implementing tests that provided essential and reliable information for validating the design and operation of the sampler.

The objectives for next year are to complete the testing of the sampler. The following tests have been accomplished to date: An autoclave test at Dresser Atlas, in Houston, Texas on March 3, 1981, in which the sampler operated perfectly in brine at 21,000 psi and 400°F; a field test in an Aminoil USA Co. steam well in the Geysers geothermal field on March 12, 1981, in which the sampler obtained a 975 ml brine sample, without problems, from a depth of 7400 feet and at a temperature of 495°F-505°F. Dresser Atlas provided the

wireline services. A hydrostatic proof test is planned that includes O-ring validation using typical geopressured brine at 25,000 psi and 450°F. Successful completion of the hydrostatic test would in LBL's opinion fully qualify the sampler for use in a geopressured design well.

TASK 2

The objective of Task 2 was to consider the design of a second-generation sampler with expanded capabilities for maintaining sample point conditions and making certain downhole measurements. A meeting was held with the Institute of Gas Technology (IGT) to compare sampler capabilities and review the design status of the LBL, IGT, and Gerhardt-Owens samplers. The following conclusions resulted from this meeting.

No particular advantage is to be found in maintaining downhole sample point conditions of temperature for chemical data; downhole measurements of properties like conductivity or compressibility are similarly viewed. Measurements of this type are difficult to make and of uncertain value. It is felt that information needed about such properties can be calculated from sample analyses or measured in the laboratory using simulated brines.

Failure to maintain downhole temperature conditions may not change the contents of the sampler after its valves have closed and would therefore not affect the results of the chemical analysis. Thus, maintaining sample temperature on the way up may be of no great advantage, unless precipitation is likely to occur.

The pH is worth trying to measure under downhole conditions because of its central importance in the chemical characterization of aqueous solutions. Making such a measurement is apparently technologically infeasible at this time, but may be possible in the near future.

Certain downhole measurements would, however, be of substantial value in reservoir characterization and engineering. Important advantages would be derived from having a tool capable of making pressure, temperature, and flow measurements at various points within the formation. Such data would be extremely useful for better understanding the fluid flow characteristics of the reservoir, the contribution of various producing zones, and would help in the prediction of future production behavior. A downhole device which would combine in one tool the capability of taking a sample and at the same time making pressure, temperature, and flow rate measurements would be highly valuable. For maximum value, a downhole sampler should be capable of taking samples from adjacent formations at specific horizons.

A preliminary proposal for development of such a combined tool was submitted to GRI for support in the next contract period, but was not accepted. No effort is currently being given to this concept.

TASK 3

The objectives of Task 3 were to review the state of knowledge of the chemical compositions of geopressured brines, from reservoir to production conditions, and to review codes that could potentially model the brines.

A review of the chemistry of geopressured brines at reservoir and well bore conditions was completed. The conclusion was that about 90 percent of analyzed geopressured brines are chemically well represented by the system $\text{NaCl-CaCl-H}_2\text{O}$ in which the Na:Ca mole ratio is greater than about 9 and the molality of chloride is less than about 2.8.

In order to understand and predict brine-rock interactions in the reservoir it is essential to know not only the brine chemistry but also the host-rock mineralogy and geochemistry. Therefore, available information on

the mineralogy and geochemistry of shale and sandstone host rock (in the Gulf Coast) was also reviewed. Such information is vital to brine modeling because the mineralogy of the grains and cements in the reservoir host rocks controls many important chemical constituents of the brines and determines the porosity and permeability of the reservoir rocks. The available information strongly suggests that the high secondary porosities, which are characteristic of economically attractive, geopressed sandstone reservoirs, are controlled by rock-water interactions involved in the diagenesis of shale and sandstone.

The first, and probably the most important, phase of this review was a critical survey of the thermodynamic data bases for minerals, aqueous species, and gases used in the various codes. No matter what code is used, theoretically predicting whether a brine will precipitate minerals depends so heavily on the thermodynamic data base in the code that this data base is the largest single source of uncertainty in such predictions at reservoir and well-bore temperatures and pressures. Data bases were reviewed for the codes HITEQ (Weres and Iglesias, unpublished data), EQ3/EQ6 (Wolery, 1979), SOLMNEQ (Kharaka and Barnes, 1973) and WATEQ2 and its relatives (Ball et al., 1980), and the Jaycor code (Levine et al., 1980). The main results of this review follow.

The only adequate thermodynamic data base for modeling geopressed brine chemistry at reservoir and well bore conditions as well as brine-rock interactions in the reservoir is that developed by Helgeson and coworkers (University of California at Berkeley) and embodied in the program SUPCRT. The only brine modeling code containing a thermodynamic data base generated by SUPCRT (and earlier work) is EQ3. EQ3 contains thermodynamic data for computations at low (steam-saturated) and high (500 bars) pressures, but data for other high pressures could be very simply generated using SUPCRT and added to EQ3.

No single published code is suitable for modeling the chemistry of geopressured brines under all possible conditions which occur from the reservoir to the surface. However, major code development is not considered necessary. Modeling the chemistry of geopressured brines under reservoir conditions (without a gas phase present) is feasible using the codes EQ3 and EQ6, which contains the best available thermodynamic data base. For modeling the chemistry of geopressured brines in surface equipment, where gas and liquid phases coexist, an expanded version of HITEQ is recommended. This would incorporate Pitzer's model of the electrolyte solutions and thermodynamic data for gas/liquid partitioning in the system $\text{NaCl-CH}_4\text{-H}_2\text{O}$ presently being measured by Prausnitz and coworkers at the University of California, Berkeley.

TASK 4

The objective of Task 4 was to examine the major problems associated with producing and utilizing geopressured brines and to propose research topics which would address those problems. Accordingly, the following tasks were proposed to GRI to be undertaken during the next contract year:

- o Complete the laboratory and field testing of the downhole sampler and fabricate a second unit to serve as a backup in the event that the first sampler is damaged or lost. Use the sampler to obtain brine samples from geopressured design test wells and wells of opportunity.
- o Complete the design, fabrication, and testing of a field sample-handling system which will receive the downhole brine and gas samples obtained and process them for subsequent laboratory analysis at LBL.

- o Conduct laboratory and theoretical studies concerning the precipitation of calcium carbonate from geopressured brines.
- o Conduct a broad program of chemical data analysis and interpretation utilizing sampler results and other petrological and mineralogical data in order to characterize the geochemistry of the geopressured reservoirs.
- o Develop a design of a downhole sampler based on the piston principle as an alternative to the flow-through sampler.

The results of this research are expected to provide data which will contribute importantly to a number of areas:

- o Establishing the chemical compositions of the brines in the reservoir;
- o Determining the causes of regional variations of reservoir fluid composition and matrix properties, such as porosity and permeability;
- o Predicting scale and sludge formation;
- o Elucidating the overall nature, distribution, and genesis of the geopressured resource.

The proposed program is a fully integrated effort between LBL design engineers, field testing personnel, and chemists.

PROJECT OBJECTIVES

The objective of the LBL program is to provide R&D support to GRI in developing the technology for recovering natural gas from geopressured reservoirs off the Gulf Coast. For this reason, LBL chose areas of investigation that would address the following:

- o Quantity of methane dissolved in the brine
- o Presence of free gas
- o Production behavior in the reservoir and well bore
- o Reservoir properties that control the production process
- o Problems likely to arise in the surface handling and disposal of geopressured brines

It was also recognized that if the above questions were to be addressed, the following data would have to be determined:

- o Volume and types of gases in place
- o Fluid-flow characteristics in the reservoir
- o Fluid-flow characteristics in the well string
- o The chemistry of the brine and its effect on fluid production and brine disposal.

Since current economic analyses of the geopressured resource are based on the amount of gas present in the reservoir and are heavily influenced by chemistry-related problems, the highest priority was given to determining the amounts of natural gas and other dissolved constituents of the brines as well as initiating an evaluation of the brine chemistry problems. This general area was identified by the National Petroleum Council, in June 1980, as one of the major areas of uncertainty requiring resolution.

SCOPE OF WORK

The project authorized and funded by GRI for the initial contract period (March 1, 1980 to February 28, 1981) consisted of four specific tasks:

Task 1: Design, construct, and test a downhole fluid sampler for use in geopressed wells. The sampler was to be cooled and depressurized at the well-head prior to or during extraction of the sample. Laboratory gas and brine constituent analyses were to be made.

Task 2: Design a downhole fluid sampler that would maintain downhole pressure and temperature and include measurement capabilities providing required input to chemical equilibrium computer programs.

Task 3: Review available brine chemistry modeling capabilities and define the requirements for extension of existing modeling codes to geopressed applications.

Task 4: Define future research projects that are of immediate value to GRI.

The first three tasks involved only 1980 activities, while work to be performed through 1982 was to be developed as part of the final proposal category.

TASK 1 DESCRIPTION

LBL was to design, fabricate, and test a flow-through sampler that would bring a sample of approximately one liter volume to the surface without leaking. Sample temperature would not be actively maintained at the downhole value while the sampler was being removed from the well. The target design specifications were:

- o Maximum operational temperature of 400°F;
- o Maximum operational pressure of 20,000 psi at 400°F.

The following describes the conceptual design approach adopted by LBL. The sampler would be a tubular pressure vessel with opposed "check valves" at both ends. These valves would be equipped with substantial closing springs which exert a forceful closing action of the valves, sufficient to ensure firm initial seating of the seals incorporated in the valves. The valves would be designed to provide some flushing action on the valve seats, as well as being relatively insensitive to silt particles deposited on the seats during the closure of the valves. Filters would be incorporated to remove all coarse particles.

The valves would be cocked open at the well-head prior to sampler descent and held open during the descent. At the desired sampling depth the valve closure would be activated by an electrical signal from the surface. This would require the availability of both a cable head assembly and an electrically operated initiation device capable of operating at downhole temperature and pressure and within the limited diameter and maximum length determined by the well bore and well-head insertion equipment.

Access to the sample fluid would be through valves incorporated in the sampler valve closure assemblies. These valves would be commercial high pressure manual valves which could be closed prior to descent and opened at the time that access to the sample was required.

The surface-controlled electrical system would be designed, constructed, and tested both in the laboratory and in a geothermal well in full tool configuration. The testing would also include both laboratory testing of isolated components, as well as the complete sampler system. The final test before application in a geopressured well was to be downhole sampling in a geothermal well.

The complete sampler would be laboratory-tested at less than 30,000 psi internal pressure at 72°F. The valve closure and electronic equipment would be tested in the LBL reservoir engineering tool chamber at pressures up to the limits of the packer assembly (10,000 psi) and at temperatures below 300°F. The valve closure mechanism would be oven tested at 400°F at 1 atmosphere.

When sampling a borehole for the purpose of performing subsequent chemical analyses, it is important that, to the extent possible, the fluid being analyzed remains the same as the original fluid that was sampled. In geopressured wells, fluids are at elevated temperatures and very high pressures. The sampling plan was to bring the sample to the surface and allow it to cool. Following depressurization, the sample would be transferred to a holding vessel until analyzed. During each of these steps, sample integrity can suffer. For example, the hot high-pressure gas-liquid mixture may react with the sampling device, particularly if H_2S is present. Sampler container walls, seals, valves, etc., should therefore be passive to the contained material during the time that it is in the sampler.

Alteration of gas species would be minimized by cooling the sampler and then transferring the gas phase to its own storage vessel via an inert carrier gas purge. A gas purge would also serve to extract dissolved gases from the liquid fraction. The liquid material could then be stored separately. If desired, the gas phase could also be separated into major components by condensation traps. Water vapor, for example, could be removed with a solid CO_2 trap. The primary gases of interest (CH_4 , CO_2 , H_2S , and other hydrocarbons) could be frozen out with a cryogenic device while the inert carrier gas passed through.

TASK 2 DESCRIPTION

LBL was to provide a preliminary design for a downhole flow-through brine sampler that could bring a sample of approximately 500 cc to the surface without leakage. This sampler was to include active maintenance of the brine temperature and was to be constructed of a nonreacting material to ensure that sample chemistry remained unchanged until the required measurements of thermal and chemical properties were completed. The measurements were to be made at the well-head after the sampler was removed from the well. This procedure was considered more practical than making downhole measurements, since satisfactory downhole electronics and transducers were not readily available. Continuous measurement of the sample temperature was to be provided to ensure accurate maintenance of the downhole conditions.

As part of Task 2 and Task 3, measurements of those constituents important in the chemical modeling were to be clearly defined. This information would ensure that all necessary measurements were taken into account during the sampler design phase.

Task 2 also included the selection and preliminary design consideration of probes and transducers to be included in the sampler. This would include the methodology and hardware required for making the necessary measurements. The final design, construction, and testing of the tool was scheduled for CY 1981.

Task 2 was also to include a review of the IGT project for design and construction of a downhole sampler. The IGT sampler is designed to provide chemical and thermal analyses of the geopressured brine at reservoir conditions. The LBL review was to emphasize the technical feasibility of the IGT plan and determine whether the proposed measurements were appropriate.

TASK 3 DESCRIPTION

A review of the current geopressured brine chemistry data was to be made to determine the range of chemical conditions in the undisturbed reservoir, the reservoir and well bore during fluid production, the reservoir (or other formations) and well bore during fluid injection, and related well-head and other surface equipment.

A review of the basic theory, equations, and computer algorithms that are incorporated in the existing operational chemistry modeling codes was to be made. The brine conditions, for which the existing computer programs are valid, were to be presented and the limitations of the theories and algorithms (if any) were to be defined. The emphasis in this part of Task 3 was to be on the limitations in existing chemistry models and on the limitations in existing computer algorithms available for modeling geopressured conditions.

The new chemistry model of Pitzer was to be fully outlined to determine if an existing computer program could be modified to incorporate this model, or if it would be more desirable to develop a new computer code.

TASK 4 DESCRIPTION

Task 4 was to define the scope and feasibility of other earth science research related to the recovery of natural gas from geopressured and other unconventional resources. Studies were to determine any additional problems associated with

- o Producing and injecting brine from geopressured reservoirs;
- o Producing natural gas from tight gas sands;
- o Acquiring gas from other unconventional sources.

Research proposals could be developed once major problems were defined and the key requirements of experimental data were identified. The research topics were to be outlined and recommendations were to be made for performing the tasks. Proposals for work in CY 1981 were to relate to topics of interest to GRI and for which LBL had expertise and facilities.

The research projects fell into two categories: reservoir studies and geochemistry/chemistry:

o Reservoir Studies

Design and construction of high pressure downhole tools;

Statistical studies to analyze field and laboratory data for evaluating natural gas fields;

Theory and calculation of gas flow near and in the well bore;

Measurement of relative and absolute permeabilities at geopressured conditions.

o Geochemistry/Chemistry

Conceptual modeling of the chemical characteristics of geopressured aquifers;

Chemical reactions between brine and the host rocks of a geopressured aquifer;

Chemical problems arising during methane recovery, i.e., scaling, injection well plugging, and air pollution;

Chemical response of reservoir rock to production;

Supporting research relating to the origin of geopressured aquifers containing methane.

TASK 1

CONCEPTUALIZATION AND PRELIMINARY DESIGN

During the contract year, LBL designed, built, and partially tested a flow-through type sampler which was specifically capable of obtaining representative samples of gas and brine from DOE "design wells" in the geopressured brine fields along the Gulf Coast of Texas and Louisiana.

The initial discussions and presentations between GRI and its advisory board and LBL researchers took place in late fall 1979. During these discussions, a flow-through sampler was selected in preference to vacuum bottle samplers or piston/aspiration samplers. The vacuum bottle sampler was, in spite of its essential simplicity, rejected because of the extreme transients in pressure and temperature that occur in the sample as it flashes into the vacuum bottle upon opening the sampling valve. It was felt that this might cause irreversible changes in the physics and chemistry of the sample and thus nullify the purpose of obtaining a geopressured well downhole sample. The piston sampler was in part rejected because the Institute of Gas Technology (IGT), which was also under contract to GRI, was using a Gearhart-Owen piston-type sampler in DOE "wells of opportunity" in the geopressured fields. It was decided that LBL should not duplicate ongoing efforts with a similar sampler, but provide a backup effort with a sampler based on a different operational principle.

Both the piston sampler and the evacuated bottle sampler leave no doubt as to where in the well the sample was obtained. Furthermore, a properly designed piston sampler can provide ideal conditions for the sampling process, including mixed flow sampling. In principle, the piston sampler is the best kind of sampler. To make use of this superiority, however, would have required considerable sophistication as well as an inherent need for sliding seals.

Reliable operation of such seals under the extreme conditions encountered in geopressured wells would present a very severe problem. Aspiration-type samplers can eliminate the sliding seals, but only with further complication. LBL concluded that the flow-through type would be a more suitable candidate for the first sampler design because of its potentially simpler basic scheme.

ENGINEERING DESIGN SPECIFICATIONS

The following engineering specifications were initially defined by the LBL earth scientists in discussions with GRI:

- o Flow-through sampler principle to produce a sampler capable of securing minimally contaminated representative gas/brine samples from geopressured wells in Texas and Louisiana and to bring them to the surface without leakage or deterioration;
- o Maximum downhole pressure of 25,000 psi;
- o Maximum downhole temperature of 450°F;
- o Sample size approximately 1000 ml;
- o Sampler operation to initiate at will by electrical means from the surface;
- o Sampler to indicate at the surface the success of the sampler operation;
- o Diameter and length of the sampler both to be as small as feasible with no limits imposed on either.

Additional specifications were added as follows:

- o Downhole environment to be typical, but slanted toward individually worst case geopressured brine constituent combination of TDS, CH₄, CO₂ and H₂S. No firm numbers were provided.
- o Maximum temperature difference between lubricator and bottomhole of 10°C or less.

- o Sampler design to permit later addition of integral instrumentation and multiplexed data transmission compartments. The design would be such that these later additions could be made with minimal expenditures of engineering, new fabrication time and cost, and modification time and cost to existing sampler(s).
- o Sampler cable to be a single conductor MP35N 10 x 16 armor logging cable manufactured by Vector Cable Company and designated 1-20 TFE. A cable design length of 20,000 ft was specified.
- o Cable to be terminated in a cone and socket arrangement similar to the Gearhart-Owen cable head termination.

CONCEPTUALIZATION AND PRELIMINARY DESIGN SYNTHESIS

Conceptualizing the flow-through sampler provided a means whereby the individual components could be assessed for suitability or compatibility. The time spent on this task was worthwhile considering the expense that would have otherwise accrued if changes were made during the detail design or implementation phases.

The design analysis and preliminary synthesis consisted of the following main elements:

- o Sampler valve locations, type, and sequencing
- o Sampler valve operation power source and operation initiation
- o Sample pressure vessel requirements and safety, sample removal port(s)
- o Material selection
- o Overall configuration, general arrangements, special schemes
- o Determination of smallest practical diameter and length
- o Identification of long delivery time items or specialty items
- o Fabrication considerations and preliminary costing.

Sampler Valve Locations, Type, and Sequencing

Two valves are required for a flow-through sampler—one at each end of the necessarily elongated sample pressure vessel. Two opposed internally seated check-valve type valves are used in the sampler. During sample retrieval the internal pressure relative to the outside pressure increases, which seats the valves more firmly. The actual seal is produced by an O-ring in the valve seating surface. Proper valve and valve seat grinding and lapping will permit no O-ring extrusion under these conditions, regardless of the pressure differential within the limits of strength of the construction materials. Valve sequencing presents a more complex problem. In the interest of simplicity, both valves were arranged to remain open during sampler descent and then to close after some suitable period at sampling depth. This requires only one set of downhole valve action closing to secure the sample.

The filters present a real problem. If filters are used in the sample intake flow path the filters might clog while descending in a dirty well and could possibly require excessive time at the sampling depth in order to obtain a representative sample. Further, their use in two-phase flow almost certainly leads to problems in obtaining representative gas fraction samples. This, however, is believed to be a generic disadvantage of flow-through samplers. Not using filters might lead to problems with valve seating and O-ring extrusion in wells producing brine with a large content of particulates leading to leakage. The sampler was designed for use with or without filters.

