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LA-7664-C

Conference Proceedings

University of California

Proceedings of Workshop on Scale Control in Geothermal Energy Extraction Systems

October 6-7, 1977

Held at Los Alamos Scientific Laboratory

Los Alamos, New Mexico

MASTER

LOS ALAMOS SCIENTIFIC LABORATORY
Post Office Box 1663   Los Alamos, New Mexico 87545

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This work was supported by the US Department of Energy, Division of Geothermal Energy.

UNITED STATES
DEPARTMENT OF ENERGY
CONTRACT W-7405-ENG. 36

CONF-7710207--

LA-7664-C
Conference Proceedings
UC-66a
Issued: April 1979

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Proceedings Editor
Roy C. Feber
Workshop Coordinators
Roy C. Feber
Charles E. Holley, Jr.

CONTENTS

PRESENTATIONS

SUMMARY

The purpose of the Workshop was to arrive at a consensus among participants concerning research and development plans to control scale in geothermal energy extraction systems, relative priorities of the needs, and whether the required technology is available. The term "systems" was taken to mean production wells, plant components, and methods for disposal of spent geothermal fluids.

Working sessions of the Workshop occupied two days. The first day was devoted to invited papers. Following a presentation by Robert Reeber/DGE on "Geochemical Engineering Programs," one or more speakers reviewed the state of the art in the areas of

- design and economics of geothermal energy extraction systems,
- field experience with scaling,
- geothermal test loops,
- chemical and engineering modeling, and
- thermodynamic and kinetic data for geothermal fluids and minerals.

On the second day, Workshop participants divided into a Chemistry Panel, Paul Needham, Chairman, and an Engineering Panel, Richard McKay, Chairman, to draw up a list of conclusions and recommendations for future work. In addition to the papers given, panel members considered written statements and/or comments and questions, which were requested on the first day, from 18 Workshop participants. A volunteer committee then identified individual items on each submission as appropriate for consideration by the chemistry panel, the engineering panel, both, or neither, and the annotated items were made available to the panels.

The panels also had a suggested format or outline for recording and elaborating on their recommendations for each identified research need. The three-part format was subdivided as shown below.

- Statement of Research Need
  - Descriptive title
  - Background
  - Research need
  - Impact
  - Estimate
- Statement of an Unresolved Issue
  - What is the issue?
  - What are the opposing viewpoints?
  - Why does it need to be resolved?
  - How should it be addressed?
- Statement of Availability of Technology
  - What is the available technology?
  - What are the constraints in applying the technology to geothermal chemistry and engineering problems?
  - What are the possible options for exploiting the available technology?

AGENDA

Thursday, October 5, 1977

8:30 a.m.	Welcome and Introduction	R. Feber, LASL
8:45 a.m.	Geochemical Engineering Programs	R. Reeber, DOE
9:00 a.m.	Plant Design and Economics	J. Hankin, Bechtel
10:30 a.m.	Field Scaling Experience	G. Tardiff and L. Owen, LLL
11:30-12:30 p.m.	LUNCH	
12:30 p.m.	Geothermal Test Loops	J. King, Dow Chemical E. Bohlmann, ORNL H. Bishop, SDGE
1:45 p.m.	Chemical and Engineering Modeling	D. Shannon, BNWL T. Merson, LASL
3:15 p.m.	Thermodynamic Data for Fluids and Minerals	H. Eugster, Johns Hopkins Univ. J. Weare, UCSD

Friday, October 7, 1977

9:00 a.m.	General Discussion and Guidelines to Panels
10:15 a.m.	Preparation of Panel Reports Chemistry Panel Chairman: P. B. Needham, Bur. Mines Engineering Panel Chairman: R. A. McKay, Jet Propulsion Lab.
11:30-12:30 p.m.	LUNCH
12:30-3:30 p.m.	Completion of Panel Reports
3:30 p.m.	Presentation of Panel Reports

Saturday, October 8, 1977

8:30 a.m.-12:00 noon	Optional Field Trip to Fenton Hill Site

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PROCEEDINGS OF WORKSHOP ON SCALE CONTROL IN GEOTHERMAL ENERGY EXTRACTION SYSTEMS

October 6-7, 1977

Held at Los Alamos Scientific Laboratory
Los Alamos, New Mexico

Proceedings Editor
Roy C. Feber

ABSTRACT

A Workshop on Scale Control in Geothermal Energy Extraction Systems was held at the Los Alamos Scientific Laboratory on October 6-7, 1977. Workshop participants included representatives of the government, universities, industry, and the national laboratories. Our purpose was to identify those areas of chemistry and chemistry-related technology deemed most critical to the control of geothermal scale. Assignment of priorities provided a basis for selecting optimum areas for additional research and development support to assist the expeditious development of a geothermal industry.

FLUID MANAGEMENT ENGINEERING PROGRAM FOR THE GEOTHERMAL ENERGY DIVISION, US DEPARTMENT OF ENERGY*

by

Robert R. Reeber
Program Manager
Utilization Technology Branch

I. INTRODUCTION

The Fluid Management Engineering Program is being developed under the auspices of the Department of Energy's Geothermal Energy Division in cooperation with industry to incorporate the production, energy extraction, and disposal aspects of geothermal development. This program has a variety of participants involving groups concerned with energy technology development, those interested in mineral recovery, waste utilization and desalination, and those with environmental concerns, such as disposal and subsidence problems.

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*This paper is a revision of the original presentation.

This presentation summarizes my views regarding approaches required to define and solve the fluid management needs of geothermal electric development. Some pertinent data or conclusions may have been omitted either due to unavailability or simply due to a lack of knowledge. It would be appreciated if they were communicated where possible to me. It is anticipated that current developments may cause important modifications for future work.

II. NEED FOR FLUID MANAGEMENT ENGINEERING

In attempting to develop a major geothermal industry, we must ask if there is indeed a need to be concerned with Fluid Management Engineering.

One major problem facing US industry is the *cost* of geothermal development. Table I illustrates the efforts of private industry to develop geothermal sources from 1927 through 1965, and the problems faced by these companies at each site, as compiled by Koenig in his article in the First International Geothermal Symposium.[1]

Excluding the Geysers, this table shows that over 158 hydrothermal wells including some deep ones (over 8000 ft) have been drilled over the past 50 years with basically no hydrothermal utilization. If we take a very rough cost figure of $250 000 per well, we see that private industry has invested approximately $40 million with virtually no return.

As shown in Table I, this failure may be principally attributed to three factors: (1) production problems, (2) corrosion and scale problems, and (3) disposal problems.

One of the major production problems is in-flow of cold water. This is primarily due to the lack of fluid flow control in the wellbore; while trying to extract the energy from the hot water, we are unable to seal it off from the cold water.

Another serious production problem is illustrated in Fig. 1. The well shown[2] is part of the Cerro Prieto plant system in Mexico. This production well has been clogged by about 30 lb. of silica, iron sulfide, and calcium carbonate scale. Such scale plugging requires periodic chemical and mechanical cleaning.

Figure 2 compares a high-pressure gas well with a geothermal well. The operating temperature of the gas well is approximately 120-176°C (250-350°F). By comparison, the operating temperature of a geothermal well can reach 300°C (570°F), with the mean temperature being around 225°C (437°F). Pressures in hydrothermal wells are approximately 100 psi or greater at the surface, not nearly as high as gas wells but still at pressures significant enough to be of some concern. In geopressured wells, pressures can exceed 10 000 psi at temperatures to 350°F.

In the gas well a production packer controls the flow of the fluid through a central tube to the energy extraction system. An annulus filled with corrosion inhibitor separates this tube from the central casing in our example. This protects the normal casing and ensures long life for the system. For the geothermal well, the corrosive chemical environment is in contact with the entire casing during operation. Also, additional stress is put on well completion materials as a result of periodic scale cleaning. Well completion and production materials are at present being tested to determine capabilities of the state of the art.

Another corrosion problem stems from periodic chemical treatments that are necessary to maintain fluid flow capacity in injection wells. Tests to evaluate these problems are planned for Fluid Management Engineering. Such chemical procedures will require that the well completion system materials be redesigned to keep present corrosion within tolerable limits. Oil field casing and cements have not been tested for this typical geothermal problem.

In addition to planned chemical treatments, plant materials are exposed to far higher temperatures and far more corrosive geochemicals, salts, hydrogen sulfide, carbon dioxide, and methane than is generally experienced in other types of power plants.