The required "parking" time at the sampling depth is a function of sample vessel volume versus the flow rate through the sampler and the desired degree of sample quality. The flow type inside the sample vessel is somewhere between perfect mixing and plug flow; given the vessel shape and valve locations, it is certainly closer to the latter. The flow rate through the

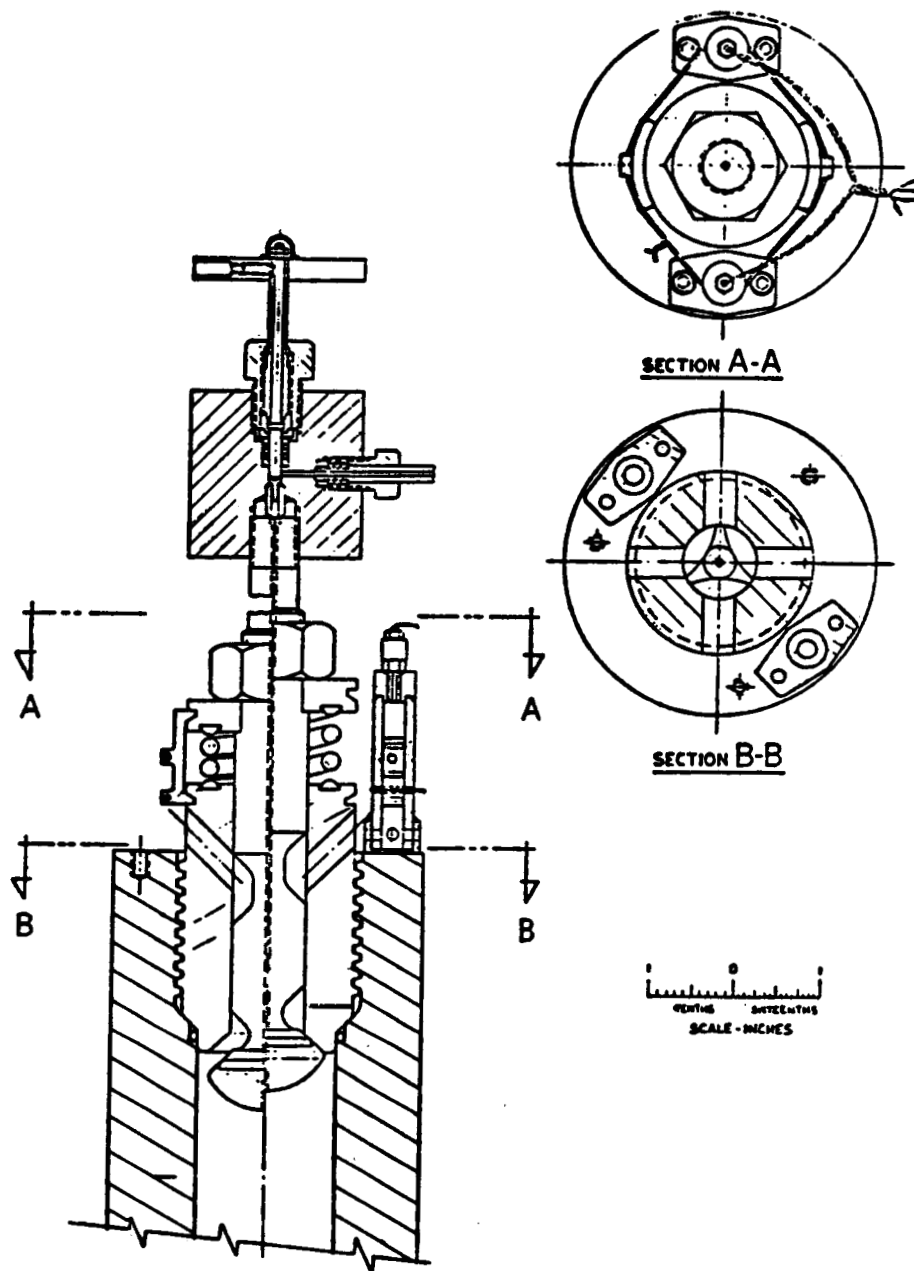
sampler depends on several conditions: the well flow rate; the well's inside diameter and surface condition; the sampler diameter; the shape of the bottom end of the sampler; the location, size, and shape of the sampler's internal flow inlet and outlet openings; and the flow resistance of the internal flow path from sampler inlet to sampler outlet compared to the external flow path resistance between the same points.

This flow analysis could be made the subject of a sizeable analytical/computational exercise, but an intelligently designed test in a suitable flow test rig (low pressure and temperature, with corrections) would be both cheaper and far more convincing, particularly if the influence of clean or clogged filters is also to be ascertained.

The sampler design based on these considerations is straightforward. The design should provide as much free internal flow path cross-sectional area as possible, including filter frontal area, taking into account the material and machining requirements. Narrow flow paths should be made as short as possible. Internal flow inlet and outlet arrangements should utilize the external flow velocity effects in order to maximize the pressure differential that drives the internal flow. The internal flow rate, however, can be only a very small fraction of the external flow rate.

Sample Valve Power Source and Initiation

Helical springs set or cocked prior to sampler descent were chosen as the simplest and most economical means of storing the required valve closure energy with very high reliability. Release of the spring driven valves at sampling depth by pyrotechnical devices was briefly considered (see Fig. 1). The scheme was simple and economical, but the problems associated with the anticipated well pressure and temperature levels caused this approach to be abandoned.



XBL 827-2311

Figure 1. Evolution of the high pressure flowthrough sampler--
first sketch.

The intent was to propel the valves toward their seats with high velocity, thus creating enough disturbance in the brine to dislodge and flush away any dirt that may have accumulated on the seats. The provision of high unit area seating force was expected to crush any remaining dirt particles, thereby obtaining tight enough seating to prevent O-ring extrusion. The firmly seated O-rings would furthermore ensure initial sealing without which the sampling scheme will fail.

For this reason, very strong valve springs were selected which required either a fairly robust release mechanism, or an intermediate mechanical amplification stage, or both. Sampling would be achieved by an electromagnetic arrangement that would release a ball lock holding the upper sampler valve open and transmit the resulting motion of the upper valve through a connecting pull rod to a ball lock holding the lower valve open, in turn releasing the lower valve.

Sample Pressure Vessel Requirements and Safety

The sample pressure vessel involved two major but unrelated problems—the magnitude of the differential pressure and the need to provide a path for removing the sample. A chief concern was the magnitude (and under certain circumstances, perhaps even the sign) of the differential pressure that the sample pressure vessel would be subjected to. No PVT data or bubble point data were available for a binary water-methane system, let alone for a mixture of water, dissolved solids, and a mixture of at least three gases with a small amount of other hydrocarbons. Steam table data for liquid water was used to establish the basic pressure differential and the first principles of thermodynamics established at least the sign of the deviations from these values.

For sampler pressure vessel design purposes, the largest conceivable differential pressure would result when the sampler is in the lubricator. This would occur at, or very near, the bottomhole temperature of a flowing well after the lubricator pressure had just been released, but before the cooling effects of the lubricator had taken effect inside the sampler. The vessel would be subjected to the well bottomhole pressure during this transient condition.

The simplest solution was to make the the sampler vessel strong enough to sustain this transient condition; the result was an increased sampler diameter. With safety as the foremost consideration, the sample pressure vessel was thus designed to simultaneously withstand a pressure differential equal to the well bottomhole pressure and a temperature equal to the highest downhole temperature.

The second problem was to find a path through which the sample could be removed from the sampler. Sample removal from either end of the vertically positioned sample vessel would make possible the removal of gaseous or liquid contents on a separate or selective basis. The solution involved hollow valve stems terminated with rupture disks, permitting retrieval of the sampler contents from either end of the vessel. In this configuration, a piercing valve could then be attached to either valve's stem outer end once the sampler had been retrieved and the pressure vessel section had been removed from the sampler. The rupture disks, properly sized and installed, also provided overpressure protection for the sample vessel, thus ensuring safety.

The upper valve stem bore along the centerline of the stem will inevitably contain a small amount of trapped air if the sampler is lowered down the well without any special measures. (The bore volume is about 1.5-2 ml or about 0.15-0.2 percent of the total sample vessel volume.) This amount of trapped

air, however small, must be considered a sample contaminant. A similar amount of air will most likely be trapped in the lower valve stem bore, since surface tension effects probably will prevent the trapped air from rising and being flushed away. Partial removal of the trapped air in the valve stems could be achieved by inserting a loosely fitting wire in the stem bore, or heating or steaming the sampler thoroughly in the lubricator prior to pressurization.

The sample vessel is designed as a high pressure vessel. The controlling dimensions were the thread and thread relief dimensions in the closure ends of the machined pressure vessel barrel. The closure utilized modified (maximum feasible bottom radius) ACME threads and was engineered for thread shear load and combined loads from bending and axial load, with a nominal stress concentration factor of 3.

MATERIAL SELECTION

The extreme environment of a geopressured well and the need for the sample vessel to act as a high pressure vessel required that certain material properties had to be satisfied, including:

- o Extremely high strength
- o Extreme toughness
- o Immunity to chloride ion stress corrosion cracking
- o Immunity to sulfide stress cracking

Maintaining the purity of the sample while it resided in the sample vessel for several hours required exceptional general corrosion resistance at high temperatures and pressures.

To keep the sampler diameter as small as possible, it was mandatory that all sampler parts adjacent to the magnetic circuit of the valve release mechanism be nonmagnetic. Fabrication of the prototype of this fairly complex piece of equipment also required single point machinability of the material.

The constraints of time and budget also made it desirable that the sampler material be readily available as bar and tubing in a variety of diameters and wall thicknesses, and preferably as semifabricated and standard items, such as spring wire, bearing balls, and fasteners. A low per-cubic-inch price was also desirable.

Nearly all conventional material choices failed some of these selection criteria. Of the candidate materials, the unique multiphase alloy MP35N most completely satisfied these material requirements. Thus, MP35N was judged to be the most suitable construction material, at least for the entire sample vessel assembly, all the springs, and any other highly stressed sampler parts. MP35N is a vacuum induction melted, vacuum arc remelted quaternary metal alloy nominally composed of 35% Co, 35% Ni, 20% Cr, and 10% Mo. It has the favorable combined properties of very high strength, good ductility, and exceptional resistance to all forms of corrosion, including simultaneous immunity to both chloride stress corrosion cracking and sulfide stress cracking. It can exhibit ultimate tensile strength levels in excess of 260,000 psi while still maintaining good ductility—a 40% reduction in area. A modest increase in ultimate strength can be further achieved by aging the alloy after work strengthening, at the expense of a very slight lowering of ductility.

Fatigue was not expected to be troublesome, since the load cycle count predictably would be low. Although fatigue cracking ultimately leads to catastrophic failure, it is neither sudden nor without warning; the crack progresses only slightly with each load cycle, thus affording ample opportunity for its detection.

The machinability of MP35N was the largest concern. Its peculiar properties, particularly related to work strengthening, make comparisons with

other high performance alloys difficult. (It is generally compared to Waspaloy, but such a comparison misses its mark.) Machining before or after aging is a matter of choice, but in any case is very difficult. The average machine shop might run into severe problems. The amount and variety of machining involved in this project proved very ambitious by comparison to other projects involving MP35N machining.

Availability of MP35N in early 1980 was questionable. Bar stock was generally available in limited diameters from the primary producer, Latrobe Steel Company. The availability of any one diameter could prove uncertain, with correspondingly long lead times.

General Considerations

The exterior of the sampler should be entirely smooth and of uniform diameter to minimize the chances of the sampler getting stuck in the well. No protuberances or appendages would be allowed.

Proper function of the sampler logically placed the sample vessel assembly at the bottom of the sampler. Maintaining the integrity of the sample pressure vessel (including machining considerations), prevented longitudinal piercing or grooving of the vessel wall to accommodate mechanical or electrical components required to operate the lower sampler valve. Threading electrical wires through the vessel interior proper for this purpose is not feasible. The only viable option is the pull rod through the center of the vessel.

Electrical wires in the sampler present both inconvenience and a reliability problem. Coiled wires, customarily used to permit screwed assembly, ought to be eliminated and replaced with a better arrangement. The number of electrical contacts, or wiring joints, should be minimized.

It was finally decided to split the sinker bars in half, centerline ball mill groove them lengthwise, and stack them on top of the sampler, hooked together with limited freedom ball and socket joints. The sinker bars would merely surround the sampler cable which would continue unbroken into a cone and socket termination inside the sampler cable head. This allowed elimination of the trouble-prone screwed and O-ring sealed mechanical and electrical joints which are normally found between the sinker bars and the sinker bar and tool. The limber yet smooth arrangement of ball-jointed sinker bars was also considered less prone to getting stuck in a well compared to a rigidly screwed sinker bar arrangement.

Diameter and Length

The design of the sampler was aimed at minimizing both the length and the diameter. A small diameter would mean that more wells would be accessible for sampling, and a short length would provide less chance of trouble in the well. Easier handling and reduced costs would result in both cases.

DESIGN

The design phase started in March 1980 with the following actions:

- o Selecting of MP35N as the sampler material for all parts that would come into external or internal contact with the brine. This amounts to the entire sampler except for the parts immersed in pressure balance oil.
- o Selecting the sampler diameter of 2.25 inches.
- o Ordering sufficient bar stock for two samplers.
- o Devising an electromagnetic type valve release mechanism.
- o Designing the sampler valve mechanisms, coupling them, and connecting them to the electromagnetic valve release mechanism.

Electromagnetic Valve Release Mechanism

The electromagnetic valve release is achieved by interrupting the current to a holding magnet. This scheme necessitates an extremely reliable magnet power source that supplies the magnet with a holding current until its armature is released, which in turn releases (e.g., closes) the sampler valves sequentially, thus, accomplishing the capture of the sample.

At ambient temperature, a holding force on the order of 175 to 200 pounds can easily be produced with a power expenditure in the coil in the range of a few tens to a few hundred milliwatts, depending on the desired safety factor. The coil power required to maintain a fixed number of coil ampere-turns increases proportionally to the temperature induced increase in the resistance of the coil conductor. At 450°F the power would not exceed 500 milliwatts. The coil needs to be energized for fairly long periods--during the descent and during "parking," a duration of up to many hours, essentially requiring continuous duty coil excitation. This was made possible by a design furnishing a very efficient heat removal path enabling the coil easily to shed its internally generated heat.

Valve Mechanisms

Ball lock arrangements, check type valves, and helical springs were the principal design elements, selected for their reliability, simplicity, and economy. These machine elements were successfully integrated with the magnet release mechanism, the setting mechanism and the valve operating mechanisms.

The final design solution was considered very satisfactory:

- o The capability of setting the fully assembled sampler at the surface facilitates predescent sampler testing and greatly simplifies sampler operations in general.

- o The setting can be achieved simply and quickly.
- o The operational status of the sampler is externally visible at all times.
- o The necessary parts are easily designed and manufactured.
- o The resulting electrical and mechanical functions, though superficially complex, in reality are straightforward and extremely reliable.

DETAIL DESIGN

The detail design started in early May 1980. The initial layout is shown in Fig. 2. This program phase centered on the design of a pressure-balanced oil immersion arrangement for the cable head, the magnet assembly and its switches. Retrofit capability for added instrumentation was also investigated and provided for. The design of the oil immersion system emphasized three areas—structure, oil compatibility, and servicing capability.

The design of the oil-brine pressure balance chamber and its outside connections involved the evaluation of the following:

- o Relative bulk modulus and volume thermal coefficients of brine and oil
- o Relative density and surface tension relationships and the mechanical clearance volume sizes and shapes
- o Damping requirements
- o Oil-brine emulsification problems
- o Internal volume changes of oil space
- o Possible suction effects of the external brine medium

Generally, below the brine breathing port an upper setting chamber was provided in which the interface (if any) between oil and brine would lie. This chamber would be separated from the lower regions with a ceramic separator made from a Norton grinding wheel. Prior to sampler use, this

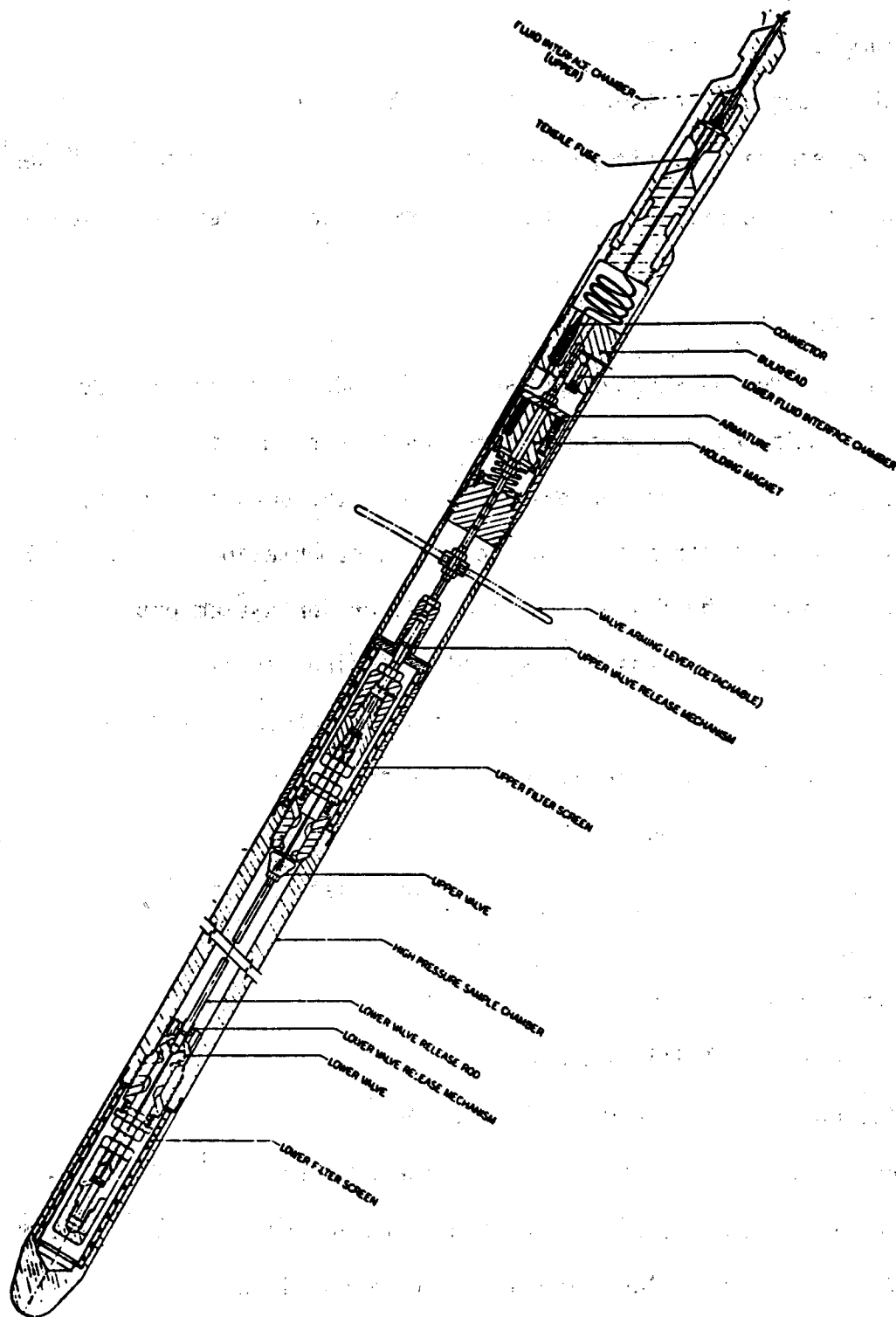


Figure 2. Initial layout (March 1980).

porous separator fills with oil as the entire system fills with oil from the injection port below. The relatively low surface tension of Krytox oil (<20 dynes per cm at 78.8°F) promotes good wetting. A principal concern was that fine emulsions might form and start to migrate about in the oil space, perhaps causing a short circuit. If emulsions form in the oil-brine balance chamber (due to shaking and rattling of the sampler), the oil drops will coalesce into the oil wetted separator surface and the water droplets will be repelled from the separator surface. The separator thus acts as an emulsion-breakdown surface for the fluid and simultaneously prevents dirt from entering the interior of the oil space.

The oil selected for these tasks had to display suitability in the following areas:

- o Evaporative loss rate
- o Thermal stability and nature of thermal breakdown products
- o Compatibility with the necessary elastomers and electrical insulation materials
- o Hydrolytic breakdown resistance
- o Catalytic breakdown resistance
- o Intersolubility of brine, oil, and air
- o Insulation characteristics
- o Emulsification properties and viscosity range
- o Flammability and toxicity

The oil filling of the oil-filled sampler parts would be achieved through oil injection ports in their lowest part. The unique Krytox fluorinated oils developed by du Pont appeared generally satisfactory. The exceptional properties of these synthetic liquids solves most of the anticipated problems. These oils exhibit extreme chemical inertness and resistance to

physical removal that permit operational temperatures far in excess of anything encountered in a geopressured well. Both Krytox oil and Krytox grease are extreme pressure lubricants and antiseizure compounds which function well at very high pressures.

The movement of the oil-brine interface in the balance chambers depends on the pressure-temperature history as the sampler moves in the geopressured well. This interface movement, of course, depends on the bulk moduli and the volume thermal expansion coefficients of the balanced fluids. Generally, oil leaves the sampler during descent and some brine enters the chambers during ascent. The balance chambers were dimensioned to handle the worst case situation with a large margin of safety, before the interface reached the separator. The sampler requires 45 milliliters of oil to fill the cablehead section and 85 milliliters to fill the magnet assembly section. The density of Krytox 143 AD oil at room temperature is approximately 1900 kg/m^3 , and at all encountered temperatures and pressures its density is higher than that of the geopressured well brine.

The oil-brine pressure balanced design provided the following advantages:

- o No limit to the downhole pressure capability of the sampler mechanisms
- o No moving parts would be subjected to unbalanced pressure forces
- o No pressure differentials across any O-rings external to the sampler vessel, which implied a higher temperature tolerance for these seals as well

- o Built-in lubrication and damping media

- o Electrical insulation immune to scuffing and leakage paths

Both of the oil-brine balance pressure systems are filled through oil injection ports equipped with spring loaded ceramic ball check valves which open at external overpressures of about 450 psi. Lower injection pressures

were preferred and therefore the injection nipple is equipped with a slitted teat that opens the valve when screwed in place for filling.

The Krytox 143 AD oil is highly viscous at room temperature. Heating of both the sampler oil spaces and the oil injection tube is necessary to make the oil move and properly fill the spaces. One hundred milliliter glass hypodermic syringes were used for this purpose. It is important to fill the space very slowly to avoid trapped air bubbles and to give gravity and the low surface tension forces time to act before a closed (i.e., stable) oil surface forms around an air volume. Filling the oil space normally takes about 30 to 60 minutes.

Heating the sampler sections is easily accomplished by flexible wraparound, snap-on, or laced, insulated silicone rubber electric heater blankets, preferably fed by a Variac transformer and equipped with a thermostat. The sampler sections should be heated to about 225°F-250°F. A heater blanket power of about 5 watts per square inch at full heater voltage is required.

Indirect heating of the fill tube is sufficient and is most simply and quite satisfactorily accomplished by insulating the tube. The syringe oil now discharges directly into a flow passage through a copper block prior to entering the flexible tube. The copper block can conveniently be heated to about 250°F with a cartridge heater controlled by a thermostat.

Integral instrumentation compartment(s), provisions for later retrofit of an instrumentation, and an electronics module would add at least one external pressure vessel compartment and one oil-filled compartment to the sampler. Thus, pressurized (and perhaps unpressurized) bulkhead and pressure vessel closure designs, 2.25 inches in diameter, would be required, as would be high-pressure high-temperature electrical feed-throughs for these bulkheads and closures.

The electronics inverted pressure vessel would therefore have to be installed between the top of the sampler and that section of the sampler containing the electromagnetic release assembly. At least one location in the sampler will have to be an oil filled space with oil-brine balance chambers to breathe radially to the brine surrounding the cylindrical sampler. The external brine flow conditions will differ from the conditions of the breathing path for the oil-brine balance chamber in the cablehead section.

The design included for test purposes a side-breathing bulkhead that separated the magnetic release section and the cablehead section, with a view toward design adaptability to a later required pressurized bulkhead with pressurized electrical feed-through for instrumentation compartment retrofit capability. The remaining detail design tasks included the following:

- o Sampler springs. The MP35N springs were calculated using available wire sizes. The magnet armature release springs were calculated to provide a safety factor of three against premature release with the magnet coil energized and a safety factor of three against non-release of the armature due to remanent magnetism after the coil had been de-energized. The sampler valve springs were designed to provide 165 pounds of seated force, to withstand further transient compression to 260 pounds force during setting, and to relax to 212 pounds force in the cocked condition.
- o Screwed joints. Arranging and marking of preferred locations of screwed joints allowed convenient subassemblies to be preassembled, checked, and serviced. In addition, the joint design permits fast and convenient removal of the sample vessel proper.

- o Mechanical security. Accidental internal or external disassembly was mainly guarded against by proper mechanical design, and, where necessary, by lock screws and pins.
- o Clearances and tolerances. In most places close clearance was not required. With a few exceptions—the pressure vessel assembly and the release magnet assembly—clearances and resulting tolerances were liberal. Catalog tolerances were used for all O-ring grooves.
- o Surface finish. In most places, surface finish was not considered critical. All surfaces were passivated after finished machining.
- o Seizure or galling. Protection against seizure or galling was a substantial problem with MP35N. To satisfactorily solve the problem, all mating and moving MP35N surfaces were treated with tungsten disulfide by the "Dicronite" process.
- o Lubrication. The tungsten disulfide dry lubricant film may be sufficient to lubricate those parts outside the oil immersion areas. However, all threads and all contact areas were additionally lubricated with du Pont Krytox 240 AD fluorinated grease, produced by thickening Krytox 143 AD oil with Vydux fluorotelomer solids. The grease was further compounded with a 5 percent by weight suspension of tungsten disulfide solids.
- o Nonimmersed parts. Providing an acceptable environment for mechanical parts not immersed in oil was a concern: sand or silt might jam the mechanisms. Silt problems were avoided by providing large clearances wherever possible. Sand was eliminated as a concern by having all internal spaces above the sample vessel assembly make contact with the outside brine solely through the sample vessel flow path exhaust filter or the sample vessel itself. Sand would therefore

be kept away from all mechanical parts by filters. Silt passing through the filter's generally would not be a problem due to adequate clearances; moreover, silt would have to move upward through stagnant brine to reach any mechanical parts. The setting piston clearance gap avoids clogging by being filled with Krytox grease during assembly and after setting.

- o Electrical insulators. Alumina was selected for the structural electrical insulators because of its indisputably high temperature capability, compatibility with Krytox oils, and compatible coefficient of thermal expansion. Its disadvantage is the fragility of ceramic.
- o Pressure vessel closure O-ring seal backup rings. The best material for the backup rings is probably annealed MP35N which will eliminate galvanic couples and will presumably be soft enough to act as a satisfactory backup ring. It might, however, cause some machining problems. Brass rings coated with Krytox grease were chosen for the prototype sampler.
- o Rupture disks. The rupture disks ought to be made from MP35N but Krytox grease-coated Inconel standard disks have been used so far with no problems.
- o Filters. An uncontroversial solution consists of wire mesh filters made from MP35N. For the prototype sampler filters, cut-down grinding wheels were used.
- o Sinker bars and fishing provisions. A general sinker bar design scheme is available, but no detail design. Final arrangements for the bars were to be agreed upon by DOE and the well operating company for execution prior to use in a specific well.

- o Setting tools for the sampler. Two simple custom designed tools were provided for the sampler.

FABRICATION

The low-bid contract was awarded in October 1980 to Humboldt Instrument Company, San Leandro, California. They finished the sampler in December 1980. The only delay occurred with the valve centerline 0.093 diameter bores, which were subcontracted and delivered in January 1981. All the single point machining performed by Humboldt Instrument Company was done with carbide tools, except drilling and tapping, which was done with high cobalt, high speed steel bits. The MP35N material and machining costs are summarized below:

Material cost	About \$11 per purchased cubic inch, as average diameter bar stock.
Complex part machining cost	About \$100 per cubic inch of material removed.
Machining time	About 0.60 cubic inches average removal per overall machining hour (includes sharpening, tool changes, head scratching, etc.).
Machining cost for a single task	About \$10 per cubic inch removed
Machining time	About 2.5 cubic inches of removal per machining hour

Both the pressure vessel bore and the valve stem bores were completed without OD machining (runout) allowance. The machining was accomplished from both ends, meeting in the middle of the work piece. The resulting meeting error was approximately 20 mils for the gun drilled vessel bore and approximately 5 mils for each of the valve stem bores.

Humboldt chose to machine the cold drawn and unaged MP35N. Aging was delayed until all parts were machined. The sampler was naturally aged during scheduled laboratory testing and in the well.

Contact assemblies were designed to permit convenient, fast and reliable assembly and disassembly of the sampler. These arrangements also allow simple and fast checkout of the sampler in the field. The sampler setting (cocking) tools were also designed during this period.

The magnet and the armature caused no particular problems. The three axial oil passage grooves in both armature and magnet body were sparked through with a full form graphite electrode.

The coil was wound manually, guided on a standard coil winding machine. A coil form was used and each layer was soaked with epoxy after winding. The winding was done with a heat lamp close to the coil, creating a coil temperature of about 170°F–190°F during winding. The epoxy was brushed on, taking care to avoid trapped air. After the winding was completed, the bulk of the epoxy coil form was machined away, the copper shorting ring and the pure silver contacts were installed, and the entire assembly was potted in a form with epoxy. Once vacuum curing in an oven was completed, the epoxy form was machined away and the coil was machined to final dimensions. The entire process worked very satisfactorily with no signs of trapped air.

A complete listing of the companies which supplied specialty items or special services for the sampler is given in Appendix B. A photograph of the finished sampler parts is shown in Fig. 3. A complete set of drawings for the sampler is available at LBL (see Appendix C).

TESTING

Ideally, the sampler should be laboratory tested in a facility that can duplicate, or closely approximate, the geopressured downhole environment. To LBL's knowledge, no such facility exists. The best approach, then, is piecemeal testing, simulating the downhole conditions either singly or in possible combinations.

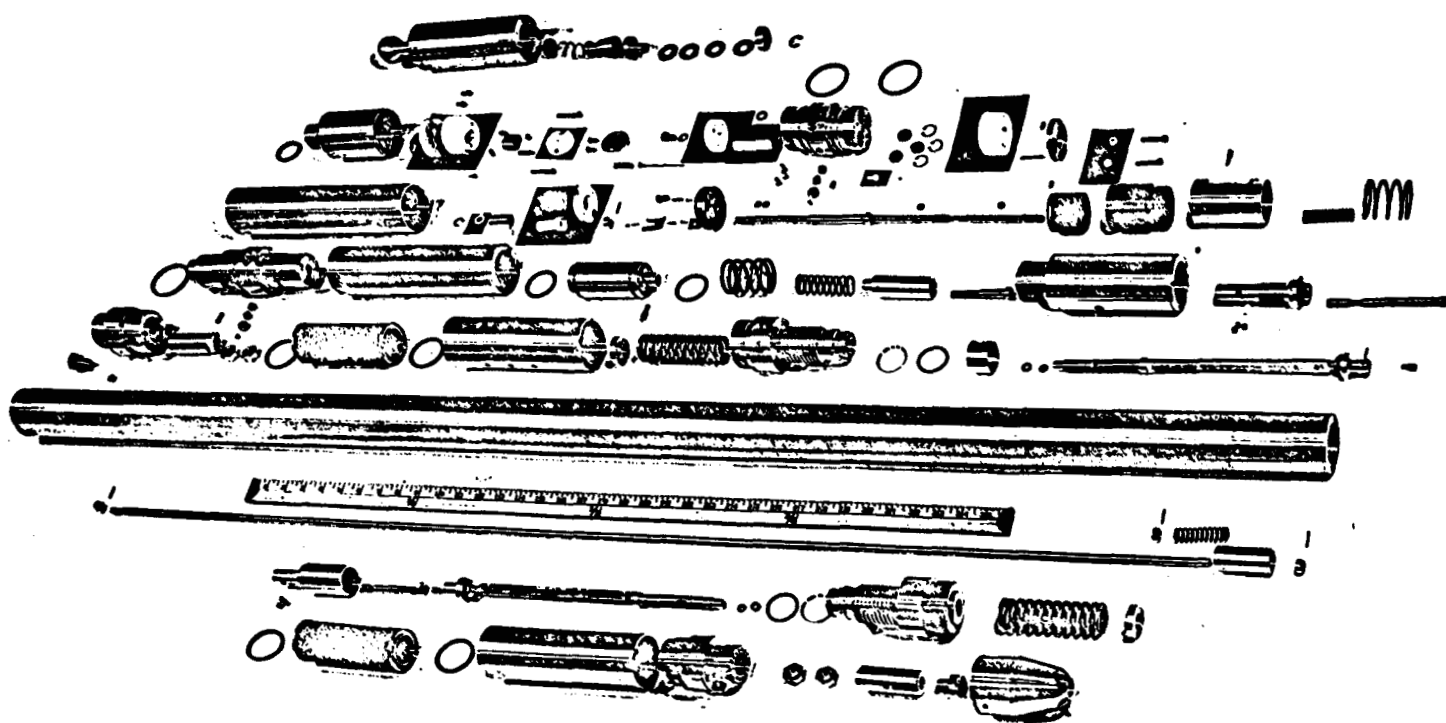


Figure 3. Flowthrough downhole sampler for geopressured brines developed for the Gas Research Institute.

The following minimum tests were scheduled:

- o Verification test of the magnet release assembly in air at a number of temperatures up to 400°F.
- o Operational test of sampler immersed (barely) in water at ambient temperature.
- o Hydrostatic test of the sample vessel assembly at pressures and temperatures up to 25,000–30,000 psi and 450°F, using artificial geopressured well brine (without the gaseous components). This test was also planned to serve as an O-ring selection test for the vessel.
- o Operational test of sampler immersed in water or brine in an autoclave at the highest pressure and temperature available within the sampler's design envelope of 25,000 psi and 450°F.

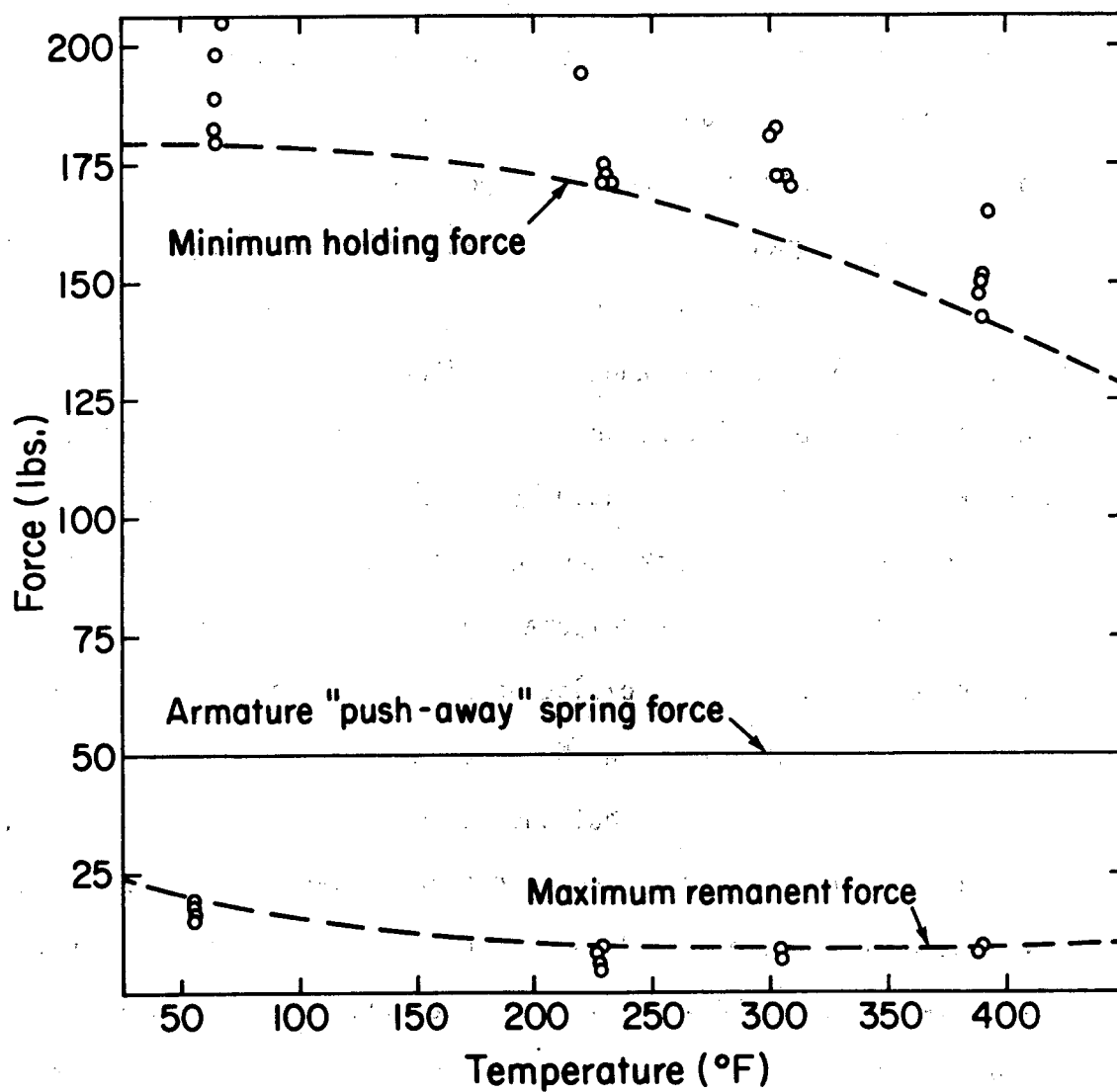
Satisfactory completion of these four tests would amply qualify the sampler for use in a DOE "Design Well" in Texas or Louisiana. If feasible, the sampler could also be tested in a geothermal well to verify that the tool, as expected and designed for, would behave well under field conditions.

A small number of sampler accessories--such as convenient oil injection gear, sampler heating jackets, and a few special assembly tools--were planned to be designed, purchased, or fabricated, as needs arose during testing.

The following tests have been performed:

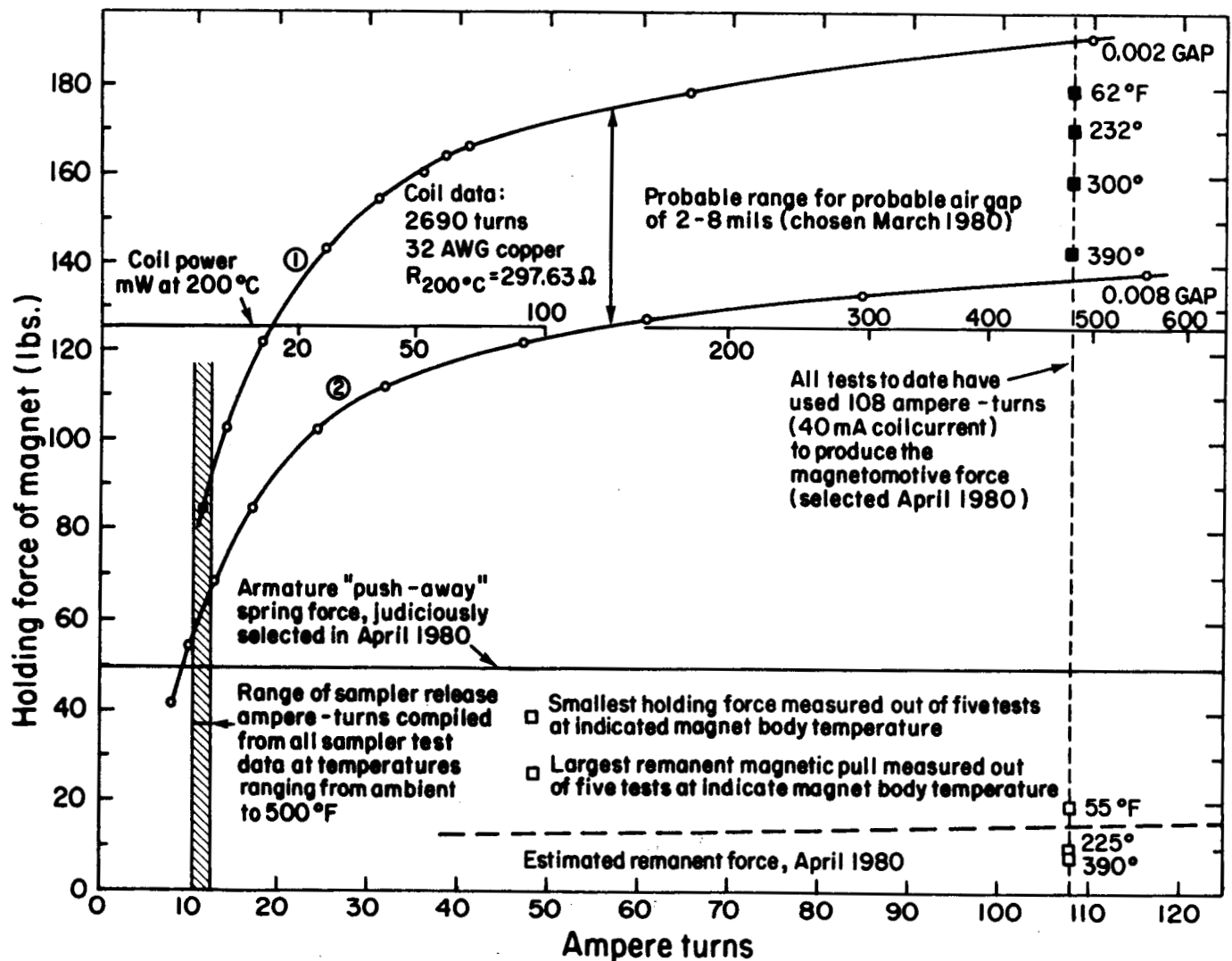
- o Magnet design verification test. The magnet and its armature were installed in an oven in such a way that the force required to pull the armature away from the face of the magnet would be measured. The maximum available oven temperature was approximately 400°F. The temperature of the magnet proper could be measured with a thermocouple. Two measurements were taken, each repeated five times for a number of temperatures up to about 400°F: Measurement of the force required to pull the armature away from the magnet face, when the magnet coil was driving the magnet iron high into saturation (well beyond the knee of the magnetization curve); measurement of the force required to pull the armature away from the magnet face after the magnet coil had been de-energized following magnetization. These tests measured the pull needed to remove the armature as held by the remanent magnetism of the magnet. The coil ampere-turns were kept constant during the tests. The results were plotted against the temperature of the magnet (Fig. 4) and exhibit the expected falloff of holding power with increasing temperature. The results are also plotted on the original design plot for the magnet (Fig. 5). It is evident that the design was entirely successful. The tests also showed that the voltage spike generated by the magnetic field collapse during accidental release under full chosen coil ampere-turns amounted to about 800-1000 volts, which might damage the coil or the cable; however, the capacity of just a few hundred feet of attached cable caused the spike to drop below 100 volts, which would be harmless to both the coil and the cable.

During normal nonaccidental release, the coil voltage spikes can be reduced to trivial levels by effecting the release by slowly reducing the supplied coil voltage until release occurs. Remanent magnetism can be eliminated as a potential problem by reversing the coil polarity and slowly increasing the voltage from zero until release occurs.



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Figure 4. Sampler magnet holding force versus temperature, five points with each temperature (December 15, 1980).



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Figure 5. Magnet force plotted against the temperature of the magnet. Holding force curves 1 and 2 were plotted on March 18, 1980, for air gaps of 2 mils and 8 mils, respectively, assuming Allegheny Ludlum relay steel No. 5, bar stock, hydrogen annealed at 1850°F (dry hydrogen). Actual steel used for the magnet was carpenter electrical iron machined from 2-1/2 in. diam. forging annealed after machining in wet hydrogen (dew point 122°F) at 1560°F for 4 hours (This steel was available; Relay No. 5 was not.) Study of Fig. 4 will resolve the apparent discrepancy between holding force, spring force, and release ampere-turns.

- o Autoclave test. The sampler performed flawlessly at 21,000 psi and 400°F in brine. The sampler was immersed in the autoclave at about 200°F and in approximately 1-1/2 hours it reached 21,000 psi and 400°F. The sampling action was then initiated and the sampler returned to the "sampling successfully accomplished" indication. It was left to cool in the autoclave overnight. Next morning the autoclave pressure and temperature were approximately 5000 psi at 250°F. After cooling to under boiling temperature, the sampler was removed. The obtained sample was released using the bottom valve setting tool to open the bottom valve. Disassembly proved all sampler parts to be in perfect condition, except for the bottom valve O-ring which was blown in several pieces when the setting tool slowly cracked the valve open. (The piercing valves still needed to be designed and built.)
- o Geothermal well sampling. A 975 ml sample was secured at a depth of 7400 feet and at a temperature of approximately 500°F in an Aminoil USA Co. steam well at the Geysers geothermal field. The pressure was unknown, but probably about 700 psi. The sampler descended the well at 275 feet per minute, spent about one minute at sampling depth prior to initiation of sampling action, returned "success" signal to the surface, and was then retrieved. The well had casing down to approximately 4000 feet. The sample was again released by cracking the

lower sample valve open with the setting tool. Subsequent inspection proved that all sampler parts were in perfect condition. A more detailed account of the results of the sampling are in Appendix D.

Both oil-brine pressure balance arrangements performed flawlessly. A trip into a hot well results, as expected, in a net loss of oil, but without any problems. All tests so far were accomplished using standard Viton O-rings. New rings were used for the Houston test and for the Geysers sampling; their condition after each test was excellent, except as noted for the bottom valve ring for the Houston test. The magnet coil was in perfect condition and the Krytox oil showed no degradation and maintained high resistivity. Krytox grease was not washed away during either test. The Krytox grease/Dicronite combination gave perfect protection against galling or seizure. The brass backup rings in the pressure vessel section remained coated with Krytox grease and showed no evidence of corrosion. The Inconel rupture discs were also coated with Krytox grease. They also were removed in perfect condition. Dimensional changes have not caused any problems. Hardness testing of the sampler has verified that well aging of the sampler is progressing.