TABLE I

EXPLORATORY DRILLING FOR GEOTHERMAL FLUIDS

Site	Number of Wells Drilled	Dates Drilled	Problem
Salton Sea (Niland)	15 >65	1927 1932-54 1957-65	Corrosion, scaling, waste disposal.
Brady Hot Springs (Magma Power Co., 10-MW binary power plant)	9	1959-65	Inflow of cold water and scaling.
Beowawe, Nevada	11	1959-65	Inflow of cold water and scaling.
Steamboat Springs	~36	1920-62	Severe scaling by $CaCO_3$, loss of production in days.
Clear Lake (Magma Power Co., Earth Energy, Inc.)	4	1961-64	Severe problem with waste disposal, 100 ppm boron.
Valles Caldera, Jemez Springs, Sulphur Springs	4	1960-64	Decline of production with time.
Calistoga, California	3	1960-61	Problems with disposal and scaling, erupting geyser well.
	~158 wells		

~$40 million privately invested with no return.

Figure 3 shows the effect of this corrosive environment on sections of pipe from the Niland Geothermal Test Facility. After less than a year in service, the pipes are already badly pitted.[3] These are ordinary steels. It is clear that overly conservative materials selection will significantly raise capital costs, whereas inadequate materials increase the probability of dangerous and expensive accidents at geothermal plant sites. The gas-geothermal well comparison has illustrated the importance of packers for fluid management and corrosion control. Some results from our laboratory screening program[4] can give an appreciation of the problems being faced. We have tested prospective new packer materials and also some commercial materials currently used as packers in the oil, gas, and aerospace industries. Figure 4 shows seals that are completely

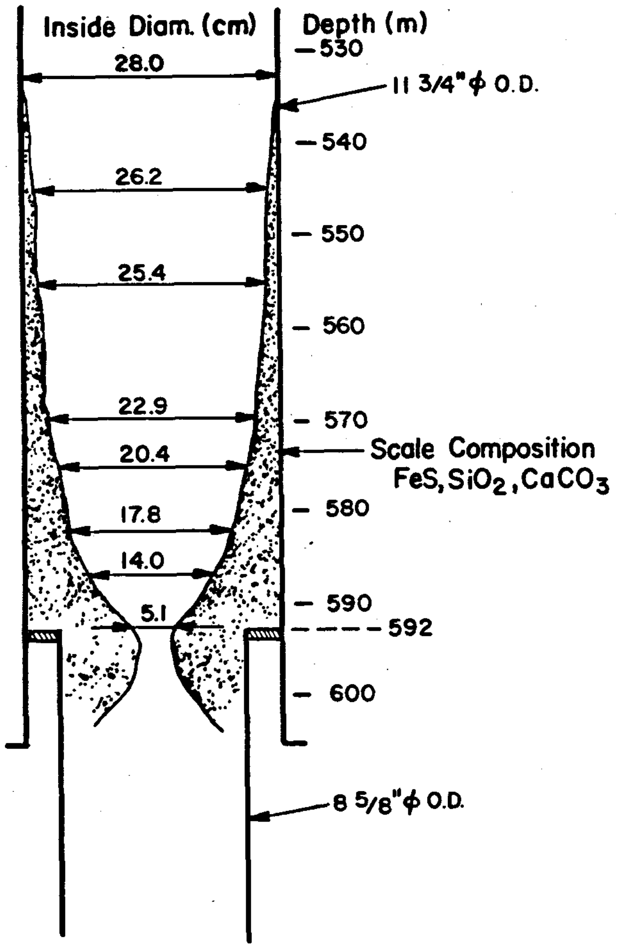

Fig. 1.
Plugged production well at Cerro Prieto.

destroyed after just 24 hours of service at 250°C (approximately 480°F). There are many other samples where the materials are actually crumbling apart after 24 h (Fig. 5). Elastomeric (rubber) seals are convenient because they can be substituted in the present oil and gas systems, thus easily upgrading equipment temperature limits. Because of the safety and materials problems, more new and complex seal systems are needed. Alternate, less versatile seals containing plastics, ceramics, and metals require redesign of equipment at a higher cost. It is clear that to ensure environmentally acceptable operation, consensus performance and safety standards, and better materials, if necessary, must be developed for tubing, casing, packers, cement, and subsurface shutoff valves.

The last, but most certainly not the least, of these major problem areas concerns the question of disposal of waste fluids under the Fluid Management Program.

Industrial options here include

- injection,
- surface disposal, or
- waste utilization.

Tables II and III give a view of geothermal injection systems, both in the United States and abroad.

Table II illustrates some of the common injection problems experienced at geothermal well sites.

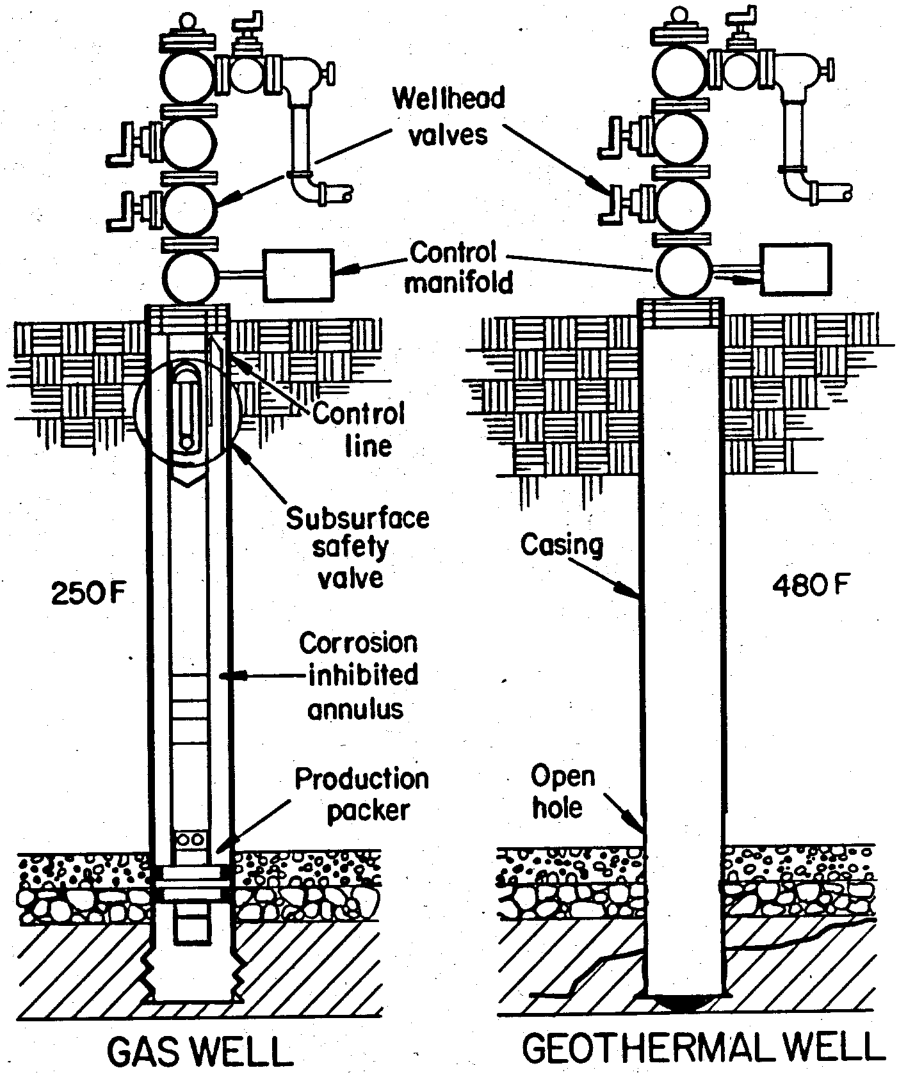

Fig. 2.
Gas vs geothermal well comparison.

These include the inflow of cold water, scaling, loss of injectivity, and surface disposal problems.

Table III illustrates five cases of successful injection. At the Geysers, an average of 4 700 000 gallons of steam condensate are being injected per day for a plant capacity of 522 MW. This condensate is low in total dissolved solids, and its amount is roughly equivalent to 6 MW for a typical hydrothermal plant.

At Salton Sea, 126 million gallons of brine were injected at a rate of 600 gal. per min. This was done over a period from 1964 through 1965. At Valles Caldera, also over a 2-yr period (1972 through 1974), 100 million gallons were successfully injected.

On the foreign scene, successful reinjection was conducted in El Salvador[9] during 1970-71 at rates of 1500 to 2700 gal. per min as part of planning for a 100-MW plant. In this case, the water was very hot, around 150°C. About 10% of the total plant investment and generating cost was estimated to be needed for reinjection. On a 50-MW scale, this is equal to about $2 to $2-1/2 million.