The magnet coil current at the instant of release was fairly constant—4–5 milliamperes for all tests, regardless of environmental conditions. The coil voltage at the same instant varied with the coil temperature. The coil power at incipient release was approximately 2–8 milliwatts (Fig. 5).

The internal damping is very satisfactory both during setting of the sampler and during the release of the sampler valves. At approximately 70°F the armature takes about two seconds to move from the face of the magnet to its fully released position.

All testing so far indicates that all design objectives have been met or exceeded. The sampler performs exceptionally well and with perfect

reliability under conditions that exceed, by a very wide margin, the average geopressured well environmental conditions. The only exception may be the possible effects of simultaneous combination of high pressure, high temperature, and high TDS brine, which unfortunately has not been tested to date. There is no reason whatever to expect that the sampler would perform any other way than satisfactorily in this case as well.

LIMITS

The reader is referred to Appendix A for a discussion of the requirements for geopressured well sampling. No upper pressure limit is believed to exist for sampling in geopressured or geothermal wells. The temperature limit for the sampler as presently designed is somewhat in excess of 500°F. The limit can be increased to somewhat more than 600°F, with 625°F as a probable absolute upper limit.

The O-ring requirements for mutual compatibility with both Krytox and brine may cause problems. So far, however, it appears that Krytox grease coating of Viton O-rings has successfully resisted removal by brine. If this consistently holds true, then the possible influence of brine constituents on the O-rings will probably be alleviated substantially.

If the parts of the sampler in contact with the sample fluid are lubricated with Krytox 240 AD grease only (not compounded with tungsten disulfide solids), then the sample should be preserved as well as the state-of-the-art permits. Based on all the design features discussed, the sampler should not leak; however, verification is exceedingly difficult. The only feasible check appears to be a bubble check in a water bath after retrieval.

Summary of Data for the Downhole Sampler

Physical Data

Overall length	120.24 in. (not including sinker bars)
Diameter	2.25 in.
Dry weight	112 lb (not including sinker bars)
Sample volume	980 ml (approximately, pending volumetric test)
Material	All parts in internal and external contact with brine are produced from MP35N alloy work strengthened bar stock, by now partially aged.
Recommended cable	MP35N monoconductor cable

Operational Limits

Maximum bottomhole pressure	No upper limit
Sample vessel maximum differential pressure	Internal overpressure 25,000 psi at 450°F (pending hydrostatic proof test); External overpressure 350 psi at any temperature.
Maximum downhole temperature	450°F (500°F is apparently feasible at present with possible extension to 625°F, pending minor modifications)
Magnet coil	2690 turns of 32AWG copper magnet wire $R_{200^{\circ}\text{C}} = 297.63 \text{ ohms}$
Operational precautions	The sampler must be kept upright at all times after filling with oil

Operation

The sample is obtained by interrupting (by slow turn-down) the 40 mA dc current supplied to the sampler holding magnet. This current must be maintained without interruption from the moment the sampler has been cocked on

the surface using the two sampler setting tools until the desired depth and time of sampling. Successful sampling is indicated by open circuit on the wireline terminals, i.e., the current drops to zero regardless of supplied voltage.

TASK 2

DESIGN CONSIDERATIONS FOR A SECOND-GENERATION SAMPLER
WITH ENHANCED CAPABILITIES

The objective of this task was to consider the design of a second generation sampler with expanded capabilities for maintaining sample point conditions and making certain downhole measurements. To this end, a meeting was held with IGT to compare sampler capabilities and review the design status of the LBL, IGT, and Gerhardt-Owens samplers (see Table 1 for a comparison of these samplers as of May 1980).

Regarding the needs for chemical data, there does not appear to be any particular advantage in maintaining downhole sample point conditions of pressure and temperature. Nor is there any apparent virtue in attempting to make downhole measurements of properties like conductivity or compressibility. Measurements of this type are difficult to make and of uncertain value. Such information can be calculated from sample analyses or measured in the laboratory using simulated brines.

Failure to maintain downhole temperature and pressure conditions would not change the contents of the sampler after its valves have closed and, therefore, would not seriously affect the results of the chemical analysis. Also, most testing and measurements would first require that the sample be cooled and depressurized. Therefore, maintaining both the sample temperature and pressure on the way up is of little value.

Only the pH (because of its central importance in the chemical characterization of aqueous solutions), is worth trying to measure under downhole conditions. However, it does not yet appear to be technologically feasible to make such a measurement.

Table 1. Comparison of downhole samplers (as of May 1980).

<u>Features</u>	<u>Institute of Gas Technology</u>	<u>Lawrence Berkeley Laboratory</u>	<u>Gerhardt-Owens</u>
Pressure (psi)	15,000	20,000+	15,000 ()
Temperature (°F)	<350	450	< 350
Dimensions			
OD	2 inches	2-1/4 inches	1-11/16 inches to 2 inches
Length		9-1/2 feet	6-9 feet
WOO	Wainoco only	N/A	OK
Design test wells	Applicability - some	Applicability - All	N/A
Date available for field use	1st Qtr 1981	October-November 1980	Now
Sample size	750 cc	1000 cc	500-700 cc
Sample analysis	Compressibility-conductivity	None	None
Operational principle	Flow-through	Flow-through	Aspirated
Material	MP35N	MP35N	4130/4340
Valve closure	Explosive	Electromagnetic	Explosive
Sealing mechanism	Metal-metal	"O" Ring	"O" ring
Sample transfer	Valve-one end	Valve-both ends	Valve-one end/piston
Design status	In process	Completed	Completed
Surface indication of closure		Yes	Yes
Sampler cleanup time	Few hours	Few hours	One-time use
Turn-around time	Few hours to one	Few hours	N/A

Certain downhole measurements would, however, be of substantial value in reservoir characterization and engineering. Important advantages would be derived from a tool capable of making pressure, temperature, and flow measurements at various points within the formation. Such data would be extremely useful for better understanding the fluid flow characteristics of the reservoir, the contribution of various producing zones, and the prediction of future production behavior. A downhole device which would combine in one tool the capability of taking a sample and at the same time make p , t , and q measurements would be highly valuable. For maximum value, a downhole sampler should be capable of taking samples from adjacent formations at specific horizons.

During these investigations, the relative advantages and disadvantages of various sampler concepts continued to be reexamined. It was concluded that a piston type sampler offers sufficient advantages over the flow-through sampler that it should be pursued as an attractive design alternative for future development. These advantages include its capability in either flowing or nonflowing wells. Moreover, the depth at which the sample is taken is more certain and the quality of the sample taken is more representative of the formation fluids. It was therefore proposed that LBL undertake a design study aimed at improving the current piston type samplers, based on experience gained with the flow-through sampler.

TASK 3

RESERVOIR CHEMISTRY AND MODELING

PART 1

CHEMICAL COMPOSITION OF GEOPRESSURED BRINES

SAMPLED AT THE WELL-HEAD

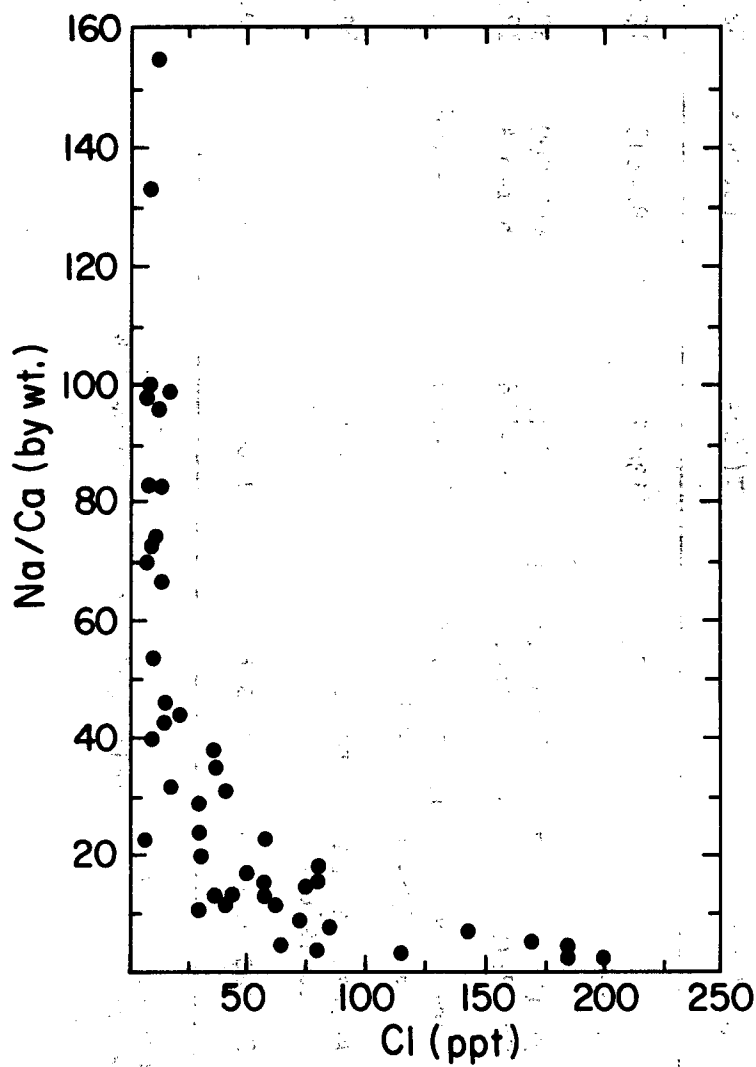
Relatively few chemical analyses of geopressured brines have been reported. However, sufficient analyses are available to demonstrate that the overall range of chemical compositions is not significantly different from the well-known chemistry of oil-field brines. A summary of the temperatures, pressures, and well-head salinities of geopressured brines is given in Table 2. In some cases, the salinities are greater than those in adjacent normally pressured units; in other cases, they are lower. Throughout the entire salinity range of 12,200 to 346,000 ppm, greater than 99 percent by weight of the nonvolatile solutes consists of chloride, sodium, and calcium. Therefore, the chemical compositions of the brines can be accurately modeled by the system $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$. The range of Na:Ca ratios is from about 1 to 150 (see Fig. 6). Despite the extreme range of Na:Ca ratios and chloride ion concentrations, most of the geopressured brine compositions have Na:Ca ratios greater than 5 by weight (about 9 by mole ratio) and chloride concentrations of less than about 100,000 ppm (2.8 molal). Thus, the majority of geopressured brine major element compositions are well represented by the NaCl-rich portion of the ternary system $\text{NaCl}-\text{CaCl}_2-\text{H}_2\text{O}$ in which the Na:Ca mole ratio is greater than about 9 and the stoichiometric molality of chloride is less than about 2.8. Less than 1 percent by weight of the nonvolatile solutes consists of dissolved Mg, K, Sr, Ba, Fe, Br, S, SiO_2 and CH_3COOH . Some pairs of aqueous species such as Ba^{2+} and SO_4^{2-} , alkaline earths (Ca, Mg, Sr) and HCO_3^- have inverse abundance ratios, as in oil-field

Table 2. Summary of known temperatures, pressures, and salinities of geopressed brines.

Reference	Locality	T(°C) ¹	P(bars) ¹	Salinity (ppm) ²
Kharaka et al. (1980)	Pleasant Bayou Well No. 2, Brazoria	138-150	787-843	108,000-132,000
Kharaka et al. (1977)	Northeast Brazoria County, Texas	117-150	463-800	50,200-73,300
	San Patricio County, Texas	100-136	521-624	12,200-36,300
Kharaka et al. (1978)	Vermilion, Iberia and St. Mary Parishes, Louisiana	105-159	431-1166	22,400-274,000
Dickey et al. (1972)	Acadia and Lafayette Parishes, Louisiana	Not reported		54,800-346,000
Schmidt (1973)	Calcasieu Parish, Louisiana	110-127	524-650	15,700-25,800

¹ Measured under downhole conditions.

² Determined by chemical analysis of samples collected at the well-head.



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Figure 6. Chemical compositions of geopressed brines in the Gulf Coast (Kharaka 1977, 1978, 1980; Dickey et al. 1972; Schmidt 1973).

brines, suggesting that the geopressed brines in the reservoirs were saturated with barite or carbonate minerals. Additional elements that could range up to concentrations of several hundred ppm in geopressed brines but are more commonly present at the 1 to 20 ppm level or less are Li, Rb, Cs, Pb, Zn, Cu, Mn, B, F, I, N. A summary of the present established range of concentrations of all these species is provided in Table 3.

The major volatile solutes in geopressed brines from the Gulf Coast are CH_4 and CO_2 . H_2S also is present in the geopressed brines in Jurassic host rocks in Central Mississippi (Grizzaffi and Thompson, 1970). The concentrations of CH_4 , CO_2 and H_2S in the brines under reservoir conditions is uncertain and at present can be estimated only from analyses of the gases separated at the surface and knowledge of gas:water ratios (see below).

CHEMICAL COMPOSITION OF BASES SEPARATED FROM GEOPRESSED BRINES AND THEIR LIKELY CONCENTRATIONS UNDER RESERVOIR CONDITIONS

Table 4 summarizes the composition of gases separated from geopressed brines in surface equipment. Clearly, the major components are CO_2 and CH_4 . Methane is, of course, the main component of the gas that is of economic value. However, carbon dioxide is more critical to chemical modeling of brine compositions because it controls the precipitation of carbonate minerals (e.g., as cements in the reservoir rocks or as scale in the well bore or surface equipment). The total CH_4 and CO_2 content of the geopressed brines under reservoir conditions is uncertain. Even after separation in the surface equipment the brines have a dissolved bicarbonate content of about 208 to 780 ppm. To date, the Pleasant Bayou Well No. 2 appears to contain brines with the highest total dissolved CO_2 . By combining the 365 ppm HCO_3^-

Table 3. Range of concentrations^a of dissolved analyzed species in well-head samples of geopressed brines.

Species	Concentration	Species	Concentration
Na	4000-84,600	Li	2-39
Ca	42-15,800	Rb	0.1-8
Cl	7000-168,000	Cs	0.5-87
K	4-1900	Pb	0.001-1
Mg	9-1500	Zn	0.003-45
Sr	4-1440	Cu	0-0.02
Ba	1-760	Mn	0.04-3
Fe	0.1-162	B	16-91
Br	6-595	F	0.07-2
SO ₄ ²⁻	0.6-691	I	10-45
S ²⁻ reduced	0.02-3.6 ^b	NH ₃	4-118
SiO ₂	26-200		
CH ₃ COO ⁻	53-1280		
HCO ₃ ⁻	200-1340		

^a All concentrations as mg per kg water

^b As H₂S

Table 4. Compositions of gases (in mole percent) separated from geopressured brines in surface equipment.

Gas	Pleasant Bayou No. 2	Fairfax Foster Sutter No. 2	Beulah Simon	Edna Delcambre No. 2
CH ₄	84.5-88.9	89.6	89.6	89.0-96.1
C ₂ H ₆	3.0-4.7	1.8	2.3	1.1-4.1
CO ₂	5.2-10.5	7.9	6.6	0.06-3.2
H ₂ S	<0.01	<0.001	--	--
N ₂	0.6-0.7	0.5	--	0.14-1.4
Reference	1	2	3	4

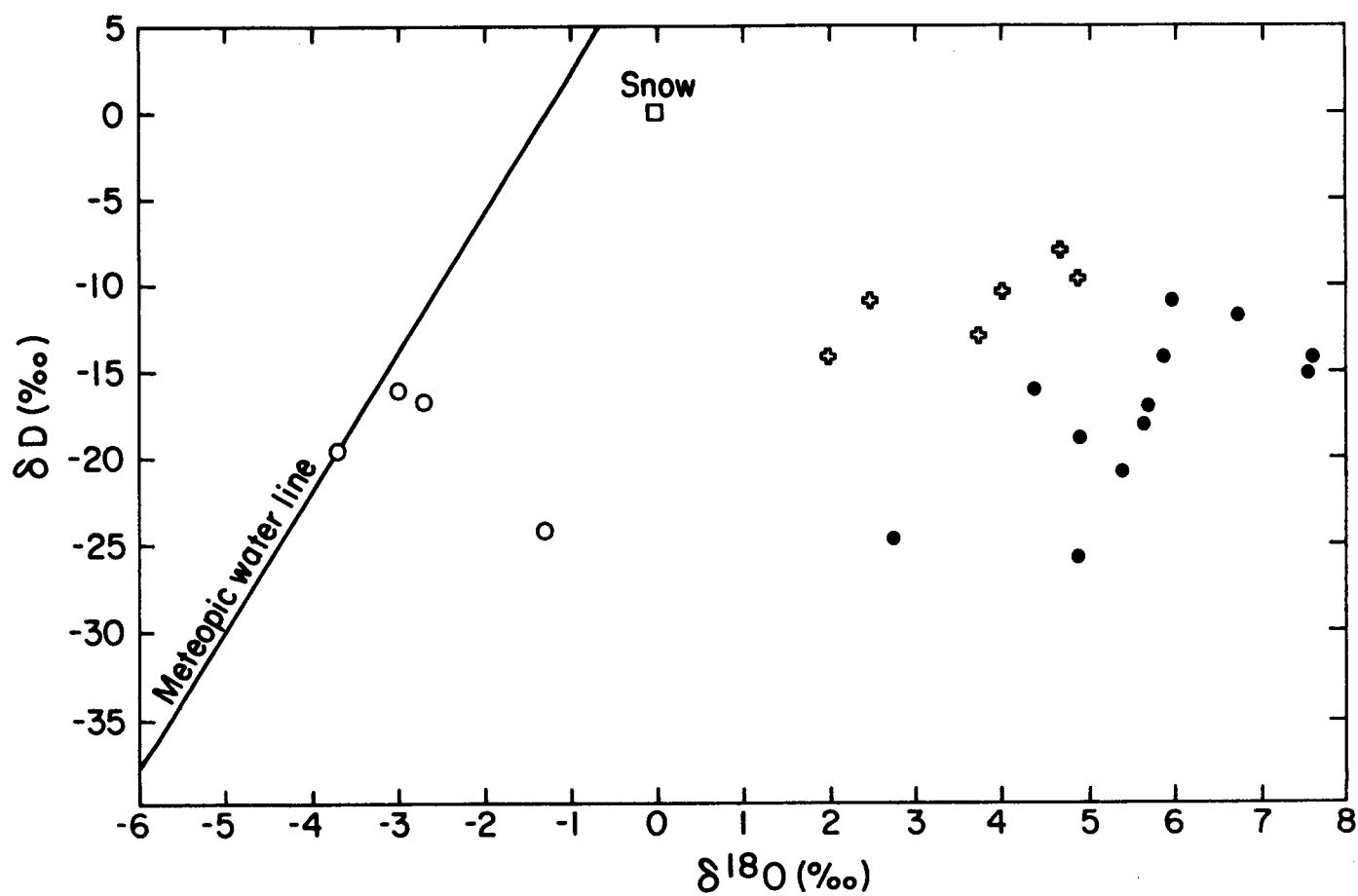
1. Kharaka et al. (1980)
2. McCoy and Hartsock (1980)
3. Randolph et al. (1980).
4. Karkalits and Harkins (1980)

from the brine analyses with the gas composition and gas:water ratio in Table 4 one arrives at total CO_2 concentration of about 0.02 molal under reservoir conditions. Calculation of methane concentrations in the brines under reservoir conditions suggests that the brines are close to saturation with methane (Kharaka et al., 1980; McCoy and Hartsock, 1980).

ISOTOPIC COMPOSITIONS OF GEOPRESSURED BRINES AND THEIR IMPLICATIONS

A very small number of D/H and $^{18}\text{O}/^{16}\text{O}$ analyses of geopressured brines have been published (Kharaka et al., 1977, 1980). These analyses are of great interest because they confirm that the water in the geopressured brines is largely of meteoric origin just as it is in oil field brines (e.g., Clayton et al., 1966). The isotopic data show a very large spread in $\delta^{18}\text{O}$ values relative to a very small spread of δD values that extends towards the isotopic compositions of present-day ground waters and the meteoric water line (Fig. 7). Kharaka et al. (1980) claim these data support a marine origin for the water; however, their interpretation is based on an unusually steep plot of the meteoric water line.

Analyses such as these could be of great practical value during flow testing of geopressured wells, particularly in combination with Cl^-/Br^- data. Important problems, such as the extent of contribution of fluids from shale beds adjacent to the sandstone reservoirs, could be very easily addressed if samples of water were analyzed over extended periods of well testing.



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Figure 7. Isotopic compositions of geopressured ($\bullet$) and associated normally pressured ($\oplus$) brines, and ground waters ($\circ$) in the Gulf Coast (Kharaka 1977, 1980).

MINERALOGY AND GEOCHEMISTRY OF THE HOST ROCKS OF GEOPRESSURED BRINES IN THE GULF COAST

The most intensive studies to date of the host rocks of geopressured brines in the Gulf Coast are limited to the shale and sandstone units of the Miocene/Oligocene Frio Formation along the Texas Gulf Coast. Important compositional variations occur in the Frio Formation laterally along the Texas Gulf Coast, corresponding to mineralogical differences in the sediments deposited, and vertically with depth through the geopressured zone because the sediments are undergoing diagenesis. The summary below of the mineralogy and geochemistry of the Frio Formation is drawn from Freed (1980), Hower et al. (1976), Bebout et al. (1978), and Perry and Hower (1970, 1972).

In shale units of the Upper Texas Gulf Coast, the most abundant minerals are mixed-layer illite/smectite clays, calcite, K-feldspar, plagioclase, quartz, kaolinite, and chlorite. The mixed-layer clays are by far the most abundant minerals, constituting at least 60 percent or more of the whole rock. No published reports are available on the variations of the mineralogical compositions of the shales along the Gulf Coast region; however, important changes occur as a function of depth below the surface. These diagenetic changes occur in response to increases of temperature and pressure and changes of pore-fluid composition caused by progressively deeper burial. Because temperature may be the most significant of these variables and because the geothermal gradient varies significantly along the Gulf Coast, the diagenetic changes are best represented as a function of temperature rather than depth (Fig. 8). The depth scale below corresponds approximately to the geothermal gradient in the Upper Texas Gulf Coast. The most important diagenetic changes in the shales are complete by about 95^o to 127^oC (12,000 ft), but they commence at temperatures of about 56^oC to 88^oC.