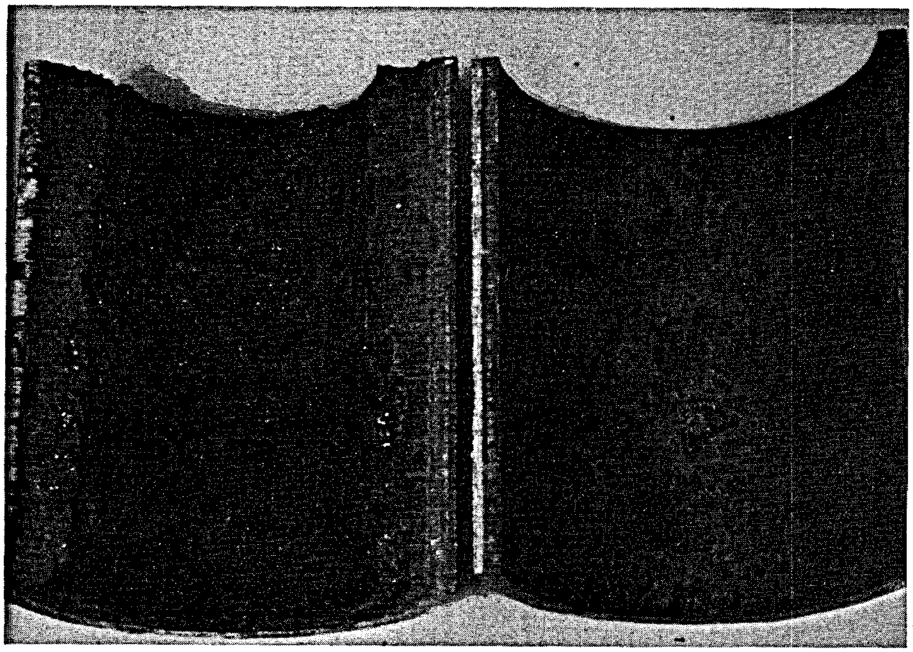

Fig. 3.
Pitted pipe.

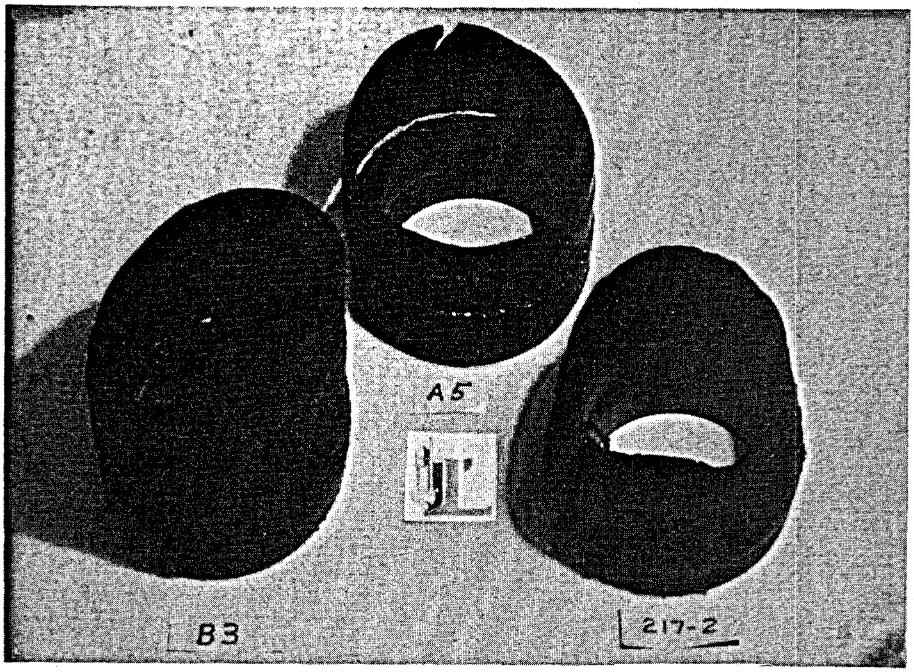

Fig. 4.
Disintegrating seals.

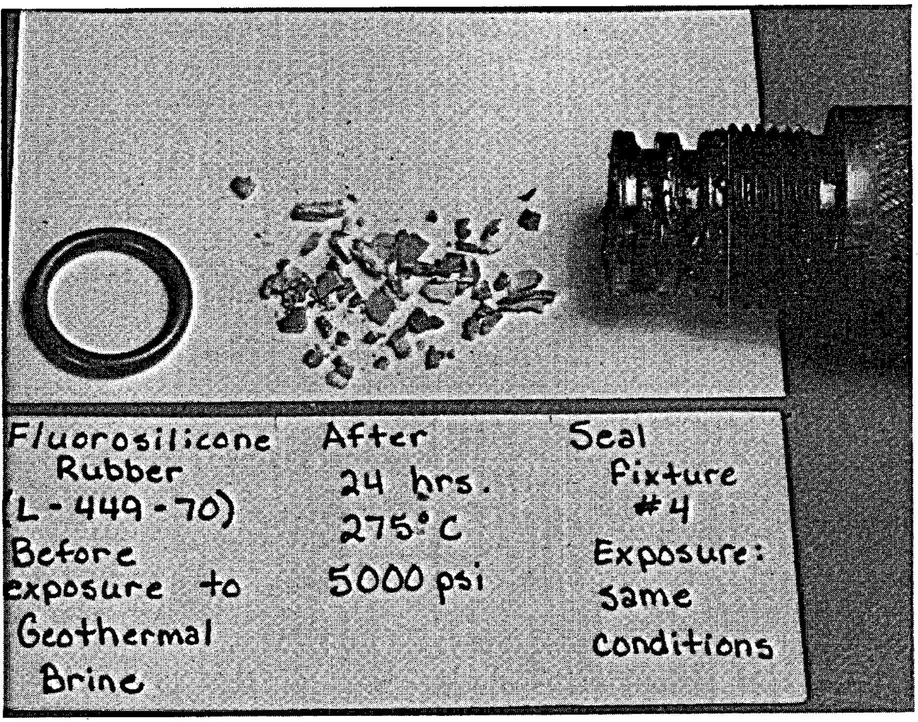

Fig. 5.
Crumbling seals.

TABLE II

INJECTION PROBLEMS

Problem	Well	Time	Remarks
Inflow of cold water, and/or scale	Brady Hot Springs, NV[1]	1959-65	Both
	Beowawe, NV	1959-65	Both
	Steamboat Springs, NV[1]	1920-62	Severe scaling
Loss of injectivity	Alfina, Italy	1977-78	6% year loss; 6600 gal./min injected
	Otake, Japan[5]	1972-Present	
	East Mesa, CA		
	Westmoreland, CA		
Surface disposal problems	Wairakei, N.Z.[6,7]	1964-74	13.5 ft subsidence; ≃200 tons arsenic discharged into local river
	Clear Lake, CA[1]	1961-64	100 ppm boron
	Calistoga, CA[1]	1960-61	

TABLE III

INJECTION SUCCESSES

Location	Description
The Geysers, CA[8]	Currently in production. 4 700 000 gal./day steam condensate. Low total dissolved solids. 522 MW installed capacity.
Salton Sea, CA[8]	Period 1964-65. 126 000 000 gallons injected (~1.5 MW). 600 gal./min injected.
Valles Caldera[8]	Period 1973-74. 100 000 000 gal. injected.
El Salvador[9]	Period 1970-71. 1500-2700 gal./min. Water was very hot ≃150°C. 10% of total investment and generating cost → injection for planned 100-MW plant.
El Salvador[10]	Period 1975-77. 60-MW hydrothermal plant. 70% of produced fluid reinjected. Water was very hot ≃150°C.

Since 1975, large-scale successful reinjection over a 2-yr period has occurred in El Salvador using up to 70% of the producing well capacity for a 60-MW plant. Future plans include injecting 30% of well capacity for maintenance of pressure in the reservoir. The remainder will be disposed of by existing surface disposal facilities (sea canals, etc.). An objective of the Fluid Management Engineering Program is to evaluate such foreign experience in terms of US needs and requirements as soon as possible.

In general, we are planning a plant module on the order of 50 MW, which would require an injection capacity of approximately 30 million gal. per day, or 20 833 gal. per min. Planned development at several sites is significantly larger, up to 1666 MW, as summarized in Table IV.[11]

The rate of injection for the first 50-MW plant module would be almost 10 times that successfully experienced with acid mine and oil field wastes, and 8 times that experienced with steam condensate injection at the Geysers. Although we have seismic and environmental base-line studies in place, without actual site experience we do not know what the consequences or long-term effects of such quantities will be. Long-term (2- to 5-yr) experience with the first 50-MW demonstration plant in New Mexico will give us invaluable information concerning this disposal approach. Smaller size injection experiments are also planned in our program (~1/2 MW).

Another impediment to disposal by injection is the quality of the water itself. We can draw a parallel here to the problems encountered in the mining industry, where acid mine drainage is disposed of by injection.[12] Because of present problems, some authors have called for restrictions on all deep-well injection for such systems.

TABLE IV

EXAMPLES OF PLANNED POWER ON-LINE THROUGH 1994

Beowawe, Nevada	650
Brady, Nevada	700
Brawley, California	900
Coso, California	600
The Geysers (Hydro), California	1 000
The Geysers (Steam), California	1 666
Heber, California	700
Puna, Hawaii	900
Roosevelt, Vermont	650
Salton Sea, California	1 000
Surprise Valley, California	700
Valles Caldera, New Mexico	750
12 sites	**10 216 MWe**

TABLE V

OIL FIELD BRINE DEEP-WELL DISPOSAL SYSTEM OPERATING COSTS

Injection Rate (gpd)	Injection Pressure (psi)	Depth (ft)	Cost ($/1000 gal.)
2 000 000	900	3 000	0.180
		7 000	0.217
		12 000	0.283
	260	3 000	0.119
		7 000	0.158
		12 000	0.223
	0	3 000	0.094
		7 000	0.131
		12 000	0.204

Table V gives estimates of the Appalachian Regional Commission for oil field brine deep-well disposal system operating costs.[12] This table summarizes the experience of 81 wells of various depths and injection rates, taking into account factors such as repairs, labor, chemicals, pumping energy, administrative expense, and equipment and replacement costs. It was estimated that operating costs for acid wastes would be 10-20% higher, due to the greater corrosivity.

Table VI shows capital costs of acid disposal wells in the Appalachia region.[12] Unlike oil field brine disposal, a high percentage of the cost is involved in the surface pretreatment facilities and pumping equipment. Small amounts of silica have caused severe injection problems. Figure 6 shows silica and other minerals that have precipitated from the Cerro Prieto plant condensate as it drains to their disposal pond. Based on mine waste disposal problems it is anticipated that successful long-term, large-scale injection will require pretreatment for silica removal.

There are also other environmental disposal problems that may stem from processing geothermal fluids. Table VII illustrates what constituents may be found in the geothermal waters of 14 of the major US known geothermal resource areas (KGRAs). Data were summarized from the compilation of Cosner and Apps,[13] and supplemented by information from Vetter[14] and Thompson et al.[15] The table shows the general ranges in parts per million of lead, barium, boron, fluoride, mercury, arsenic, zinc, and hydrogen sulfide for these principal KGRAs. In cooperation with industry, present R & D is quantifying the large uncertainties in our knowledge of the chemistry of the natural resource.

Although other contaminants may not cause as large an environmental concern, from a technical standpoint they are significant in that they affect plant performance, plug production and injection wells, and add to production costs (Fig. 7). These include silica, calcium carbonate, sulfates, and heavy metals sulfides. Waste water with these contaminants will have to be processed in expensive pretreatment facilities before fluid surface disposal due to the quantity of these sludge materials.

TABLE VI

CAPITAL COSTS, ACID WASTE DISPOSAL WELLS, APPALACHIA REGION

Well Location	Eastern Ohio	Western Pennsylvania		Southwestern New York	
Total depth (ft)	3 300	4 800	6 000	3 060	4 300
Design injection rate (gpm)	100	100	100	300	100
Design injection pressure (psi)	700	300	4 000	---	---
Total system cost	$564 000	$960 000	$770 000	$502 000	$447 000
Surface equipment	400 000	400 000	220 000	125 000	147 000
Completed well	164 000	560 000	550 000	377 000	300 000
Cost averages					
Per ft	$ 170.00	$ 200.00	$128.00	$164.00	$104.00
Per psi	806.00	3 200.00	192.00	---	---
Per 1 000 gal.	3.92	6.66	5.34	1.16	3.10

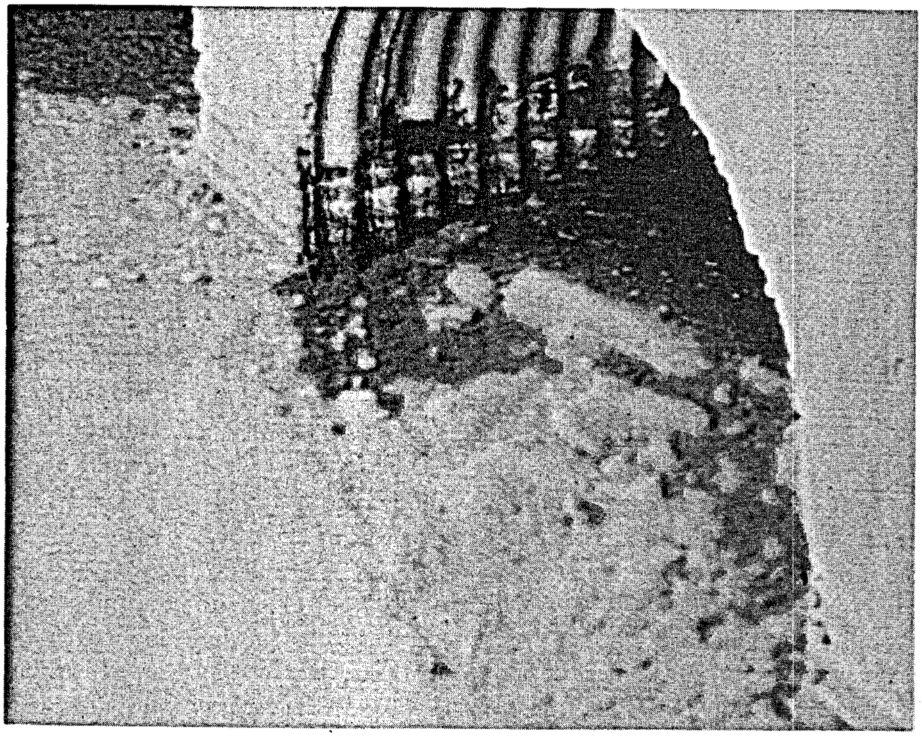

Fig. 6.
Cerro Prieto disposal pond.

TABLE VII

FLUID CONTAMINANTS

(parts per million)

KGRA	1	2	3	4	5	6	7	8	9	10	11	12	13	14
TDS	290	855	1100	1596	1804	5610	6000	6442	7034	13168	19000-22000	26300	52625	151 237-319 000
Temp (°C)	80	242	238	146	180	238	280	240	294	190	305	204	147	200-340
Pb	<0.005	---	---	---	<0.5	---	---	---	---	1.6	<0.002 −0.2	---	---	<4.-155.
Ba	<0.2	---	---	<0.4	<0.2	---	---	---	---	6	12	14	---	85-570
B	0.14	1	11	0.3	1.5	0.56	---	29	---	4.1	4.5-20	9.75	---	100-745
F^-	2-14	6	20	7.3	---	3.8	---	5	---	1.7	1.-2.	0.99	---	2.4-18
Hg	<0.02	---	---	---	0.0008	---	0.0005-0.0444	---	---	---	---	---	---	0.006-<0.2
As	<0.05	---	0.2	---	---	---	---	---	---	---	0.38-2	0.26	---	0.16-15
Zn	---	---	---	---	0.5	---	---	---	---	0.3	0.01-0.03	0.07	---	283-740
H_2S	<0.001	6	14	0.1	---	---	~200	---	1.5-6	~2	300-600	3	---	10-30

KGRA

1 Boise
2 Beowawe
3 Mono-Long Valley
4 Raft River
5 East Mesa
(Vetter et al.)
6 Coso
7 Puna
8 Roosevelt
9 Baca
10 Heber
11 Cerro Prieto
12 East Mesa
13 Brawley
14 Salton Sea