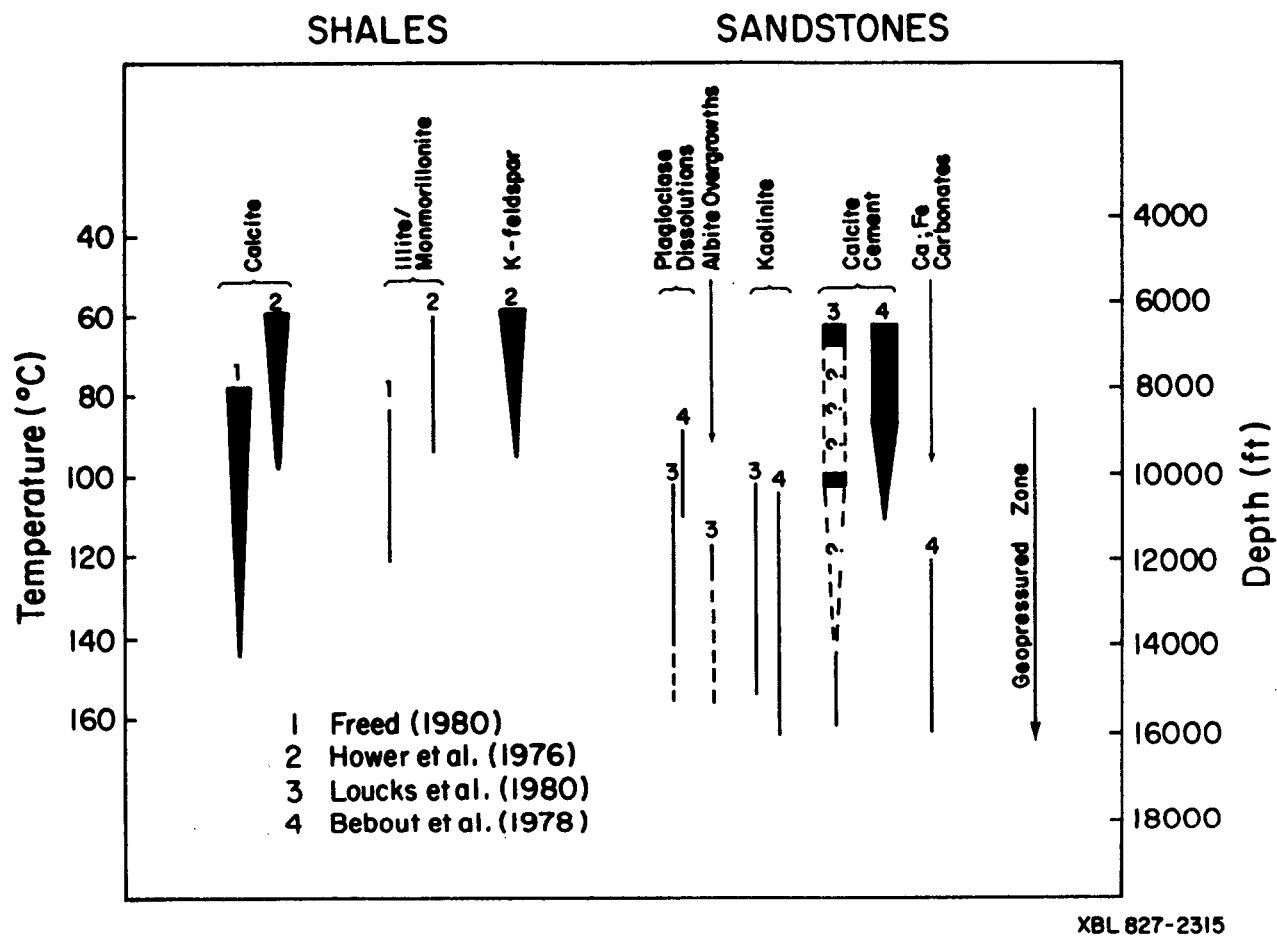


Figure 8. Diagenetic changes in the Frio Formation, Upper Texas Gulf Coast.

Mixed-layer montmorillonite (80 percent)/illite (20 percent) changes to montmorillonite (20 percent)/illite (80 percent), calcite disappears, plagioclase is converted to albite, and either K-feldspar or detrital illite disappear. Small changes in the quantities of chlorite or kaolinite may also occur. The final mineral assemblage that persists with depth to temperatures of at least 175°C is mixed-layer illite (80 percent) montmorillonite (20 percent), albite, chlorite, quartz, and kaolinite.

The sandstones of the Frio Formation consist of detrital quartz, plagioclase, K-feldspar, and volcanic and carbonate rock fragments. The proportions of quartz, feldspar and rock fragments vary from subarkose and sublitharenite in the Upper Texas Gulf Coast to feldspathic litharenite and litharenite in the Lower Texas Gulf Coast. In particular, carbonate rock fragments in the sandstones of the Lower Texas Gulf Coast are far more abundant than in the Upper Texas Gulf Coast. Changes in the sandstones as a function of depth and temperature are summarized below.

In the shallow subsurface, to depths of about 8500 feet (93°C), the most significant changes in the sandstones are development of calcite or quartz-rich cements, which reduce the primary porosity of the sediment from about 0.40 to about 0.15. Over a relatively narrow depth interval (to about 11,000 feet, 120°C) a significant porosity increase occurs to values of about 0.30, and petrographic evidence suggests partial dissolution of rock fragments, plagioclase, calcite cements, and carbonate rock fragments. Overgrowths of albite, quartz, and kaolinite occur partly within this interval and below it to depths of at least 16,000 feet (176°C). Kaolinite occurs as a replacement of feldspar and as a cement with iron carbonates that tend to reduce the porosity of the rock to about 0.10 to 0.20 at depths below 12,000 feet and extending to at least 16,000 feet. In core from the Pleasant Bayou

No. 2 well, Loucks et al. (1980) found that kaolinite occurred as described over the depth interval of about 11,000 to 15,000 feet, but neither kaolinite nor iron carbonate occurred below about 15,000 feet. Moreover, additional detailed mineralogic, petrographic, and chemical studies are needed to establish the precise mineral assemblages (including mineral compositions) for the purposes of modeling the water-rock interactions during burial and establishing the mineralogical controls over the porosity and permeability of the sandstones.

PART 2

DATA BASES FOR SIMULATING THE CHEMISTRY OF GEOPRESSURED BRINES

Computer codes for simulating the chemistry of geopressured brines and their interactions with rocks are here discussed in four sections:

- o Review of thermodynamic data bases for minerals and aqueous species
- o Review of methods of calculating activity coefficients of aqueous species
- o Computational capabilities of brine modeling codes
- o Potential applications of brine modeling codes to the study of geopressured fluids

Probably the most important part of such a review is a critical survey of the thermodynamic data bases for the minerals, aqueous species, and gases used in the various codes. Regardless of the code, theoretically predicting whether or not a brine will precipitate minerals relies so heavily on the thermodynamic data base in the code that the data base is generally the largest single source of uncertainty in such predictions, particularly at elevated temperatures and pressures. The second phase of this review is a survey of the models used in the codes for calculating individual ion activity coefficients. Activity coefficients are important because they relate measured

concentrations of aqueous species to the thermodynamic activities in the chemical modeling. The uncertainties in calculated activity coefficients are much smaller than the uncertainties associated with the thermodynamic data base, except for relatively simple chemical systems at low temperatures and pressures. The third phase is a survey of the actual makeup of the computer codes for modeling brine chemistry. The final review phase details potential applications of brine modeling codes to the study of geopressured fluids.

THERMODYNAMIC DATA BASES FOR MINERALS AND AQUEOUS SPECIES

Data bases have been compared for the codes EQ3/EQ6 (Wolery, 1979), HITEQ,^{*} SOLMNEQ (Kharaka and Barnes, 1973), and WATEQ2 and its relatives (Ball et al., 1979). All these codes contain data bases consisting of thermodynamic equilibrium constants for the dissolution of minerals and the dissociation of aqueous species or standard free energies of the minerals and aqueous species. Uncertainties in these equilibrium constants (or free energies) are the largest source of uncertainty in chemical modeling (Nordstrom et al., 1979), yet accurate knowledge of these equilibrium constants at elevated temperatures and pressures is essential. Two different approaches to this problem are discussed below with reference to the codes cited above and the special situation of geopressured brines.

Equilibrium Constants for Dissolution of Minerals Determined Experimentally from Solubility Studies at High Temperatures and Pressures

Most of the codes make direct use of, or interpolate, equilibrium constants that were determined by high temperature/pressure experimental

^{*}Documentation for HITEQ has not been published. However, HITEQ is discussed and its use demonstrated by Weres, Tsao, and Inglesias (1980).

studies. However, the amount of such data is relatively small. Therefore, the data bases in these codes need to be constantly revised and updated to ensure that the best experimentally determined data are used and that new values adopted are not inconsistent thermodynamically with previous determinations. Ultimately, accurate experimental determinations of mineral solubilities will be the best check on the types of calculation described below.

Equilibrium Constants for dissolution of Minerals at Elevated Temperatures and Pressures Calculated from Standard State Thermodynamic Data Referenced to 25°C and 1 Bar

Where equilibrium constants have been determined at 25°C and 1 bar, or can be calculated from estimated standard free energies, thermodynamic theory provides the means of calculating them at elevated temperatures and pressures (Helgeson, 1967, 1969, and Helgeson et al., 1978). The following are general equations for calculating an equilibrium constant at arbitrary T and P from standard enthalpies, heat capacities, and volumes:

$$\log K(T, P_r) = \log K(T_r, P_r) - \frac{\Delta H^0(T_r, P_r)}{2.303R} \left(\frac{1}{T} - \frac{1}{T_r} \right) + \frac{1}{2.303R} \int_{T_r}^T \Delta C_p^0(T', P_r) \left(\frac{1}{T'} - \frac{1}{T} \right) dT' \quad (1)$$

$$\log K(T, P) = \log K(T, P_r) - \frac{1}{2.303RT} \int_{P_r}^P \Delta V^0(T, P') dP' \quad (2)$$

where

K is the equilibrium constant of interest

T_r and P_r are the "reference" values of temperature and pressure (usually 298.15 K and 1 bar)

T and P are the temperature and pressure for which K is to be calculated.

ΔH^0 is the heat of reaction

ΔC_p^0 is the change in heat capacity associated with the reaction

ΔV^0 is the change of volume associated with the reaction

R is the Universal Gas Constant = 8.314 J/mol K, and

T' , P' are dummy integration variables

K , ΔH^0 , ΔC_p^0 , and ΔV^0 are functions of T and P .

The practical utility of these equations depends on how well the constants $K(T_r, P_r)$, $\Delta H^0(T_r, P_r)$, and the functions $\Delta C_p^0(T', P_r)$ and $\Delta V^0(T, P')$ are known. If they have been fitted to adequate experimental data that spans the values of T and P of interest, Eqs. (1) and (2) essentially serve as a means of interpolation and give good values of K . If these values are poorly known, if the equations are used outside of the range for which empirical data is available, or if the equations are approximated, the values obtained will be no more than estimates.

In the WATEQ2 codes, equilibrium constants at T and P are calculated using only the first two terms on the right-hand side of Eq. (1). Such an approach is a very crude approximation to calculating the temperature dependence of equilibrium constants, and it completely ignores the pressure dependence. Consequently, codes such as WATEQ, WATEQF, and WATEQ2 are useless in calculating values for temperatures above about 50°C (L.N. Plummer, USGS, Reston, Va., pers. comm.). They are, therefore, totally inadequate for modeling the chemistry of geopressured brines under reservoir conditions in the well bore and probably in most of the surface equipment as well.

The data base in the code SOLMNEQ, as originally published, was calculated using the methods and data given in Helgeson (1967) for temperatures to

350°C and pressures corresponding to the liquid-vapor equilibrium of water (165.13 bars at 350°C (Helgeson and Kirkham, 1976)), by using an approximation to the last term on the right-hand side of Eq. (1).

Consequently, the equilibrium constants calculated using this method for the dissolution of minerals, such as calcite and barite, are accurate. However, pressure dependence (the last term in Eq. (2)) is not included in the thermodynamic base in SOLMNEQ. Therefore, the code is only useful for modeling geopressured brines under surface conditions after the pressure is reduced at the choke. Similar constraints apply at present to HITEQ.

The only code containing a thermodynamic data base adequate for modeling geopressured brines under reservoir and well-bore conditions is EQ3/EQ6. The equilibrium constants in EQ3/EQ6 are taken directly from the output of the computer program SUPCRT (Helgeson et al., 1978) which is the only published code that uses equations similar to Eqs. (1) and (2) without neglecting any of the terms. The thermodynamic data in SUPCRT are internally consistent, as well as consistent with most available high temperature/pressure and low temperature/pressure experimental data and contains sufficient thermodynamic data to calculate equilibrium constants for the dissolution of minerals at both elevated temperatures and pressures (to 600°C and 5 kilobars).

At present, EQ3/EQ6 contains thermodynamic data for computations at low (steam-saturated) and high (500 bar) pressures, but data for other high pressures could very simply be generated using SUPCRT and added to the data files of EQ3.

Equilibrium Constants for the Dissociation of Aqueous Species at Elevated Temperatures and Pressures

The values of equilibrium constants for the dissociation of aqueous species such as HSO_4^- , H_2S , H_2CO_3 , and HCO_3^- at elevated temperatures are essential for

modeling brine chemistry and are known more precisely than are equilibrium constants for the dissolution of minerals (Helgeson, 1967, 1969).

This is not the case for the dissociation constants of aqueous complexes (for an indication of the uncertainties involved, see Helgeson, 1969). Fortunately, at the temperatures and pressures of geopressured brines, complexes such as NaCl^0 , MgCl^+ , and CaCl^+ are essentially completely dissociated. However, complexes of Mg, Ca, Sr, and Ba with anions such as SO_4^{2-} and HCO_3^- may be important, because they are relatively stable. Uncertainties in the log K values of complexes such as MgCO_3^0 and CaSO_4 are at least of the order of ± 0.3 at about 150°C and 1 bar; whereas, for NaSO_4^- and KSO_4^- , the uncertainties under the same conditions are at least ± 0.5 (Ball et al., 1980). Species such as MgCO_3^0 , MgHCO_3^+ , CaCO_3^0 , and CaHCO_3^+ have log K values known to within ± 0.1 at 100°C (Ball et al., 1980).

Such uncertainties are perhaps inevitable. Frequently, these complexes appear in geochemical calculations mostly as a convenient artifice which compensates for the fundamental inadequacy of the most commonly used models of electrolyte solutions. Their physical reality sometimes is debatable.

The most important complexes of transition metals, under the conditions of low total dissolved sulfur common in geopressured brines, are the chloride complexes. The only consistent set of data for these complexes, used by essentially all subsequent workers, are those of Helgeson (1969). Uncertainties in the dissociation constants of these complexes are relatively high because most of them are calculated at high temperatures by using equilibrium constants measured at low temperatures and entropies of dissociation estimated

from entropy-radius correlation considerations. For example, the average standard deviation for an entropy of dissociation is about 3 cal. mole^{-1} , which results in an uncertainty for $\log K$ of about ± 0.7 .

Dissociation equilibria are not greatly affected by pressure at temperatures less than 300°C (Helgeson, 1969; Wolery, 1979). For example, over the range 5 to 500 bars at 150°C , $\log K$ for MgCO_3^0 decreases by about 0.24.

Review of Thermodynamic Data Bases for Gaseous Species and Gas-Liquid Partitioning

Of the codes SOLMNEQ and WATEQ and its derivatives EQ3/EQ6 and HITEQ, only the last was designed to calculate conveniently the partitioning of gases between liquid and vapor, and to predict the effect of phase separation on liquid phase chemistry. Ideally, for modeling geopressured brines under all possible pressure-temperature conditions, it would be necessary to have solubilities and Henry's law constants for CO_2 , CH_4 , C_2H_6 , H_2 , and N_2 , with respect to $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ solutions over a range of temperatures and pressures. Very little of this data is available. For CO_2 and CH_4 , the data are sufficient for solubilities in NaCl solutions at the temperatures of interest, but there are no such data for H_2 , C_2H_6 , or N_2 . Henry's law constants are even more poorly known. Only those for CO_2 in Na/Cl-salt solutions are known at elevated temperatures (Ellis and Golding, 1963), although gas-liquid partitioning is being determined for the system $\text{NaCl-CH}_4\text{-H}_2\text{O}$ by Prausnitz and coworkers (University of California, Berkeley).

Despite the lack of thermodynamic data for gaseous species and gas-liquid partitioning at elevated temperatures and pressures, there are sufficient data for the partitioning of CO_2 between gaseous and liquid phases at the

relatively low pressures and temperatures expected during surface treatment of geopressured brines. Consequently, HITEQ may be used for such applications; HITEQ was, in fact, developed to treat just such problems. However, gas-liquid equilibria in the reservoir, at elevated temperatures and pressures, cannot yet be realistically modeled.

For the purposes of modeling the chemistry of geopressured brines under reservoir, well-bore, and surface conditions, there is no single code available with a thermodynamic data base covering temperatures in the range of 25°C to 160°C and pressures in the range of 400 to 1200 bars, which also models gas-liquid-mineral equilibria. However, the code EQ3/EQ6 is suitable for modeling the chemistry of geopressured brines under reservoir and well-bore conditions, provided a gas phase does not exist, because it has a thermodynamic data base covering the entire temperature range of interest at 500 bars pressure. Data files for higher pressures could very simply be added to EQ3/EQ6 from the output of the code SUPCRT. In order to model the chemistry of geopressured brines under surface conditions, HITEQ or a derivative of it could be used. Most of the thermodynamic data needed for this purpose appears to be available.

METHODS OF CALCULATING ACTIVITY COEFFICIENTS OF AQUEOUS SPECIES

Extended Debye-Hückel Equations

The codes SOLMNEQ, HITEQ, and EQ3/EQ6 all use some form of the extended Debye-Hückel model to calculate individual ion activity coefficients--generally the method outlined by Helgeson (1969). Helgeson's method uses the following equation for the individual ion activity coefficient of the j^{th} aqueous species in sodium chloride-rich solutions at elevated temperatures and saturation pressures:

$$\log \gamma_i(T, \bar{I}) = \frac{-A(T)Z_i^2\bar{I}^{1/2}}{1 + a_i(T)B(T)\bar{I}^{1/2}} + B^\bullet(T)\bar{I} \quad (3)$$

where

γ_i is the activity coefficient of the i^{th} aqueous species

Z_i is the charge of species i

$\bar{I}$ the true ionic strength of the solution

a_i is the size parameter for the i^{th} ion

$A(T)$ and $B(T)$ are functions of temperature

$B^\bullet$ is the "deviation function" and is also a function of temperature.

The two most uncertain parameters in this equation are a_i and $B^\bullet$. The former is assumed to be independent of temperature and equal to the values given for individual ions by Kielland (1937). The latter was calculated as a function of temperature by Helgeson (1969), who also demonstrated that $B^\bullet$ was essentially independent of ionic strength.

Equation (3) was designed for predicting activity coefficients in aqueous solutions with ionic strengths to about three in which more than 80 percent of the solute is NaCl. The range of temperatures covered is 25°C to 300°C at pressures of the liquid-vapor equilibrium for water. These chemical constraints correspond very closely to the bulk of chemical compositions of geopressured brines (see Task 3, Part 1).

This very simple equation is attractive because it allows predictions to be made over a wide range of conditions, knowing only a few parameters. Predictions may easily be made at higher pressures as well (that is, pressures greater than the vapor pressure of the given solution).

All electrolyte models of the extended Debye-Hückel type are approximate, and are used only because they are easy to apply over a wide range of

conditions. The values for the ion activity coefficients that the models give may be quite accurate under certain circumstances, but they are essentially only estimates.

A specific weakness of such extended Debye-Hückel treatments is that they are incapable of describing the strong pairwise interactions between ions of opposite charge that are important for divalent and polyvalent ions at room temperature, and may be important even for univalent ions at high temperature. To overcome this deficiency, recourse is made to the concept of "ion-pairing." It is debatable if such pairs actually exist except in special, and relatively limited cases; in practice, ion pairing is liberally used as a crutch to prop up a model which is, in essence, overly simplistic. Also, introducing ion pairs greatly complicates the algorithms of brine modeling codes and causes them to be slower than they might be otherwise.

Nonetheless, if carefully and consistently applied, this whole body of theory can lead to useful results. In many geochemical applications, the uncertainty in the values of the ion activity coefficients is the smallest uncertainty among many; usually, the uncertainty in an activity coefficient is less than an order of magnitude, while the stabilities of the solid phases present, or the fugacities of gases, may be uncertain to several orders of magnitude. Also, the extended Debye-Hückel model offers the only practical means of making with some degree of confidence the breathtaking extrapolations that are frequently required in geochemical calculations.

The leading work in this area has been that of H. Helgeson and his students at the University of California at Berkeley. In recent years, they have developed a far more general method of calculating activity coefficients of aqueous species (Helgeson and Kirkham, 1974ab, 1976). This method is consistent with the thermodynamic data base of these workers (discussed above) to 600°C and 5 kilobars.

Pitzer's Model of Electrolyte Solutions

The Debye-Hückel model can be further extended and made more accurate by adding additional terms that are fitted to experimental data. This approach is often referred to as the virial coefficient method. Although virial expansions are capable of high accuracy given sufficient data to fit the formulas, their practical utility is severely limited by the number of coefficients that must be fitted, very often drawing on limited data.

Recently, a relatively simple and powerful virial coefficient model of electrolyte solutions has been developed by K.S. Pitzer and his students at the University of California, Berkeley (Pitzer, 1973; Pitzer and Mayorga, 1973; Pitzer and Kim, 1974).

By carefully considering the thermodynamic and structural properties of electrolyte solutions, Pitzer has succeeded in recasting the virial equations into a form that involves a relatively small number of adjustable parameters. This model is the most accurate and easiest to use in its class. The following summation closely follows that of Pitzer (1979).