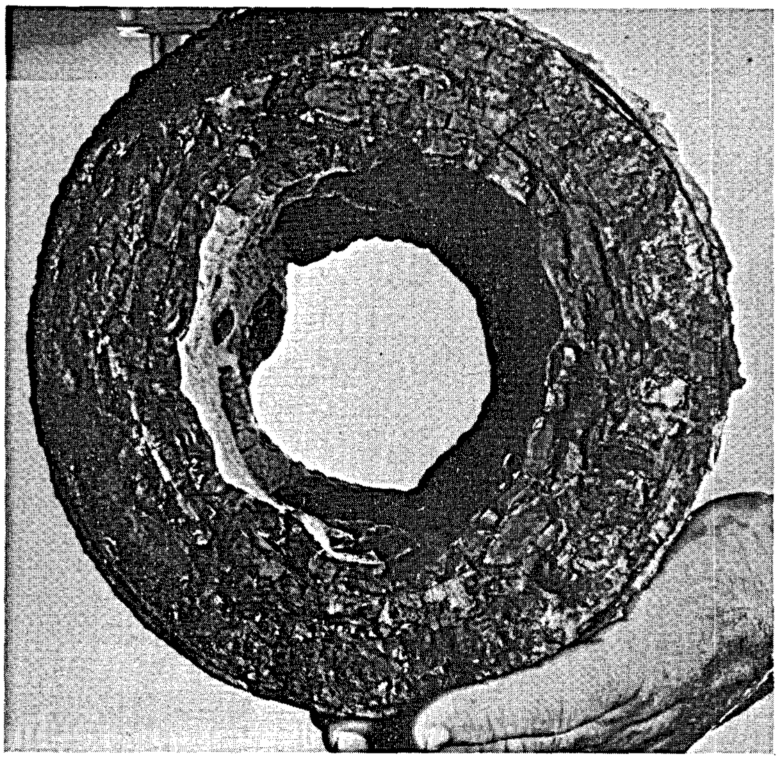

Fig. 7.
Clogged pipe.

"Silica for example, is highly soluble in hot geothermal water and solubility decreases as water is cooled in a geothermal power plant. Calculations indicate as much as 30 000 tons per year could pass through a 100-MWe water cycle plant. The major cost impact will be on the reinjection well system where costs of 1-10 mills per kWhr of power produced could accrue to waste handling alone."[16]

No final regulations presently exist for geothermal fluid disposal due to the lack of operating experience and geothermal plants. Some conception of possible problems to be faced can be obtained from experience in other industries. As an illustration of regulations developed for part of the mining industry, EPA standards for specific acid mine waste effluent[12] require that the heavy metals in total must comprise no more than 3 ppm, that total dissolved solids cannot exceed 52 ppm, and that the pH range must be between 6 and 8.5. These are fairly strict standards sustained by the EPA. They are lower, in fact, than most natural waters. The EPA is reviewing these standards.[17] Because of detoxification effects of some impurities on others, there is a high probability that some of them will be revised and raised.

III. WHAT DO WE KNOW ABOUT THE NATIONAL RESOURCE?

Initial research by the DOE Reservoir Assessment Branch indicates that approximately 95% of the national resource reservoirs have a salinity less than sea water and can be classified as brackish water (Table VIII).[18]

TABLE VIII

CLASSIFICATION OF GEOTHERMAL RESOURCES BY TEMPERATURE AND SALINITY

Down-Hole Fluid Temperature[a]	Very Low Salinity ($0\text{-}2 \times 10^3$ ppm)	Low Salinity ($2 \times 10^3\text{-}2 \times 10^4$ ppm)	Intermediate Salinity ($2 \times 10^4\text{-}10^5$ ppm)	High Salinity ($>10^5$ ppm)
Very high temperature >240°C	Yellowstone, Wyoming	Puna, Hawaii Valles Caldera, New Mexico Roosevelt Hot Springs, Utah	Cerro Prieto, Mexico	Salton Sea (Niland), California
High temperature 150°C-240°C	Mono-Long Valley, California Beowawe, Nevada	East Mesa, California Heber, California Steamboat Springs, Nevada Roosevelt Hot Springs, Utah	Brawley, California	
Intermediate temperature 90°C-150°C	Raft River, Idaho Fly Ranch Hot Springs, Nevada	Brady Hot Springs, Nevada		
Low temperature 40°C-90°C	Klamath Falls, Oregon			

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[a] Temperature is based on actual well measurements.

Up to the present, field experience has addressed the more saline portion of the resource. But small amounts of scale can cause problems even for brackish water systems. New field experiments are planned to evaluate fluid management problems for this larger portion of the resource.

Injection can, of course, only be a viable alternative where the geology permits. It would be easy to dispose of the waste water by dumping it into a river or by some other form of surface effluent disposal; however, the problems cited above with contaminant levels do not usually make this a feasible alternative. Where injection is not possible, controls must be imposed upon the effluent in the same manner as for acid mine drainage. This would naturally require treatment before disposal in many cases, and could add significantly to the cost of geothermal development. Such pretreatment is site specific and a prime purpose of the program is to obtain field data.

The problem of these high costs and possible solutions was recently addressed by DuPont at its Chambers Works Plant in Deepwater, New Jersey. This facility produces a highly variable chemical effluent, which is being treated with a powdered, activated carbon sludge process called PACT.[19] Before discharge to the Delaware River, the treated waste water is mixed with 1-1/2 times its volume of clean condensate and is passed through a settling basin where suspended solids are reduced to 30 ppm or less. This amount of suspended solids meets current EPA standards for minimum effluent levels in the mining and milling industries.[12]

DuPont expects capital costs for that portion of its process designed to treat 26 400 gal. per min of inorganic waste water to be $13 million (1975 dollars) and predicts $7.2 million (1977 dollars) for yearly operating costs. It is fortuitous for our costing that this size system is about that of a 50-MW plant. It is hoped that pretreatment for injection can be accomplished at a significantly lower cost, especially by direct integration and optimization of control equipment in the whole plant.

In any case PACT technology with adaptation may be applicable to geothermal waste effluent treatment problems for the final and perhaps most desirable alternative; that is, waste water utilization. In some cases the brackish water can be purified to a point where it is usable in agriculture, drinkable by livestock, or put to some other public use (Fig. 8). Low-cost techniques have not yet been perfected for geothermal, and there is very little documented experience in utilization of waste effluent from geothermal wells. In addition to evaluating the retrofit of available equipment, long-term R & D is currently addressing improved waste utilization processes.

We have reviewed some of the important production, corrosion and scaling, and disposal problems. During this review we touched briefly on the need for subsurface safety valves (Fig. 2).

When materials performance standards are established and a significant level of actual field experience is obtained, we will be able to specify design criteria for such valves and also develop them. Why are these valves important?

In the case of our high-pressure gas well, if the surface equipment should blow off, the subsurface valve will react to shut off the system. Environmental damage would be minimized. In the geothermal well, if an accident or corrosion deteriorates or damages the surface equipment, we could face a very major catastrophe that would entail considerable time and expense to bring under control, with potentially serious environmental consequences. Two such blowout accidents have occurred in Mexico and Iceland; fortunately they were not near populated areas. As more and more geothermal wells are drilled without improved materials and well control systems, a greater possibility for such accidents exists. If it is not practical to have subsurface safety valves in geothermal wells, then a high standard of materials performance specifications must be maintained in completing and operating geothermal wells.

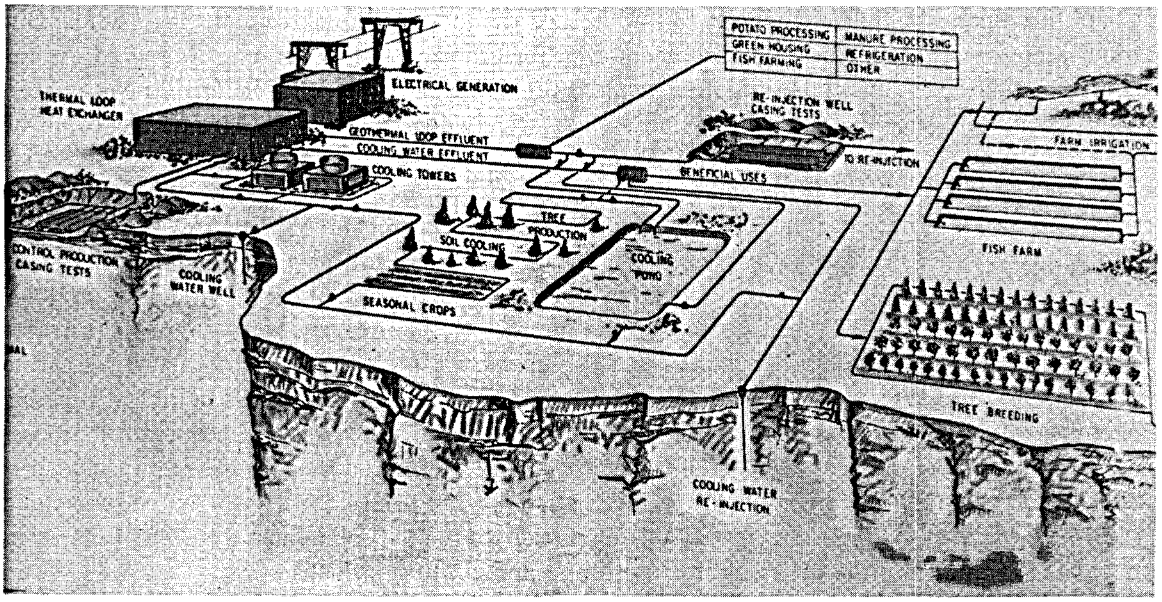

Fig. 8.
Medium-temperature geothermal reservoir test facility.

With many problems still unsolved, it is then no wonder why there is a reluctance in the private sector to invest large amounts of capital in the range of $50 million for one power plant without the assurance that the geothermal fluid can be produced, processed, and disposed of in a safe, environmentally acceptable, and cost-effective manner.

IV. HOW THE DIVISION OF GEOTHERMAL ENERGY PROPOSES TO TREAT IDENTIFIED PROBLEMS

The Division of Geothermal Energy proposes a four-part Fluid Management Engineering Program. To accelerate this process, all elements are being developed simultaneously and will provide us with working solutions to the most serious of these problems. The goal of the program is to provide necessary technology for management of the fluids.

The areas defined for analysis under the Fluid Management Engineering Program are

1. characterization,
2. monitoring,
3. modeling, and
4. systems research and development.

The relationships between these areas and the identified problems are shown in Fig. 9.

Industrial field experiments are necessary to define the site-specific nature of the fluid, and how this will be affected by changes in the conversion system. A series of projects has been planned accomplishing this. Results from these projects will enable industry to identify which systems will best apply to a particular resource, or to the types of resources available in the United States.

Field, and later plant, equipment will need to be monitored. This will ensure optimization of the process and, more important, control over the process at all times. Such monitoring will allow for expeditious shut-down in emergency cases. It will provide maintenance periods, and it will also help compile permanent records of critical plant variables, and thus prevent possible long-term operating problems. The data gathered from industrial field locations and pilot plants will give us the basis on which to model the processes.

The third step will help to improve efficiency, improve reliability, and develop processes for waste utilization and disposal.

Systems R & D, the fourth component, will help us develop the variety of hardware and chemical treatments necessary for most efficient use of the national resource. The ultimate goal

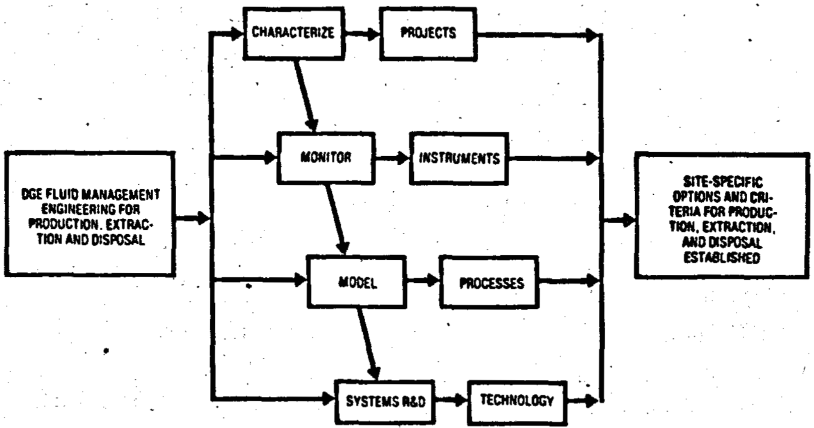

Fig. 9.
Fluid Management Engineering Program flow chart.

of this program is to establish technology for site-specific options and criteria in production, energy extraction, and disposal. This would enable industry to quickly determine for each particular site what sort of production systems would be most appropriate, what production criteria would be applicable to extend the life of the wells and reservoir, what sort of monitoring would be needed for the equipment, and what would be necessary to take care of the waste effluent. One important goal is to develop environmentally acceptable disposal systems that are integrated into total plant design. This goal will achieve significant cost benefits when compared with retrofit waste processing systems.

V. SPECIFIC PARTICIPANTS IN THE EFFORT

Table IX gives a breakdown of these participants. In the Department of Energy, Division of Geothermal Energy, project investigators are working on utilization technology, reservoir engineering, environmental problems, and large projects. Additional work in the Department of Energy is carried out by the Environmental Control Technology Division and the Office of Energy Research. Participants include personnel from the Menlo Park and Reston offices of the US Geological Survey; the Nevada and Cincinnati offices of the Environmental Protection Agency; the College Park Research Center, Reno Mineral Recovery Laboratory, and Columbia Plaza Project Office of the Bureau of Mines. The Bureau also has scattered programs of related interest to the Fluid Management Program in other laboratories.

Representing private industry are the Electric Power Research Institute; major utilities, GE and Elliott Turbine; major oil companies such as Union, Phillips Petroleum, and Chevron; primarily geothermal developers, Republic Geothermal and Magma Power; and, working through government Programs, the national laboratories and universities.

VI. PROBLEM IDENTIFICATION

Table X gives an overview of the workshops and meetings that served to define some of the problems of fluid management engineering. These have brought together government, industry, and university representatives in an effort to coordinate development activity.

In August 1976, DOE (then ERDA) sponsored a Scale Management Conference in San Diego, California; and in December 1976, a Brine Chemistry Overview in Washington, DC. Participants in this conference included government representatives from the Department of Energy (ERDA); from the Geology and Mineralogy Data Center of the US Geological Survey; national laboratories were represented, as were members of private industry. The focus of early work was primarily on

TABLE IX

PARTICIPANTS

DOE DGE
  GEOCHEM. ENG.
  RESERVOIR ENG.
  ENVIRONMENTAL
  PROJECTS OFFICE
DOE
  ENVIR. CONTR. TECH.

USGS
  MENLO PARK
  RESTON
EPRI & INDUSTRY
EPA NEVADA
BM COLLEGE PARK
  RENO

TABLE X

WORKSHOPS AND MEETINGS

1. Scale Management Conference, ERDA, San Diego, California, August 1976.
2. Brine Reinjection Subpanel Meeting, ERDA, Washington, DC, July-August 1976.
3. Brine Chemistry Overview, ERDA, Washington, DC, December 1976.
4. Int. Symp. Geothermal and Oil Field Chemistry, Soc. Petroleum Engineers, San Diego, California, June 1977.
5. Reservoir Management Meeting, Electric Power Research Institute, Warm Springs, Oregon, July 1977.
6. Fluid Management Workshop, DOE-LASL, Los Alamos, New Mexico, October 1977.
7. Sampling and Analysis Meeting, EPA, Las Vegas, Nevada, March 1977.
8. Sampling and Analysis Round-Robin Review Meetings, ERDA-PNL; Seattle, Washington, July 1977; San Francisco, California, September 1977.
9. Mineral Recovery-Fluid Management Coordination Meetings; Bureau of Mines-ERDA, December 1976, February 1977, and July 1977; Bureau of Mines-ERDA-USGS, January 1977.

problems with above-surface equipment; as experience in the program developed it was realized that a total systems approach to fluid management including wells and the reservoir was the more critical problem. The need for more site-specific field work and characterization was found to be necessary.

The Brine Reinjection subpanel met in July and August 1976 in Washington, DC, to discuss field work on an agency-by-agency basis. The subpanel discussed the feasibility of high-volume injection with its attendant environmental and technical constraints. A report was submitted to Research and Technology panel members.

DOE helped plan and also encouraged DOE-funded project papers for the Society of Petroleum Engineers International Symposium of Geothermal and Oil Field Chemistry in San Diego, California, in June 1977; a second conference will be held in 1979.

We have coordinated plans and programs with the Electric Power Research Institute at their Reservoir Management Meeting in Oregon in August 1977; with LASL's Fluid Management Workshop in October 1977; sampling and analysis work with the Environmental Protection Agency in Las Vegas, March 1977, and with Pacific Northwest Laboratories under contract in Seattle, July 1977, and San Francisco, September 1977, in a series of round-robin review meetings.

In addition, there have been a number of interagency geothermal research and technology panel meetings. These included representatives of DOE, the EPA, the Office of Saline Water, Bureau of Mines, National Science Foundation, NASA, and the Bureau of Reclamation. There have also been coordination meetings between DOE's Fluid Management Program and the Bureau of Mines' Mineral Recovery Group with input from the US Geological Survey.