The development of Pitzer's model starts with an expression for the excess Gibbs free energy of the solution per kilogram of solvent in the form

$$G^{\text{ex}}/(n_w RT) = f(I) + \sum_i \sum_j \lambda_{ij}(I) m_i m_j + \sum_i \sum_j \sum_k \mu_{ijk} m_i m_j m_k \quad (4)$$

where

$f(I)$ is a Debye-Hückel term describing long-range electrostatic forces

$m_i, m_j, \dots$ are the molalities of the various ions present

λ_{ij} and μ_{ijk} account for short range binary and ternary interactions

It is assumed that the μ_{ijk} are independent of ionic strength and are negligible if ions i, j, k are all of the same sign.

Suitable manipulations of this formula ultimately yield the following equations for the individual ion activity coefficients of a cation M or an anion X :

$$\ln \gamma_M = z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) + \sum_c m_c (2\theta_{Mc} + \sum_a m_a \psi_{Mca}) \quad (5a)$$

$$+ \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} \psi_{aa'} M + |z_M| \sum_c \sum_a m_c m_a C_{ca}$$

$$\ln \gamma_X = z_X^2 F + \sum_c m_c (2B_{cX} + ZC_{cX}) + \sum_a m_a (2\theta_{Xa} + \sum_c m_c \psi_{Xac}) \quad (5b)$$

$$+ \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} \psi_{cc'} X + |z_X| \sum_c \sum_a m_c m_a C_{ca}$$

where

$$Z = 2 \sum_c m_c Z_c = 2 \sum_a m_a |Z_a|$$

$$F = A(T) [I^{1/2} / (1 + bI^{1/2}) + (2/b) \ln(1 + bI^{1/2})] + \sum_c \sum_a m_c m_a B'_{ca}$$

$$+ \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} \theta'_{cc'} + \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} \theta'_{aa'}$$

The osmotic coefficient of the solution is given by

$$(\phi-1) = \frac{2}{(\sum_i m_i)} \left\{ -\frac{A(T) I^{3/2}}{1 + bI^{1/2}} + \sum_c \sum_a m_c m_a (B_{ca}^\phi + ZC_{ca}) \right.$$

$$+ \frac{1}{2} \sum_c \sum_{c'} m_c m_{c'} (\theta_{cc'}^\phi + \sum_a m_a \psi_{cc'a}) + \frac{1}{2} \sum_a \sum_{a'} m_a m_{a'} (\theta_{aa'}^\phi$$

$$+ \sum_c m_c \psi_{aa'c}) \left. \right\} \quad (6)$$

The B's and θ 's are combinations of λ 's and the C's and ψ 's are combinations of μ 's. Unlike the individual λ 's and μ 's, the B's, θ 's, and ψ 's may be evaluated from experimental data.

The coefficients B_{MX} and B_{MX}^ϕ are functions of ionic strength. For 1-1 and 1-2 electrolytes,

$$B_{MX} = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} g(\alpha I^{1/2})$$

$$B_{MX}^\phi = \beta_{MX}^{(0)} + \beta_{MX}^{(1)} e^{-\alpha I^{1/2}}$$

$$B_{MX}' = \beta_{MX}^{(1)} g'(\alpha I^{1/2})/I$$

where $\alpha = 2$, and the functions g and g' are given by

$$g(x) = 2[1 - (1+x)e^{-x}]/x^2$$

$$g'(x) = -2[1 - (1 + x + 1/2 x^2)e^{-x}]/x^2$$

The parameters, C_{MX} , are related to the tabulated parameters of Pitzer and Mayorga (1973), C_{MX}^ϕ , as follows:

$$C_{MX} = \frac{C_{MX}^\phi}{2|Z_M Z_X|^{1/2}}$$

If there is only one salt present in the solution (that is, only one kind of anion and only one kind of cation, the θ 's and ψ 's all equal zero. Therefore, the properties of a pure electrolyte solution are completely

defined by the values of the β 's and C's for the solution. The values of the β 's are, in turn, determined by the values of $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$. $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, and C_{MX}^ϕ are functions of temperature. It is these three functions that must be fitted to the experimental data in order to completely describe the properties of the solution of a single electrolyte.

θ_{ij} is nonzero only when both i and j are cations or if both are anions. ψ_{ijk} is nonzero only when i , j , and k are all different ions, and are not all of the same charge type. Thus, they appear in the expressions for γ_X , γ_M , and $(\phi-1)$ only if the solution contains three or more kinds of ions. The θ 's and ψ 's are collectively referred to as the mixing terms, and express the effects of interactions between ions of like sign. θ and ψ functions may be determined from the properties of solutions that contain no more than three ions--the so-called common ion binary mixtures (e.g., a solution that contains NaCl and Na₂SO₄). However, once the β 's, C's, θ 's, and ψ 's have been determined from the properties of pure electrolyte solutions and common ion binary mixtures, they allow the properties of solutions that contain any number of ions to be accurately predicted. This is a major attraction of Pitzer's model.

When both i and j have the same charge, θ_{ij} is a function of temperature only. When i and j differ in charge, so-called unsymmetrical mixing terms also appear:

$$\theta_{ij}^\phi \rightarrow \theta_{ij} + E_{\theta_{ij}}(I) + I E_{\theta'_{ij}}(I)$$

$$\theta_{ij} \rightarrow \theta_{ij} + E_{\theta_{ij}}(I)$$

$$\theta'_{ij} = E_{\theta'_{ij}}(I)$$

Equations for calculating $E_{\theta'_{ij}}(I)$ and $E_{\theta_{ij}}(I)$ have been derived and published by Pitzer (1975); therefore, these functions are known, and

θ_{ij} remains the only adjustable parameter which must be fitted to the experimental data.

The ψ functions are functions of temperature only.

Pitzer's model also allows most "ion pairs" to be completely dispensed with; the effect of "ion pairing" is simply incorporated into the values assumed for B_{MX} , and it need not be treated separately. This feature holds great promise for dramatically simplifying geochemical calculations if fully exploited in practice.

The intrinsic limitation on the use of Pitzer's model is that $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, C_{MX}^{θ} , θ'_{ij} and ψ_{ijk} must be fitted to experimental data.

There is, as yet, no way of predicting the values of these functions, or even predicting how they vary with temperature. This has the effect of restricting the practical utility of the model to the solutions whose pure electrolyte and common ion binary subsystems have been experimentally studied at the temperatures of interest.

To date, many pure and mixed electrolyte solutions have been accurately described using Pitzer's model at 25°C, but only a few systems have been fitted up to high temperature and concentration. What is available is briefly summarized in Table 5. What has been fitted using Pitzer's model essentially reflects the range of reliable experimental data that is available.

The publication of Pitzer's model has stimulated efforts to generate new and improved experimental data needed to expand its range of utility. Therefore, the situation in this regard is improving rapidly.

To date, almost all detailed studies of electrolyte solution properties have been limited to pressures not much greater than the vapor pressure of the given solution itself. Pioneering work in high pressure solution chemistry is now underway by Pitzer and his students (for example, Rogers, 1981). However,

Table 5. Systems fitted using Pitzer's model of electrolyte solutions.

Systems	Temperature range	Concentration range	Reference
Many pure electrolytes of the 1-1, 1-2, 1-3, 1-4, and 1-5 type	25°C only	Various	Pitzer and Mayorga (1973)
Pure sulfate salts of Mg^{+2} , Ni^{+2} , Cu^{+2} , Zn^{+2} , Cd^{+2} , Co^{+2} , Ca^{+2} , Be^{+2} , Mn^{+2} , and UO_2^{+2}	25°C only	Various	Pitzer and Mayorga (1974)
52 common ion binary systems, and 11 binary systems without common ions	25°C only	Various	Pitzer and Kim (1974)
Phosphoric acid and its ions	25°C only	0-6 m	Pitzer and Silvester (1976)
Sulfuric acid and its ions	25°C only	0-6 m	Pitzer, Roy, and Silvester (1977)
NaCl	0-300°C	To saturation	Silvester and Pitzer (1977)
Pure chlorides, nitrates, and perchlorates of the rare earth elements	25°C only	0-2 m	Pitzer, Peterson, and Silvester (1977)
Temperature derivatives of Pitzer parameters for various pure electrolytes, mostly of the 1-1 or 2-1 type	Derivatives at 25°C allow limited extrapolation	Various	Silvester and Pitzer (1978)
Ionization of water in NaCl solutions	0-300°C	To saturation with NaCl	Busey and Mesmer (1976)
Ionization of $Si(OH)_4$ in NaCl solutions	0-300°C	1-5 m in NaCl	Busey and Mesmer (1977)
KCl	109-201°C	1.2-7.0 m	Holmes, Baes, and Mesmer (1978)
$CaCl_2$	109-201°C	0.8-3.5 m	Holmes, Baes, and Mesmer (1978)
$MgCl_2$	109-201°C	0.8-3.2 m	Holmes, Baes, and Mesmer (1978)
Mixture of NaCl and KCl	110-201°C	0.6-6.0 m total Cl	Holmes, Baes, and Mesmer (1979)

Table 5. (Continued)

Systems	Temperature range	Concentration range	Reference
Seawater without Ca^{+2} or HCO_3^{2-} , but including solid phases produced on evaporation; that is, the system H_2O - $(\text{Na}^+, \text{Mg}^{+2}, \text{K}^+)(\text{Cl}^-, \text{SO}_4^{2-})$	25°C	To complete crystallization	Harvie and Weare (1980)
Mixture of NaCl and CaCl_2	110-201°C	Up to 6 m NaCl	Holmes, Baes, and Mesmer (1981)
Pure NiCl_2 and CoCl_2	100 and 130°C	To limit of hydrolysis	Holmes and Mesmer (1981)
NaCl	25-300°C, 1-1000 bar	0-4 m	P.S.Z. Rogers (1981)
NaSO_4	30-200°C, 1-200 bar	0-2 m	P.S.Z. Rogers (1981)
Solubility of CaSO_4 in evaporated seawater	25°C only	0.3-5 m ionic strength	P.S.Z. Rogers (1981)
Solubility of SrSO_4 , and BaSO_4 in NaCl solutions and MgCl_2 solutions	25°C only	0-2.0 m in NaCl or MgCl_2	P.S.Z. Rogers (1981)
Mixtures of NaCl and NaHCO_3	25°C only	0-1.0 m total sodium	Pitzer and Peiper (Work in Progress)

barring a dramatic breakthrough in ability to predict what has not yet been measured, it is not likely that Pitzer's model will ever be able to span the range of conditions and components that are of interest to geochemists.

There is also the danger that attempting to use Pitzer's model when not all needed parameters are known will lead to gross errors. Generally, the B^o method is to be preferred in such cases, since it is at least systematic and its limitations are well understood.

However, in those cases for which needed data is available and has been fitted using Pitzer's model, this model will give the best predictions possible. This will soon be the case for a suite of problems which arise in connection with various energy extraction and conversion technologies. Using Pitzer's model, great accuracy ought to be soon achieved when modeling the following important saline waters—sea water, cooling tower water, oil field brines, and geopressured brines at moderate pressure.

In such cases, the prediction and control of solution pH, the partition of gases between liquid and vapor, and scaling potential are usually of greatest concern. Such calculations normally concern themselves with only a relatively few important components and species. It is precisely these important components that have received most attention in the work summarized in Table 5.

Finally, such practical applications require much greater predictive accuracy than most geochemical research applications. Thus, the greater accuracy of Pitzer's model offers real advantages here. Such calculations have traditionally been performed using electrolyte models of the extended Debye-Hückel type; very often they have yielded unreliable results.

COMPUTATIONAL CAPABILITIES OF BRINE MODELING CODES

All codes reviewed are capable of calculating the concentrations and thermodynamic activities of the species in an aqueous solution, given a complete chemical analysis of the solution. This is a species distribution calculation, after which the degree of saturation of the solution with respect to minerals can be calculated.

The species distribution calculation has been approached thermodynamically in two distinct ways--the equilibrium constant approach and the Gibbs Free Energy approach (Nordstrom et al., (1979). Use of one of these approaches in any particular code defines the characteristics of the code by limiting the choice of numerical techniques available. The equilibrium constant approach results in a set of nonlinear equations that are solved by using either the technique of successive approximation or the Newton-Raphson method. The Gibbs free energy approach results in a set of nonlinear equations that are solved by numerical techniques such as pattern search, linear programming, steepest descent, or gradient methods. The codes EQ3, SOLMNEQ, and HITEQ use the equilibrium constant approach to the species distribution problem; the JAYCOR code uses the Gibbs Free Energy approach.

EQ3

The codes EQ3 and EQ6 are extremely general in nature and capabilities. They were written by T. J. Wolery and are described in Wolery (1979) and Wolery and Walters (1975). Input to the program EQ3 consists of the concentrations of all simple aqueous species in a fluid, e.g., total sodium concentration, together with the pH, some measure of the redox state of the solution (E_h , pe^- , oxygen fugacity, dissolved oxygen content, or concentrations of a redox couple, such as sulfate and sulfide), temperature,

and pressure. From consideration of mass balance requirements on cations and anions, together with mass action expressions, the equilibrium concentrations and activities of all aqueous species of geochemical importance are calculated for the particular fluid under consideration. The program then calculates the state of saturation of the fluid with respect to all relevant minerals in the thermodynamic data base.

EQ6

The program EQ6 uses the output of program EQ3 to carry out computations of chemical equilibrium and mass transfer according to models developed by Helgeson (1968, 1979). A fixed mass of the aqueous solution specified in the output of EQ3 is allowed to react with a reactant subsystem, consisting of a set of minerals, with which it is not initially in equilibrium. Progressive addition of the reactant subsystem results in chemical reactions and mass transfer that are computed by assuming that partial equilibrium is obtained after each increment of reaction progress. Overall equilibrium is achieved when the solution finally equilibrates with the reactant assemblage. The output of EQ6 predicts the changes in solution composition and the amounts of product minerals as a function of reaction progress. The reaction progress variable may, if desired, describe changes of temperature and pressure as well as irreversible reaction of the solution with the reactant subsystem.

HIT EQ

HIT EQ was developed specifically for modeling surface treatment processes associated with production of geothermal brines. The input to HIT EQ specifies the pressure, the amount of water in the system, the total heat content of the system, and the amount of each of about 15 chemical components of practical

importance. HITEQ then calculates the partition of water, heat, and chemical components between the liquid phase and the vapor phase, the temperature, the pH, the concentrations of various species in the liquid phases, and the saturation ratio for each of the major scale-forming carbonate and sulfate minerals. At present, the thermodynamic data base in HITEQ is limited to the simple sulfate and carbonate minerals of the alkaline earth elements (e.g., strontianite, calcite, witherite, barite, celestite, etc.) for which thermodynamic data were taken from Helgeson (1969) as outlined in this report.

The capabilities of HITEQ and the chemical components that it incorporates reflect the practical needs of geothermal brine treatment process design. These needs are essentially the same as those of geopressured brine treatment process design. Incorporation of Pitzer's model of electrolyte solutions into HITEQ and updating its data base would give a state of the art tool for use in these and related areas.

An attractive feature which HITEQ shares with its relatives EQBOX and KINBOX is the simplicity of its algorithm: the overall problem to be solved is reduced to a single nonlinear equation in hydrogen ion activity which is solved using the Newton-Raphson method. Two outer loops iteratively solve for the ion activity coefficients and the partition of the various components between the liquid and vapor phases. In practice, all three loops converge rapidly, and, as a result, the codes are very fast running. Putting Pitzer's model into HITEQ would actually simplify the algorithm further, and possibly make it run even faster.

The listing and documentation of HITEQ have not been published, but HITEQ is discussed and its use demonstrated by Weres, Tsao, and Iglesias (1980).

Preliminary Technical Assessment of the JAYCOR Code and Its Use in Modeling the Chemistry of Geopressured Brines

JAYCOR's code is a recent addition to a family of codes whose use in geochemistry started in the 1960's. It is similar in purpose to EQ3/EQ6, but when fully developed may have more capabilities. However, it differs from almost all other similar codes in three important respects. First, in expressing the chemical equilibrium problem, it uses a free energy minimization approach rather than one based on equilibrium constants. It is claimed that the code has an elegant and rapid numerical method for solving this problem, but, assessing this particular advantage of the code must be deferred until the code is documented.

Second, the JAYCOR code, at present, has a very inadequate thermodynamic data base for solids that in no way represents the present state of knowledge of the thermodynamic properties of minerals. Properties of solids that have no geological significance, such as calcium chloride, are included in the data base. Also, there is no data base for volumes of minerals in the code. This is serious because it will not permit any modeling of the high pressure regime characteristic of geopressured reservoirs. There is no mention in the preliminary account of the code available (Levine et al., 1980) of the extensive thermodynamic data base for minerals developed by Helgeson and coworkers (1978) and used in EQ3/EQ6.

Third, JAYCOR has attempted to develop a liquid phase model based on Pitzer's model of electrolyte solutions, and a vapor phase model capable of dealing with the very high densities and pressures under which the vapor is in equilibrium with geopressured brine in the wellbore. The electrolyte model is similar to the one that Weres has proposed be put into HITEQ.

The problem with the electrolyte model chosen is that many empirical parameters are needed to specify it. It is unlikely that the range of species that the Jaycor code will ultimately be able to properly model using Pitzer's model will be much larger than that covered by HITEQ because of the lack of such data. Indeed, Levine et al. (1980) do not appear to be familiar with important recent literature in this area. In particular, they seem to be unaware of the high temperature fits for the dissociation of water in NaCl solutions (Busey and Mesmer, 1976), the dissociation of monosilicic acid in NaCl solutions (Busey and Mesmer, 1977), the dissociation of boric acid in NaCl solutions, (Mesmer et al., 1972), the osmotic coefficients and mean activities of MgCl_2 , CaCl_2 , and SrCl_2 , in aqueous solutions, (Holmes et al., 1978, 1979), and the recent work on the evaporation of brines by Harvie and Weare (1980).

In addition, Levine et al. (1980) apparently intended to approximate many of the empirical parameters in the Pitzer model from the available high temperature data for NaCl and the room temperature data for other salts. However, the formulas proposed by them to make these estimates (eqs. 3.14 and 3.17 in Levine et al., 1980) are incorrect, as may quickly be determined by comparing their predictions with the available data of Silvester and Pitzer (1978). In fact, the approximations introduced by these formulas may well result in a loss of accuracy, rather than any improvement over the simple extended Debye-Hückel theory. The latter is at least self-consistent and has well-known limitations.

More generally, the JAYCOR code may not be suitable to some problems that are important in practice. The thermodynamic formulation and algorithm in the code may be elegant and efficient, but, in fact, the code does not seem capable of precisely the very important kind of liquid-vapor equilibrium

problem for which HITEQ was specifically developed (H. Levine, JAYCOR, pers. comm., 1980). Even if modified, it simply appears not to be designed to deal with the basic kind of modeling problem that arises in the design of brine treatment processes. However, it should be able to solve problems involving only a liquid phase as conveniently as does HITEQ.

A related concern is the running time and the complexity of input. Because HITEQ is designed to deal with only one kind of problem, it reduces the fundamental mathematical problem to just one equation which is quick and easy to solve numerically. Because of its more general capabilities, JAYCOR is far more complicated. Therefore, it is expected that the JAYCOR code would be slower in solving problems of the sort that HITEQ was developed for. Likewise, each component in each phase and each chemical reaction to be modeled would require a separate line of interactive terminal input or input card. For example, a typical brine modeling problem using HITEQ would probably require about four lines of input, while the JAYCOR code would require about 25.

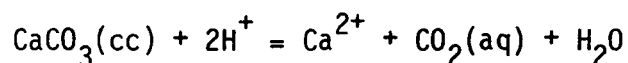
The JAYCOR code appears not to offer any great advantage over HITEQ in the range of problems that HITEQ was developed for. Its ultimate value might be as an advanced and improved substitute for codes of the EQ3/EQ6 type; that is, once fully developed and provided with an adequate thermodynamic data base it might be used for rock-water interaction modeling and related problems under geopressured reservoir and downhole conditions. Developing the JAYCOR code is a very general and long-term project that in our opinion requires a substantial amount of additional work, including work by geochemists.

POTENTIAL APPLICATIONS OF BRINE MODELING CODES TO THE STUDY OF GEOPRESSURED FLUIDS

Reservoir Fluid Chemistry

EQ3 can establish the chemical compositions, equilibrium speciations, and states of saturation of geopressured brines in the reservoirs. This is a direct application of the results of the downhole sampling program. The information gained will be vital to realistic predictions of scaling during testing and production, and, in addition, will help to establish the important brine-rock interactions influencing reservoir porosities and permeabilities.

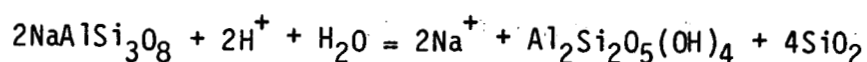
The result of well head sampling (summarized earlier in this report) can be used as a check on the reservoir fluid compositions established by the downhole sampling program. For example, one compositional parameter of great interest is the total dissolved carbon dioxide contents of geopressured brines under reservoir conditions. This parameter will be measured directly on downhole samples retrieved under the downhole sampling program. However, it can also be estimated from well head analyses in at least two ways. First, the results of the gas phase analysis at the surface and the measured gas:liquid ratio can be used to calculate the total dissolved carbon dioxide under downhole conditions (Kharaka et al., 1980). Second, from the results of petrographic studies, it can be assumed the brines are probably in equilibrium under reservoir conditions with a carbonate mineral, such as calcite or dolomite, e.g.,



The mass action expression for this equilibrium is

$$\log K = \log a_{\text{Ca}^{2+}} / (a_{\text{H}^+})^2 + \log a_{\text{CO}_2}$$

This expression can be used to calculate the concentration of carbon dioxide in the brine from the activity coefficient of CO_2 in NaCl solutions (Helgeson, 1969), the activity of Ca^{2+} (which can be calculated from the well head analysis), the equilibrium constant K (calculated using the data in Helgeson et al., 1978), and the pH. The pH of the brine can be calculated by further assuming from the results of petrographic studies, that the brine is in equilibrium with the assemblage albite, kaolinite, and quartz under reservoir conditions, e.g.,



The mass action expression for this equilibrium can be written

$$\log K = 2 \log (a_{\text{Na}^+} / a_{\text{H}^+})$$

$$\text{i.e., pH} = 1/2 \log K - \log a_{\text{Na}^+}$$

Using thermodynamic data from Helgeson et al. (1978) the equilibrium constant can be calculated. The activity of Na^+ can be calculated from the well head analysis for total dissolved sodium and the method of calculating activity coefficients described by Helgeson (1969).