VII. SPECIFICS OF THE PROGRAM

Let me elaborate on each of these elements in more detail (Fig. 10).

A. Characterization

Characterization is needed to determine the nature of the site, its fluids, and fluid-reservoir interactions. Environmental base-line studies, managed in the field, evaluate both the immediate impacts and the long-term impacts of subsequent geothermal power plant construction.

Next, after predicting the specific resource location, resource assessment is conducted with the assistance of industry to establish the magnitude of the resource from drilling and testing of flowing wells. Preliminary well chemistry is obtained during this step.

Because some data existed prior to DGE involvement in development, an initial characterization project has summarized all of the US geothermal fluid well data available in the open literature and obtainable from geothermal operations.

From a review of these analyses we determined a need for a sampling and analysis project. For specific sites there may also be environmental problems we cannot address as thoroughly as we would like with methods developed in this initial sampling and analysis project. It is expected that environmental concerns will stimulate the continued evaluation of these areas and eventually lead to the compilation of an ASTM handbook containing sampling and analysis standard methods for geothermal fluids.

An important part of the input for this manual will be the results of the round-robin comparisons provided by a variety of government, industrial, and private laboratory participants. They include the Environmental Protection Agency, the US Geological Survey, the Department of Energy, national laboratories (Livermore, Battelle Northwest, and Ames), Union Oil Company, Chevron Oil Field Research, and several private laboratories involved in geothermal analysis work. There are also several university-affiliated laboratories participating in this effort. By incorporating end users at the beginning of the project, we are able to relate it to their analytical needs. As an end product of the consensus, industry will have available in one location

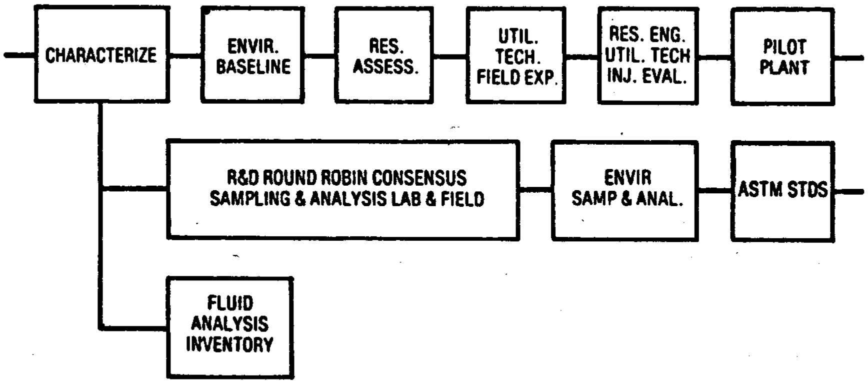

Fig. 10.
"Characterization" flow chart.

the current state of the art of standard methods of sampling and analysis. This project will have improved data reliability and provide for immediate technology transfer of government R & D to industry.

Other industrially coupled projects essential for characterization are the "production chemistry" field experiments (Fig. 11). These take into account that the extraction of large amounts of fluids from an equilibrium condition in the reservoir will produce a nonsteady state. In places where a significant amount of fluid will be extracted, it is expected that a new quasi-equilibrium will eventually be established in time, with correspondent changes in the fluid. Such changes can significantly affect the design and specification of later plants on that site. We have one example among our field experiences where initially the fluids indicated a very high level of noncondensable gases; after 6 months of production, this had dropped enough to completely alter the preliminary design choices based on the initial chemistry assessment.

In the assessment and injection technology evaluation, industrially coupled projects would examine the underlying geology and geochemistry of the region and how they determine the type of pretreatment necessary to permit disposal of the waste fluids.

This information will enable a determination, before major commitments of private and public dollars are made, of the relative timing for the development plan for the site in question and also an early identification of technical problems that can be addressed by associated R & D.

1. Implementation of Field Characterization. Early in program planning, a variety of field experiments, for example, at East Mesa (Fig. 12), were performed. This indicated that field data

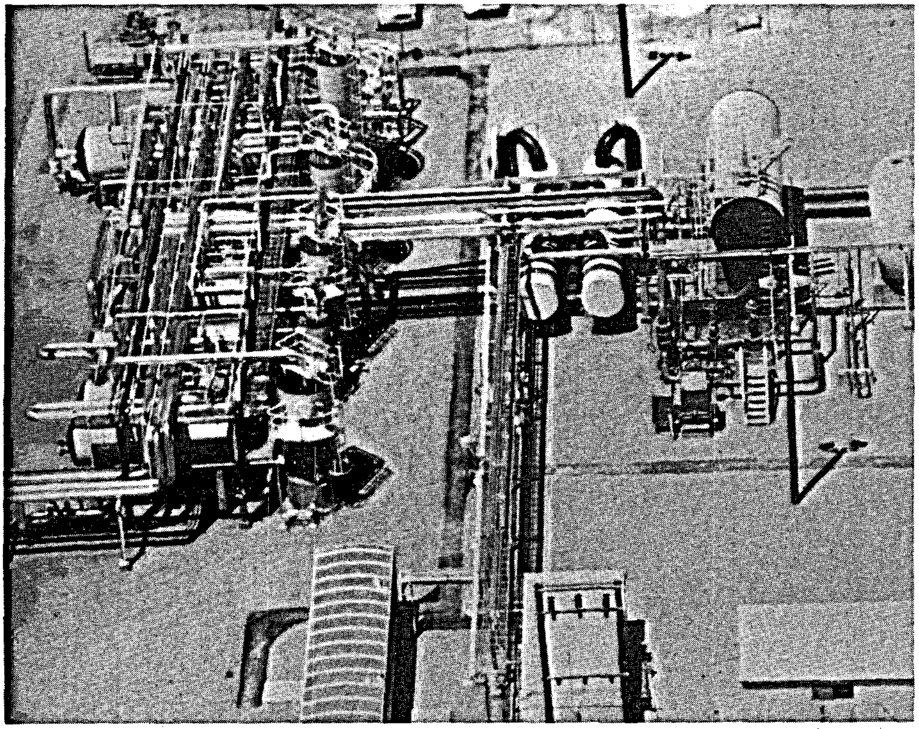

Fig. 11.
The Niland test facility.

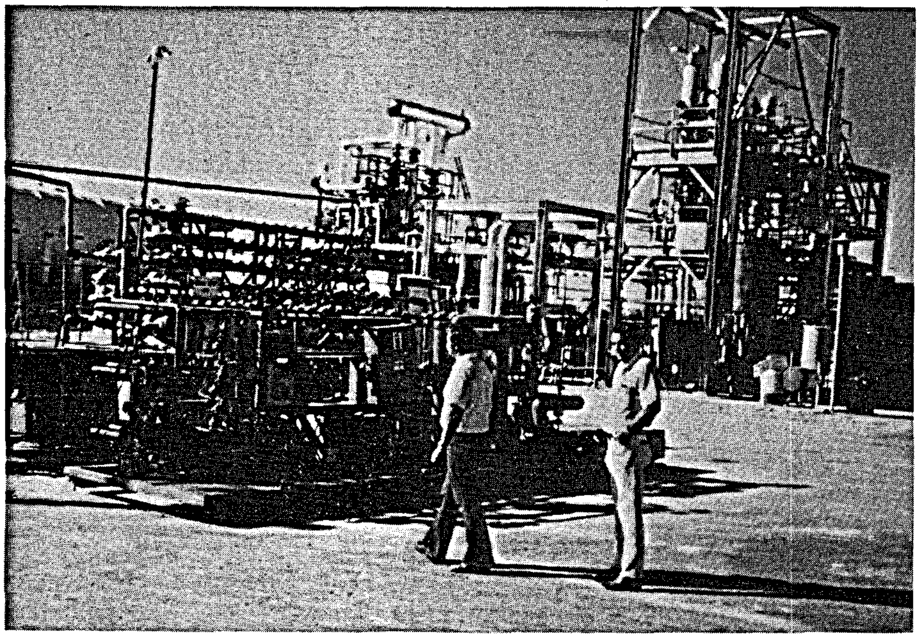

Fig. 12.
The East Mesa facility.

are required from systems at high flow rates. A prototype design was made for a 1-MW geothermal scaling and injection mobile test unit (Fig. 13). Major developers are evaluating their reservoirs with similar technology. Industrial information obtained from their experiments will provide input for modeling, necessary fluid management treatment and disposal procedures, and equipment planning and implementation.