Consequences of Cooling the Reservoir Fluid and Irreversible Reaction of the Fluid with Its Host Rocks

EQ6 was specifically created for applications like the prediction of the consequences of cooling or decreasing pressure on a fluid or fluid-plus-rock

system. Even though EQ6 does not at present model gas-liquid equilibria, it is still useful because many geopressured problems do not involve a vapor phase. For example, it is of great interest to predict the effects on the fluid of processes such as small but significant amounts of cooling, e.g., in a nonflowing well bore. In addition, if significant drops in pressure occur in the reservoir around the well bore, the fluid may undergo irreversible reaction with its reservoir host rocks that could affect their porosity and permeability. Either of these two applications could be made by taking the degree of reaction progress in EQ6 to be some (arbitrary) function of temperature or pressure.

Reservoir Geochemistry

The combined EQ3/EQ6 package is ideally suited for modeling the specific mineral precipitation and dissolution reactions that influence porosity, permeability, and scaling during production of geopressured brines. Integration of all the results of the downhole sampling project with available knowledge of the petrology, mineralogy, and mineral chemistry of the reservoir rocks could be used as constraints during such modeling of rock-water interactions. In addition, by establishing the burial history of the reservoir, it should be possible to predict more accurately maximum likely depths for exploitation of geopressured reservoirs and their possible response to production.

Such work would utilize the results of the chemical analyses made of brines collected at the well-head by LBL and other researchers, IGT, McNeese State, USGS, as well as those collected under LBL's downhole sampler program, to establish the chemical compositions and equilibrium speciations in the brines under reservoir conditions. In particular, the relationship of brine

composition to the petrology of the reservoir rocks would be studied. Accurate documentation of changes of the mineralogy and chemistry of Gulf Coast shales and sandstones as a function of depth are necessary for understanding the controls of petrology over brine chemistry and porosity. Much descriptive work of this kind has been and will be carried out by both the Bureau of Economic Geology at Austin, Texas, and Louisiana State University at Baton Rouge (under DOE sponsorship). Many of their results are useful but should be supplemented by additional more detailed studies to establish accurate mineral compositions and abundances. For example, quantitative results for the changes in abundance of the minerals in the core and cuttings as a function of depth are necessary and the clay mineralogy of the sandstone reservoir rocks needs investigation. The standard laboratory techniques of microscopy, X-ray diffraction and fluorescence, and electron microprobe analysis could be used for such studies.

All above laboratory and theoretical work could then be used to establish the specific mineral precipitation and dissolution reactions that have controlled the porosities and permeabilities of the reservoir rocks during their burial history. As a consequence, the chemical compositions, equilibrium speciation, and states of saturation of the reservoir brines would be firmly established as a function of the burial histories of the reservoirs. It should then be possible to make realistic predictions of porosity and permeability changes caused by chemical reactions in the reservoirs that occur in response to production.

Practical Problems of Brine Handling

Depressurizing geopressured brine to separate the dissolved gases from it causes a large chemical perturbation; in particular, the removal of CO_2 from

solution increases the pH and causes calcium carbonate to precipitate. So far, this is the only type of scale that has been observed in geopressured brine handling operations. Brine disposal by reinjection usually involves mixing the brines from different wells, and also mixing of the brine being injected with the brine in the receiving formation. Such mixing of brines of different composition has often been observed to cause scaling in oil field and geothermal field operations, and the same danger exists in the case of geopressured brines as well.

Predicting and controlling such scale deposition processes often requires accurate calculations of liquid phase equilibria and pH, and of the partition of gases between liquid and vapor. Usefully predicting these things requires more accuracy than is the case with most geochemical research applications.

To be sure, in oil field practice such problems have often been solved by trial and error testing, and the generous use of threshold type scale inhibitors. In principle, chemical problems associated with the handling of geopressured brines might also be addressed in this way. However, the case of geopressured brines (and geothermal brines) appears to be fundamentally different in practice. An obvious difference is the much higher temperature of these brines; this limits the use of "beaker experiments," and narrows the range of additives to choose from. An even more important and practical distinction is the very large volume of brine that must be handled and disposed of in utilizing geopressured and geothermal resources. Typically, this is one or two metric tons per dollar of ultimate product value. This is one or two orders of magnitude higher than is the case with oil field brines.

The very large amount of brine to be handled and disposed of means that any brine treatment process used must be inexpensive. This militates against

the routine use of exotic additives, and places a premium on cleverness in brine treatment process design. Such cleverness demands a thorough understanding of the chemistry of the brine, and this, in turn, requires good brine modeling capability. (See Weres, Tsao, and Inglesias, (1980) for an example of practical geothermal brine treatment design.)

HITEQ was purposefully designed to model just such problems of scaling and gas-liquid equilibria. After updating its data base and incorporating Pitzer's electrolyte model, HITEQ could be used to calculate the following:

- o Degree of supersaturation of the brines with the common carbonate and sulfate minerals
- o Partition of volatile components between brine and vapor at relatively low pressures
- o Chemical effects of separating the vapor from the brine
- o Effects of chemically modifying the brine.

This information could be used to study the chemistry of brines that are obtained in the downhole sampling project and to help develop extraction and preinjection brine treatment processes that are suitable for these brines.

Use of Pitzer's model appears to be a practical proposition in this case, because the temperatures and pressures of greatest interest are moderate and experimentally accessible, and only a limited number of components are of practical importance. For the most part, these components are just those that are receiving the most careful study. (Compare the lists below with Table 5).

Listed here are the various ions, solids, and gases that are of greatest practical importance in the context of scale formation and control. Those that are known to be important in the case of geopressured brines are underlined.

The following ions are frequently present in high concentration in saline waters: Na⁺, K⁺, Mg⁺², Ca⁺², Cl⁻, and SO₄²⁻. The following are the common scale forming minerals: Calcite and aragonite (both CaCO₃); anhydrite (CaSO₄), gypsum (CaSO₄·H₂O), strontianite (SrCO₃), celestite (SrSO₄), barite (BaSO₄), witherite (BaCO₃), amorphous silica (SiO₂).

The following are important in determining the solution phase pH (along with their conjugate acid and base forms): CO₂, H₂S, HN₃, CH₃COOH, Si(OH)₄, B(OH)₃.

The following frequently are important components of the vapor or gas phases that may coexist with such fluids: CH₄, CO₂, H₂S, NH₃, N₂, O₂, C₂H₆, H₂.

Most of the ions, solids, and gases underlined are included in the present version of HITEQ.

TASK 4

RESEARCH PROJECTS

Task 4 aimed to examine the major problems associated with the development of geopressured brines and to propose research topics which addressed those problems. Accordingly, during the contract year, LBL proposed the following tasks to GRI:

- o Complete laboratory and field testing of the downhole sampler and fabricate a second unit to serve as a backup in the event that the first sampler is damaged or lost. The downhole sampler is designed to obtain brine samples from DOE geopressured Design Test Wells and Wells of Opportunity.
- o Complete the design, fabrication, and testing of a field sample-handling system which will receive the downhole brine samples and process them for subsequent laboratory analysis at LBL.
- o Conduct laboratory and theoretical studies of the precipitation of calcium carbonate from geopressured brines.
- o Conduct a broad program of chemical data analysis and interpretation, utilizing sampler results and other petrological and mineralogical data, in order to characterize the geochemistry of the geopressured reservoirs.
- o Develop a design of a downhole sampler based on the piston principle as an alternative to the flow-through sampler.

The results of this proposed research are expected to provide important data which will contribute importantly to a number of areas:

- o Establishing the chemical compositions of the brines in the reservoir
- o Determining the causes of regional variations of reservoir fluid composition and matrix properties, such as porosity and permeability.

- o Predicting scale and sludge formation
- o Elucidating the overall nature, distribution, and genesis of the geopressured resource.

The proposed program is a fully integrated effort between LBL design engineers, field testing personnel, and analytical, theoretical, and geochemical scientists.

A detailed description of these proposals was presented to GRI in an LBL document entitled Outline of LBL Research Proposals for Submission to the Gas Research Institute (October 1980).

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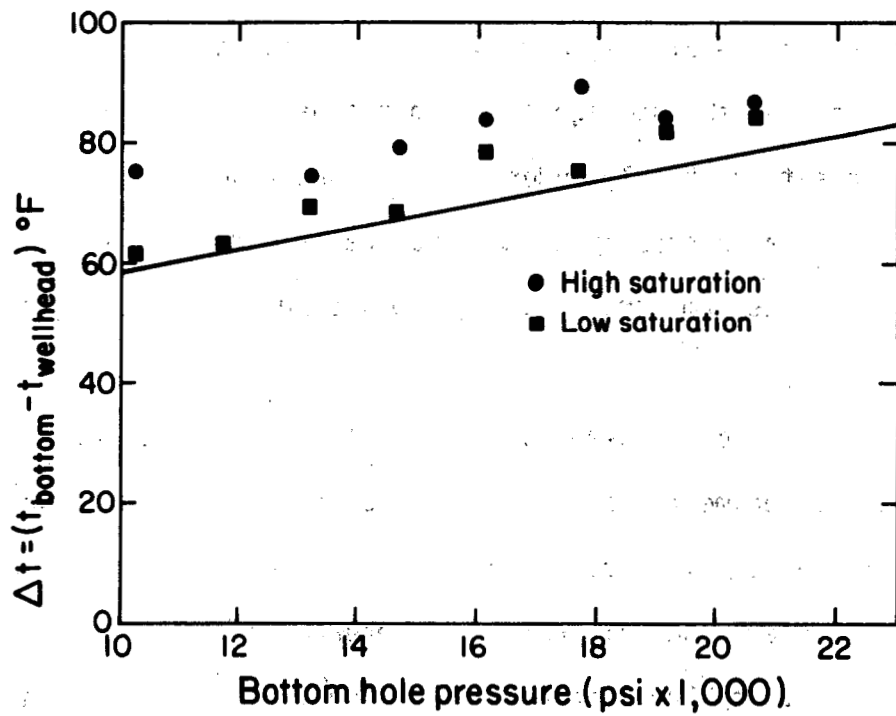
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APPENDIX A
CALCULATIONS OF PRESSURE-TEMPERATURE EFFECTS
ON LBL FLOW-THROUGH SAMPLER OPERATION

The LBL sampler is designed to take advantage of the characteristics of geopressured wells, that is, a regime where methane and brine are under unusually high pressures at high temperatures. It is this high temperature that maintains the relatively high pressure in the sampler, relative to the well-bore fluid, as the sampler comes up the well. To ensure that the sampler would operate satisfactorily under various conditions of pressure and temperature, it was necessary to mathematically model the water-methane system in the well and the sampler. This work was conducted by E. Iglesias at LBL under DOE funding.

This computer program used for these calculations predicts the pressure and temperature regime for a fixed volume of methane and pure water in any compositional ratio. The sampler will remain sealed after the valves close so long as the sampler internal pressure is greater than the well bore pressure. The computed results show that this condition is predominantly a function of temperature; thus, the temperature profile within the well largely determines whether the sampler can be successfully used.

Figure A-1 shows the range of conditions under which the sampler will operate properly. In this figure, the differential temperature (bottom hole temperature, less well-head temperature) is plotted against bottom hole pressure. If the well conditions in the field fall below the line shown in Fig. A-1, the sampler is expected to work satisfactorily. If the conditions fall within the scatter of points in Fig. A-1, the sampler will probably work well, but with less certainty.



XBL 827-2310

Figure A-1. Differential temperature versus bottom hole pressure.
Area below the line is safe operation condition.

Figure A-1 was constructed using data from Fig. A-2, which shows the pressure and temperature distribution for various methane saturations in pure water. The stippled area indicates the range of methane concentrations expected (assuming saturation) for geopressed wells. For any given bottom hole pressure the temperature should fall within the stippled zone. To construct Fig. A-1, a series of pressures were assumed and the corresponding temperatures were read from Fig. A-2. This is illustrated by the lines drawn at 15,000 and 10,000 psi in Fig. A-2. A high and low temperature is defined as each pressure line intersects the edge of the stippled area. These temperatures correspond to the maximum and minimum concentrations of methane expected in geopressed wells.

Each of these pressures and temperatures were taken as bottom hole conditions. The mathematical model then calculated the pressure for a fixed volume of fluid as the temperature decreased to 75°F. Figure A-3 is an example of one of these plots. The initial bottom hole pressure was assumed to be equal to the lithostatic load of 1 psi per foot. Thus, a 15,000 psi bottom hole pressure was assumed to represent a well 15,000 feet deep. This does not represent the actual case in the wells tested to date, since in geopressed wells pressures are typically greater than hydrostatic, but less than lithostatic; however, this approximation provides a margin of safety. The hydrostatic load (0.43 psi/ft) was then subtracted from the bottom hole pressure to approximate a well head pressure. Again, this is not the real situation because the well is filled with brine which is heavier than water, but the error gives an additional margin of safety. This well head pressure represents the minimum pressure needed in the sampler to keep it closed. The sampler internal pressure is predominantly a function of its temperature. The minimum sampler temperature is indicated where the sampler's internal pressure

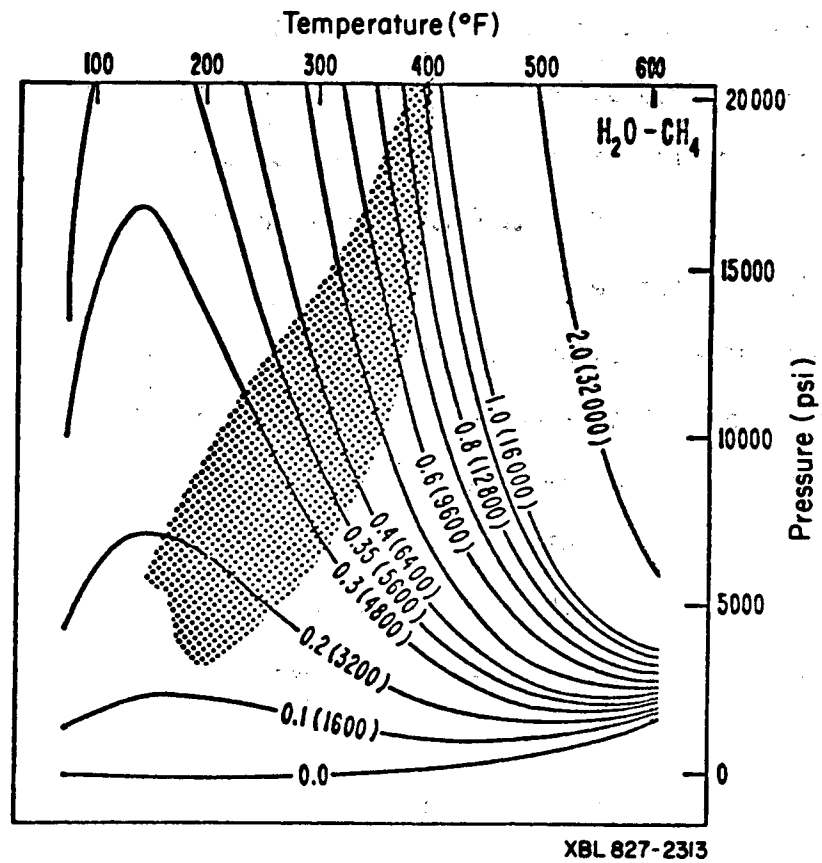
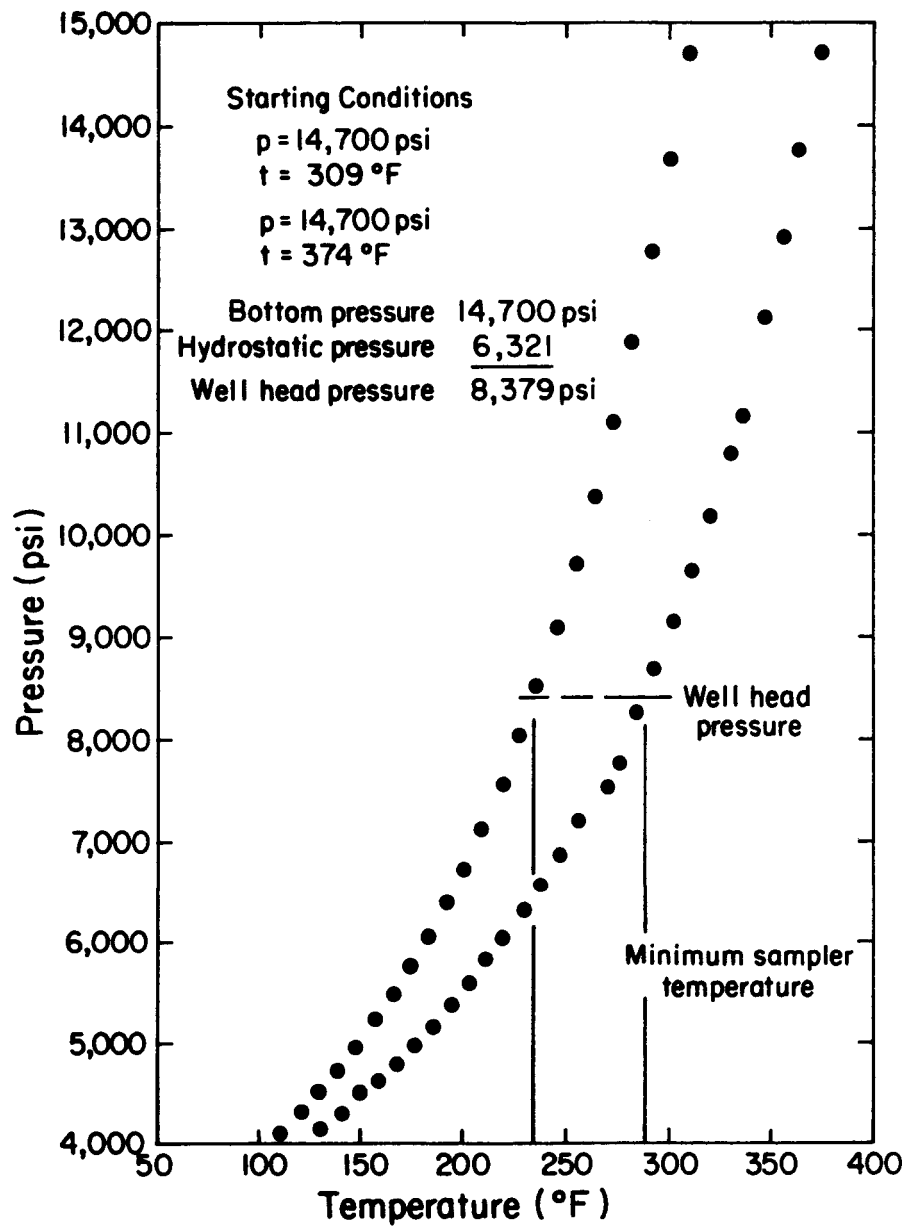


Figure A-2. Methane saturation in water as a function of temperature. Zone of methane saturation found in wells (:::); ppm methane, 3200.



XBL 827-2312

Figure A-3. Sampler internal pressure versus temperature.

line crosses the well head pressure, as shown in Fig. A-3. Thus, the temperature gradient under which the sampler will work is defined for this bottom hole pressure and the maximum and minimum expected methane saturations.

The process was repeated for eight pressures from 20,580 to 10,290 psi. The sixteen differential temperatures are plotted against bottom hole pressure in Fig. A-1. It is remarkable that the differential temperature from the high and low end of the methane saturations are so close. The methane saturation appears to have little or no practical effect on the sampler operation.

A line was arbitrarily drawn below all the data points in Fig. A-1. The area below the line indicates where the sampler will work as designed. Because of the safety factors in the calculation, we suspect that sampler would function properly even if the well condition fell within the area of scattered data points in Fig. A-1. For the three wells of opportunity tested by Eaton Operating Co., the sampler would have worked in the G. M. Koelmay No. 1 and the P. R. Girouard No. 1 well without any problem. The A. Sacdana Well No. 2, which was abandoned because of low flow, would have fallen in the "probably would work" range of Fig. A-1.

Generally accepted sampling procedures require that a well be flowed for long periods prior to sampling, thus reducing the temperature differential in the well. Therefore, proper operation of the sampler is anticipated to proceed without encountering any difficulty under anticipated well conditions.

APPENDIX B

LIST OF COMPANIES SUPPLYING SERVICES

The following companies supplied specialty items or provided special services for LBL in the fabrication and assembly of the downhole sampler.

American Hollow Boring Company 1901 Raspberry Street Erie, Pennsylvania 16512 G. T. Clover (814) 452-3664	Gun drilling 1-1/4 in. bore through one MP35N sample pressure vessel. Cost \$586. Delivery 3 weeks
Autoclave Engineers, Inc. 2930 West 22nd Street Erie, Pennsylvania 16512 (814) 838-2071	Inconel rupture disks
E. I. du Pont Nemours and Company 1007 Market Street Wilmington, Delaware 19898 Charles B. Miller (303) 774-0027 or (800) 441-9475	Krytox oil and grease
Humboldt Instrument Company 400 Preda Street San Leandro, California 94577 Alan Day (415) 638-3957	Machining all MP35N parts for one sampler. Cost, \$27,000; Delivery 2 months Machining two required sampler setting tools; Cost \$2,500; Delivery 2 weeks
Latrobe Steel Company Latrobe, Pennsylvania 15650 C. J. Stalnaker (412) 537-7711	Supplied all required MP35N bar stock for two samplers, including allowances. Approximately 593 pounds total, delivered during spring 1980. Total cost, \$19,863.
Northwest Dicronite 1954-H Old Middlefield Way Mountain View, California 94043 Mark Feely (415) 967-6940	Dicronite process dry film lubrication treatment of the sampler and its setting tools. Cost, \$440; Delivery, 4 days
Rea Magnet Wire Company, Inc. 3600 East Pontiac Street Fort Wayne, Indiana 46896 Richard D. Murphy (219) 743-8032	32 AWG Pyre-ML insulated (single build) copper magnet wire (NEMA thermal rating 220°C), purchased locally for approximately \$7 per pound (6 inch spool)

Spring Engineering Company
P. O. Box 94150
Houston, Texas 77018
Tom Upton
(713) 686-9488

Ten complete sets of MP35N springs for one
sampler. Total cost, \$1,696; Delivery, 3
months

Ultraspherics, Inc.
1390 Industrial Park Drive
Sault Ste. Marie, Michigan 49783
Nancy Marklevits
(906) 632-7310

One hundred balls, aged MP35N, 0.250 in.
diameter, grade 50. Cost, \$625; delivery,
4 months, complete

Viking Metallurgical Corporation
544 Cleveland Avenue
Albany, California 94710
S. Courtney
(415) 526-4881

Bar, forging, 2-1/2 in. diameter x 28 in.
long, annealed, forged from Carpenter
Electrical Iron, Carpenter Heat No. 27252.
Cost, \$235; delivery, 3 weeks

APPENDIX C

LBL DRAWING LIST OF THE DOWNHOLE SAMPLER

CATEGORY CODE 473001

1883113 PAGE 053

DATE MO-YR	DRAWING NUMBER	REV TYPE	CATEGORY CODE	DRAWING TITLE	
03-81	1883113	D	47 30 01	CONE	S.O.1884074
03-81	1883121	D	47 30 01	CONE RETAINER	S.O.1884074
04-81	1883143	D	47 30 01	CABLEHEAD SLEEVE	S.O.1884074
04-81	1883154	D	47 30 01	CONNECTOR BULKHEAD	S.O.1884083
04-81	1883161	D	47 30 01	FLOW RESTRICTOR	S.O.1884083
04-81	1883173	D	47 30 01	PISTON ROD	S.O.1883815
04-81	1883182	D	47 30 01	COLLAR	S.O.1883815
03-81	1883191	D	47 30 01	ARMATURE	S.O.1884092
03-81	1883202	D	47 30 01	CONTACT HOUSING, INSULATED	S.O.1884092
03-81	1883221	D	47 30 01	GUIDE BUSHING, INSULATED	S.O.1884092
03-81	1883231	D	47 30 01	CONTACT PIN	S.O.1884092
03-81	1883262	D	47 30 01	MAGNET HOUSING	S.O.1883815
03-81	1883272	D	47 30 01	MAGNET BODY	S.O.1883815
04-81	1883282	D	47 30 01	MAGNET ASSEMBLY	S.O.1883815
03-81	1883291	D	47 30 01	MAGNET RETURN SPRING	S.O.1883815
03-81	1883301	D	47 30 01	ARMATURE RETURN SPRING	S.O.1883815
04-81	1883311	D	47 30 01	UPPER VALVE RELEASE ROD	S.O.1883815
04-81	1883322	D	47 30 01	MAGNET RETAINING SLEEVE	S.O.1883815
04-81	1883331	D	47 30 01	RETAINING SCREW MAGNET	S.O.1883815
04-81	1883341	D	47 30 01	PISTON ROD KEYING PIN	S.O.1883815
04-81	1883353	D	47 30 01	MAGNET BULKHEAD	S.O.1883815
04-81	1883361	D	47 30 01	PLUG	S.O.1883815
04-81	1883371	D	47 30 01	ALL RETAINER	S.O.1883815
03-81	1883382	D	47 30 01	UPPER JAW	S.O.1883815
04-81	1883391	D	47 30 01	SPRING RETAINER, CHECK VALVE	S.O.1883815
03-81	1883401	D	47 30 01	CHECK VALVE SPRING	S.O.1883815
03-81	1883412	D	47 30 01	PISTON GUIDE PIN	S.O.1883815
04-81	1883422	D	47 30 01	ARMING PISTON	S.O.1883815
03-81	1883431	D	47 30 01	PISTON RETURN SPRING	S.O.1883815
04-81	1883442	D	47 30 01	UPPER TRANSITION SLEEVE	S.O.1883815
03-81	1883451	D	47 30 01	UPPER VALVE ARMING SPRING	S.O.1883815
04-81	1883462	D	47 30 01	UPPER BALL RELEASE SLEEVE	S.O.1883815
04-81	1883472	D	47 30 01	UPPER VALVE BALL CAGE	S.O.1883815
03-81	1883481	D	47 30 01	LOCK BALL	S.O.1883815
03-81	1883492	D	47 30 01	UPPER VALVE ARMING ROD	S.O.1883815
03-81	1883501	D	47 30 01	CLAMP INSERT	S.O.1883815
04-81	1883512	D	47 30 01	UPPER VALVE RELEASE HOUSING	S.O.1883815
04-81	1883521	D	47 30 01	VALVE PLUG	S.O.1883815
04-81	1883532	D	47 30 01	VALVE COUPLING	S.O.1883815
04-81	1883542	D	47 30 01	HOLD - DOWN RING	S.O.1883815
04-81	1883552	D	47 30 01	VALVE GUIDE PIN	S.O.1883815
04-81	1883563	D	47 30 01	VALVE GUIDE, UPPER	S.O.1883815
04-81	1883573	D	47 30 01	VALVE STEM	S.O.1883815
04-81	1883582	D	47 30 01	RETAINING SCREW	S.O.1883815
03-81	1883592	D	47 30 01	FILTER END CAP	S.O.1883815
03-81	1883602	D	47 30 01	VALVE STEM NUT	S.O.1883815
03-81	1883612	D	47 30 01	SPRING RETAINING WASHER	S.O.1883815
03-81	1883623	D	47 30 01	FILTER ASSEMBLY	S.O.1883815
03-81	1883632	D	47 30 01	INTERMEDIATE TRANSITION SLEEVE	S.O.1883815
03-81	1883642	D	47 30 01	CLOSURE	S.O.1883815
03-81	1883653	D	47 30 01	PRESSURE VESSEL BODY	S.O.1883815
03-81	1883662	D	47 30 01	BACK - UP RING	S.O.1883815

CATEGORY CODE 473001

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DATE MO. YR	DRAWING NUMBER	REV TYPE	CATEGORY CODE	DRAWING TITLE	
03/81	18B3672	D	47 30 01	RETAINING RING	S.O.18B3815
03/81	18B3682	D	47 30 01	ORIFICE REDUCER	S.O.18B3815
03/81	18B3692	D	47 30 01	ARMING/RELEASE ROD RETAINING NUT	S.O.18B3815
03/81	18B3702	D	47 30 01	RETAINING PIN, FIXED	S.O.18B3815
03/81	18B3712	D	47 30 01	LOWER VALVE RELEASE ROD	S.O.18B3815
03/81	18B3721	D	47 30 01	LOWER VALVE ARMING SPRING	S.O.18B3815
03/81	18B3732	D	47 30 01	LOWER BALL RELEASE SLEEVE	S.O.18B3815
03/81	18B3742	D	47 30 01	LOWER VALVE ARMING ROD	S.O.18B3815
03/81	18B3753	D	47 30 01	LOWER BALL CAGE	S.O.18B3815
03/81	18B3772	D	47 30 01	LOWER TRANSITION SLEEVE	S.O.18B3815
03/81	18B3781	D	47 30 01	VALVE SPRING	S.O.18B3815
03/81	18B3793	D	47 30 01	LOWER VALVE GUIDE	S.O.18B3815
03/81	18B3803	D	47 30 01	BULLET NOSE	S.O.18B3815
04/81	18B3815	A	47 30 01	ASSEMBLY	S.O.18B3815
06/80	18B3831	D	47 30 01	FILTER PLUG	
06/80	18B3852	D	47 30 01	RETAINING PIN, REMOVABLE	S.O.18B3815
06/80	18B3872	D	47 30 01	CONTACT HOUSING - GND -	S.O.18B4092
06/80	18B3881	D	47 30 01	GUIDE BUSHING - GND -	S.O.18B4092
04/82	18B3893	R	47 30 01	INSTALLATION AND MARKING DUG.	S.O.18B3815
04/82	18B3902	D	47 30 01	FILTER ELEMENT	S.O.12B3803
04/82	18B3912	D	47 30 01	PRESSURE VESSEL	S.O.18B3653
04/82	18B3992	D	47 30 01	SEPARATOR	S.O.18B4074
04/82	18B4053	D	47 30 01	CABLEHEAD	S.O.18B4074
04/81	18B4061	D	47 30 01	COMPRESSION RING	S.O.18B4074
03/81	18B4074	A	47 30 01	CABLEHEAD SUB - ASSY	S.O.12B3215
03/81	18B4083	A	47 30 01	CONNECTOR SUB - ASSY	S.O.18B3815
04/81	18B4092	A	47 30 01	ARMATURE SUB - ASSY	S.O.18B3815
04/81	18B4101	D	47 30 01	CONTACT RETAINER	S.O.18B3815
04/81	18B4112	D	47 30 01	CONTACT SLEEVE	S.O.18B3815
04/81	18B4122	D	47 30 01	INSULATOR BUSHING	S.O.18B3815
04/81	18B4141	D	47 30 01	PIN	S.O.18B4334
04/81	18B4151	D	47 30 01	FEEDTHRU ADAPTER	S.O.18B4083
04/81	18B4161	D	47 30 01	PLUNGER GUIDE	S.O.18B4083
04/81	18B4171	D	47 30 01	CAP	S.O.18B3815
04/81	18B4181	D	47 30 01	BUSHING	S.O.18B4083
04/81	18B4191	D	47 30 01	HOLD - DOWN DISC	S.O.18B4074
03/81	18B4201	D	47 30 01	FEEDTHRU RETAINER	S.O.18B4083
04/81	18B4211	D	47 30 01	INSERT	S.O.18B4074
04/81	18B4221	D	47 30 01	CONTACT RING	S.O.18B4083
03/81	18B4231	D	47 30 01	FEEDTHRU PIN	S.O.18B4083
04/81	18B4241	D	47 30 01	BASE, RECEPTACLE	S.O.18B4083
04/81	18B4251	D	47 30 01	CONTACT PAD	S.O.18B4083
04/81	18B4262	D	47 30 01	INSERT HOUSING	S.O.18B4074
03/81	18B4272	D	47 30 01	BASE, CONTACT	S.O.18B4074
04/81	18B4282	D	47 30 01	SETTING TOOL T - BOLT	
04/81	18B4292	D	47 30 01	SETTING TOOL PIVOT PIN	S.O.18B4334
04/81	18B4302	D	47 30 01	SETTING TOOL HANDLE	S.O.18B4334
04/81	18B4313	D	47 30 01	SETTING TOOL LEVER	S.O.18B4334
04/81	18B4323	D	47 30 01	SETTING TOOL YOKE	S.O.18B4334
03/81	18B4334	A	47 30 01	SETTING TOOL ASSEMBLY	
02/81	18B4352	D	47 30 01	MAGNET COIL	S.O.18B3283
04/81	18B4362	D	47 30 01	GREASE FITTING	

CATEGORY CODE 473401

DATE MO-YR	DRAWING NUMBER	REV TYPE	CATEGORY CODE	DRAWING TITLE
04/81	1854372	D	47 30 01	VACUUM FITTING
03/81	1384382	D	47 30 01	CLAMP LOWER JAW
03/81	18F4392	D	47 30 01	CARRYING CASE
03/81	18B4401	D	47 30 01	ARMING ROD RETAINING SCREW
02/81	18P4412	D	47 30 01	INTERIM VALVE COUPLING

S.O.18D3S15

APPENDIX D

FIELD TEST OF THE SAMPLER AT THE GEYSERS

On March 12, 1981, the flowthrough downhole brine sampler designed and fabricated by LBL for GRI was successfully field tested in a well at the Geysers geothermal field in California. This well, which belongs to Aminoil USA, is located near the extreme southeastern extension of the field. The area is believed to be near the transition between a vapor dominated reservoir to the northwest and a liquid dominated reservoir further to the southeast. Neither the name of the well nor its exact location were given to LBL for proprietary reasons.

The sample was taken at a depth of 7400 feet (2.25 km) subsurface. A survey taken two days earlier indicated the water level to be at 7200 feet. The steam temperature at moderate flow rates was about 500°F (260°C), and this is probably close to what the downhole temperature was at the time of actual sampling.

The steam saturation pressure at this temperature is 680 psi (47 bar), which probably approximates the downhole pressure at the time of sampling. If the sampler actually reached thermal equilibrium with the wellbore fluids during the sampling run, this would also have been the pressure inside the sampler at the moment it was removed from the lubricator. In any case, the pressure inside the sampler was no higher. Therefore, during this test, the sampler was operated above its rated temperature (450°F), but at far lower than its rated pressure (25,000 psi).

The test was successful and constitutes the first time that a liquid water sample has ever been taken downhole and brought up from the Geysers reservoir. (There had been several previous attempts using another downhole sampler.)

The test was performed under the supervision of mechanical engineers Leif Hansen and Bruce Dudak who together designed the sampler. They and mechanical technician Ray Solbau actually operated the sampler in the field. Chemists Oleh Weres and Leon Tsao received the sample from the engineers, performed several measurements and titrations while still in the field, and prepared and bottled the remainder of the sample for shipment to LBL for further analysis. Geothermal group leader Norman Goldstein, reservoir engineer Sally Benson, and electrical technician Don Lippert were also present to familiarize themselves with the procedures. Robert Galbraith was not able to be present. Aminoil was represented by geologist Richard Dunlap.

Although the sampler and the LBL personnel arrived at the well site at about noon, the sampler did not actually begin its trip down the well until nearly five o'clock due to several delays. First, the relatively cool weather at the site made it difficult to fill the cablehead with the very viscous Krytox oil. The high viscosity of the Krytox also made it difficult to cock the sampler valves open. The sampler was finally preheated with steam by putting it into the lubricator for a few minutes. This made it possible to cock the sampler. Before the sampler is actually used in a geopressured well, an electrical heating mantle to preheat the sampler and a powered positive displacement grease pump will be fabricated. These auxiliary tools will eliminate such problems.

The battery-powered current supply that had been hurriedly put together for this test failed due to a wiring error. The dc power supply in the logging truck was used instead. Since the sampler valves close if the current is turned off, a battery supply would provide protection against a generator

failure. This test, combined with the current and voltage data from other tests, has provided the input necessary to finalize our design for an ac-powered supply with internal battery backup. This power supply has now been fabricated and bench tested.

Inspection of the sampler the day after testing showed that all seals worked properly and the oil bath protected the critical electrical parts. The magnet coil exhibited no deterioration from the high temperature.

Because the decision to conduct the sampling run preceeded the run itself by only one week, the chemists did not have sufficient time to properly prepare for it. The techniques employed in handling the sample in the field were rudimentary. Overall, however, the whole operation served as a practice run, whose main function was to familiarize the chemists and field staff with the operational problems involved, rather than a fully mature data gathering run. Nevertheless, an adequate chemical analysis of the water was obtained. The data that has been and will be obtained from this sample will be essentially all that is normally obtained in properly designed and executed geothermal well sampling operations.

The results of the analyses performed by the LBL chemists in the field and at LBL are summarized in Table D-1 and discussed below.

From the chemists' point of view, the greatest deficiency of this field test was that a system for handling the brine sample in the field, without exposing it to air, was not available. Therefore, the water sample was

Table D-1. Analysis of sample from the Geysers.

Component	mg/l	mg-moles/l	Analytic method
Na	400	17.4	Atomic absorption
K	37	0.95	Atomic absorption
Rb	0.3	0.003	X-ray fluorescence
Mg	<0.1	<0.004	Atomic absorption
Ca	10	0.25	Atomic absorption
Sr	0.6	0.007	X-ray fluorescence
SiO ₂ (a)	353	5.9	Molybdate yellow
B	27	2.5	Carmines red
H ₂ S+HS ⁻	4.3	0.13	Specific ion electrode
HCO ₃ ⁻ (b)	480	7.8	Titration with acid
NH ₄ ⁺ (c)	(50)	(3)	Titration with base and calculation
Cl ⁻	504	14.2	Specific ion electrode
SO ₄ ²⁻	<11	<0.11	Nephelometric
pH(d)	6.2		
T(d)	29.8		

(a) Total silica determined by analyzing an aliquot that had been digested with NaOH. Molybdate active silica alone, as determined four days after sampling, was 199 mg/l = 3.3 mg-moles/l.

(b) Under these conditions, bicarbonate accounts for the total titratable alkalinity. The initial pH value (6.2) indicates that about 500 mg/l = 11 mg-moles/l of dissolved CO₂ was also present.

(c) Estimated from base titration data using known concentrations of other components and the principle of charge balance.

(d) Determined at the beginning of the first titration procedure, which began about 15 minutes after the brine was removed from the sampler.

exposed to air while being handled in the field, and no attempt could be made to analyze the small amount of vapor that probably was present in the unopened sampler.

The greatest problem encountered by the chemists was the temperature of the water when it was removed from the sampler—only 35.4°C. The major reason was that, prior to opening the sampler, the engineers had to hose it down with cold water for several minutes to be able to handle it comfortably and safely—but apparently with negative effects. It ought to be possible to avoid this problem when sampling actual geopressured wells.

The low sample temperature caused much of the dissolved silica to polymerize by the time the sampler was opened, as indicated by the distinct opalescence of the brine at that point. This makes the values determined for molybdate active silica concentration meaningless except for interpreting base titration data. It is possible and easy to reconvert polymerized silica to monomeric silica by digesting an aliquot of the water with NaOH in a boiling water bath before performing the molybdate analysis. Theoretically, this procedure ought to give the total concentration of silica that was present, both monomeric and polymeric, when the sample was originally taken. However, polymeric silica tends to settle out and adhere to the walls of containing vessels. Therefore, once the silica has polymerized, some of it is usually irreversibly lost from the sample, and the total concentration of silica in the sample decreases irreversibly. It is an easy matter to prevent further polymerization by diluting the sample after it has been removed from the sampler, but nothing can undo the effect of the polymerization that has occurred within the sampler.

Therefore, the total silica concentrations determined using NaOH digestion were erratic—304, 256, 352, 271, and 201 mg/l. Because polymerization and

precipitation can only cause the silica concentration to decrease, the highest of these values (352 mg/l) is probably the closest to fact. This is still suspiciously low since it corresponds to saturation with quartz at only 214°C. Saturation with quartz at the inferred well-bottom temperature of 260°C would have given a dissolved silica concentration of about 506 mg/l.

This uncertainty in the silica concentration would be less of a problem in the case of geopressured brine because these are usually at a much lower temperature and contain less dissolved silica. Therefore, even if cooled to ambient temperatures, the degree of supersaturation in amorphous silica (which is what actually precipitates out, rather than quartz) probably would not be high enough to cause any problems.

In this concentration range, ammonia would ordinarily be determined by a specific ion electrode. Unfortunately, because of the short notice, an ammonia electrode was not available, and the ammonia concentration had to be calculated from the concentrations determined for the other components by using the principle of charge balance. This value is only an estimate but is probably a fairly good one.

In calculating the ammonia concentration, the concentration of monosilicic acid was taken to be what was actually determined by the molybdate yellow method without first digesting the sample with NaOH. This was 199 mg/l = 3.3 mg-moles/l. Fortunately, the calculation of the ammonia concentration was not very sensitive to the value assumed for the silica concentration. This same calculation also excluded the possibility of ionic components not listed in Table D-1 from having been present in concentration >1 meq/l.

Sulfate was determined by the nephelometric method at LBL. The value obtained in this way was 11 mg/l = 0.11 mg-mole/l. This is suspiciously close to the value that had been determined for sulfide, and this strongly suggests

that the sulfate was actually formed by the oxidation of sulfide after the sample had been exposed to air. This is a common problem that arises in sampling geothermal wells. In general, determining small concentrations of sulfate in either geothermal or geopressured brines must be considered an unsolved problem. We intend to study it further in preparation for sampling geopressured wells.

The other components listed in Table D-1 were determined by standard methods, and the values probably are reliable.

A trace of chromium was also detected (between 0.2 and 1.2 mg/l not shown in Table D-1). Nickel was not detected (detection limit = 0.3 mg/l). This confirms the expected extreme corrosion resistance of the MP35N alloy of which the sampler is made.

The substantial concentrations of sodium, potassium, and calcium present in this water indicate that it is at least in part derived from actual reservoir brine rather than being all condensate. On the other hand, the total salinity of the sample is lower than is usually the case with geothermal brines in other areas. Therefore, substantial dilution of the brine with steam condensate is indicated. The substantial concentrations of bicarbonate, boric acid, and ammonia are consistent with this interpretation in that these are typical steam condensate components. (The silica concentration would not be very much effected by dilution since condensate would come to chemical equilibrium with quartz in a few days or weeks time.)

The Na-K geothermometer temperature that corresponds to this brine composition is 179°C. The Na-K-Ca geothermometer temperature is 199°C. That these geothermometer temperatures are so much lower than the measured temperature at the wellhead may simply be due to analytical error. On the other hand, it may also be geochemically significant. For example, it may

indicate that the water in the wellbore leaked into it from much shallower and much cooler horizons. (This particular well is cased down to only about 3800 feet subsurface).

The Na-K-Ca geothermometer is also affected by dilution, and it is highly probable that the water actually consists of brine diluted to some degree with steam condensate. For example, assuming that the actual brine has been diluted tenfold with condensate (which contains no sodium, potassium, or calcium) and correcting the calculation of the Na-K-Ca geothermometer temperature to compensate for this gives a revised temperature estimate of 223°C. Assuming that it has been diluted two-hundred-and-fiftyfold gives a revised temperature of 260°C, which is what was actually measured at the wellhead. In the latter case, the original, undiluted brine would be inferred to contain about 240 g/l of dissolved solids. This value is high, but it has been matched and exceeded in analyses of geothermal and geopressured brines in other areas; therefore, it is plausible.

When the results of the isotope analyses become available they will give a good, independent indication of the extent to which the "initial brine" has been diluted by steam condensate.

ACKNOWLEDGMENT

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