2. Status of Characterization. Our LBL project has compiled 286 geothermal well fluid analyses for a report that will be available in February 1978.[18]

Battelle Pacific Northwest Laboratories has developed industrially coupled follow-on projects such as the standard sampling and analysis work to fill the gaps identified. Major chemical industrial service laboratories, geothermal operators, universities, and national laboratories have collaborated in this effort. Field data have been obtained from the Niland and Raft River pilot plant projects, with Bureau of Mines, LLL, and INEL cooperation. Field experiments involving production and disposal of large quantities of fluids at other locations are being planned for FY 1979.

B. Monitoring

Monitoring is essential for obtaining maximum operating efficiency from pilot and demonstration plants (Fig. 14). At the present time, industry is operating in an area of complex chemistry at high temperatures and pressures where instrumentation does not exist. Adequate instrumentation must be developed as early as possible to gain the maximum benefit from DGE field tests and larger demonstrations.

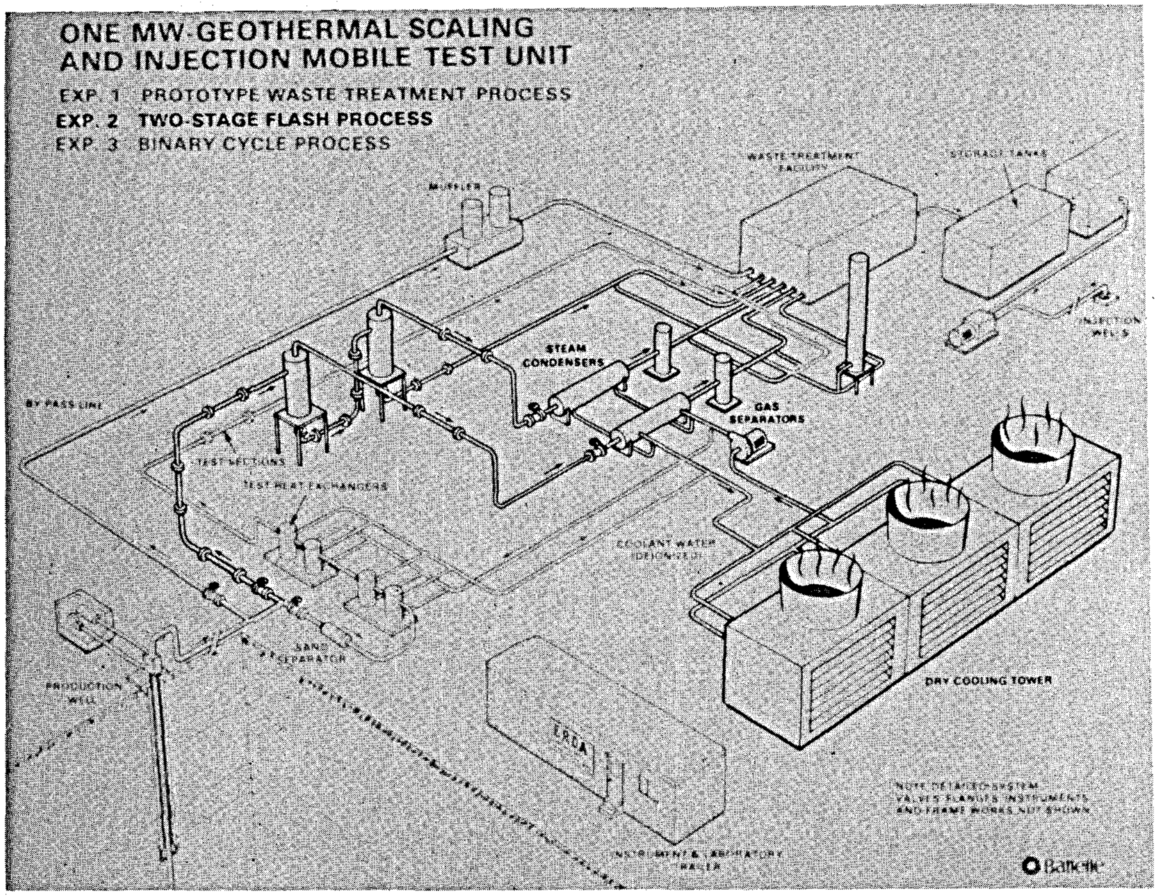

Fig. 13.
Mobile test unit.

1. **Addressing the Monitoring Problem.** To ensure program relevance to industrial problems, we enlisted the aid of a National Academy of Sciences Committee.

The suggestions made in the NAS committee report[20] will be implemented through a management and research and development effort operated by Battelle Northwest (Table XI).

Some examples of current monitoring research at Battelle Northwest are illustrated by the following figures. This project is to develop downhole and in-line fluid analysis probes to aid in our monitoring efforts. These probes will be designed to determine the brine chemistry at high temperatures and pressures in piping systems and downhole. The probe output will be analyzed and interpreted to help predict and control scaling and corrosion problems, and to aid in well and system operation.

We have developed an electrodeless conductivity probe that performed successfully in the laboratory at tests up to 250°C. Figure 15 is a cross section of the electrodeless conductivity probe developed in the Battelle Northwest Laboratory. This device is resistant to scale buildup, and can be calibrated without the necessity of shutting off the well.

Battelle plans to continue tests to develop other electrodes, and an RFP has been prepared for industry subcontracts for a pH electrode and downhole package design. Planned field tests of developed equipment are also an important part of the monitoring segment of this program (Fig. 16). They will assist us in interpretation of any failures in present or planned plants and provide

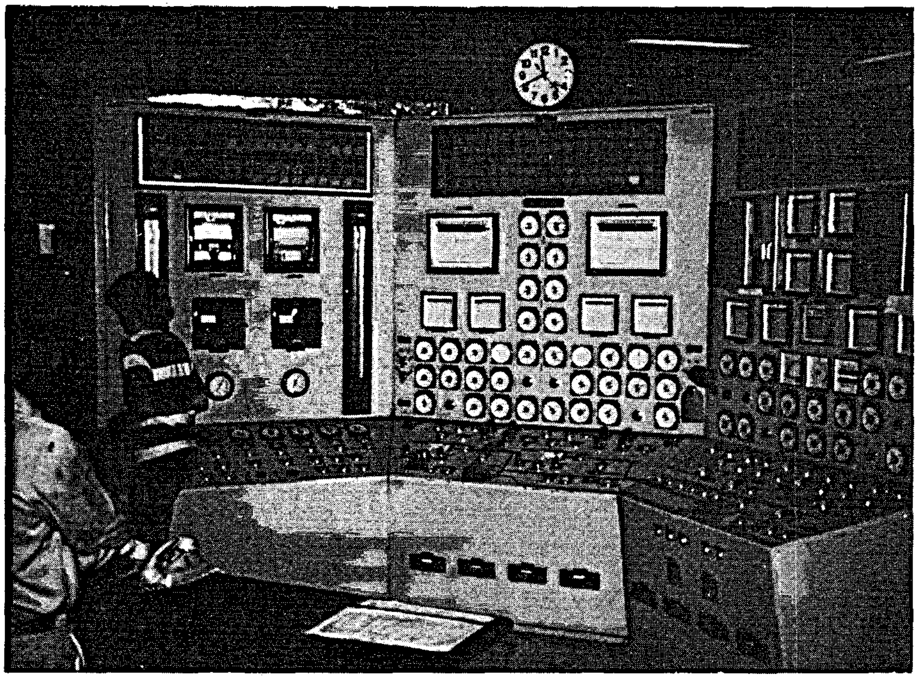

Fig. 14.
Cerro Prieto control panel.

TABLE XI

PACIFIC NORTHWEST LABORATORY PROGRAM

Inhouse R & D
Instrument R & D Subcontracts
Instrument Field Tests
Sampling and Analysis ASTM Coordination

us with tested instrumentation necessary to build better plants and maximize the use of information from present and planned facilities. After our successful 250°C laboratory tests on the conductivity meter, we successfully tested it in the field at an East Mesa test site at 161°C.

Additional field tests on new equipment will be integrated into the overall assessment/field technology test program. Instruments planned for the PNL subcontract (FY 1978 and 1979 starts) are shown in Table XII. These include the glass electrode and flash point indicator. The research subcontracts will lead to further development of a novel reference electrode, a H^+-sensitive electrode, a small rugged CO_2 sensor and a sulfide-sensitive electrode. Temperature/pressure monitors and integrated thermionic circuits recommended by the NAS study for early development are being pursued actively by LASL and Sandia in the logging program (Table XII). Logging is generally for short-term use, but it is anticipated that application to long-term use will result from later extensions of this work.

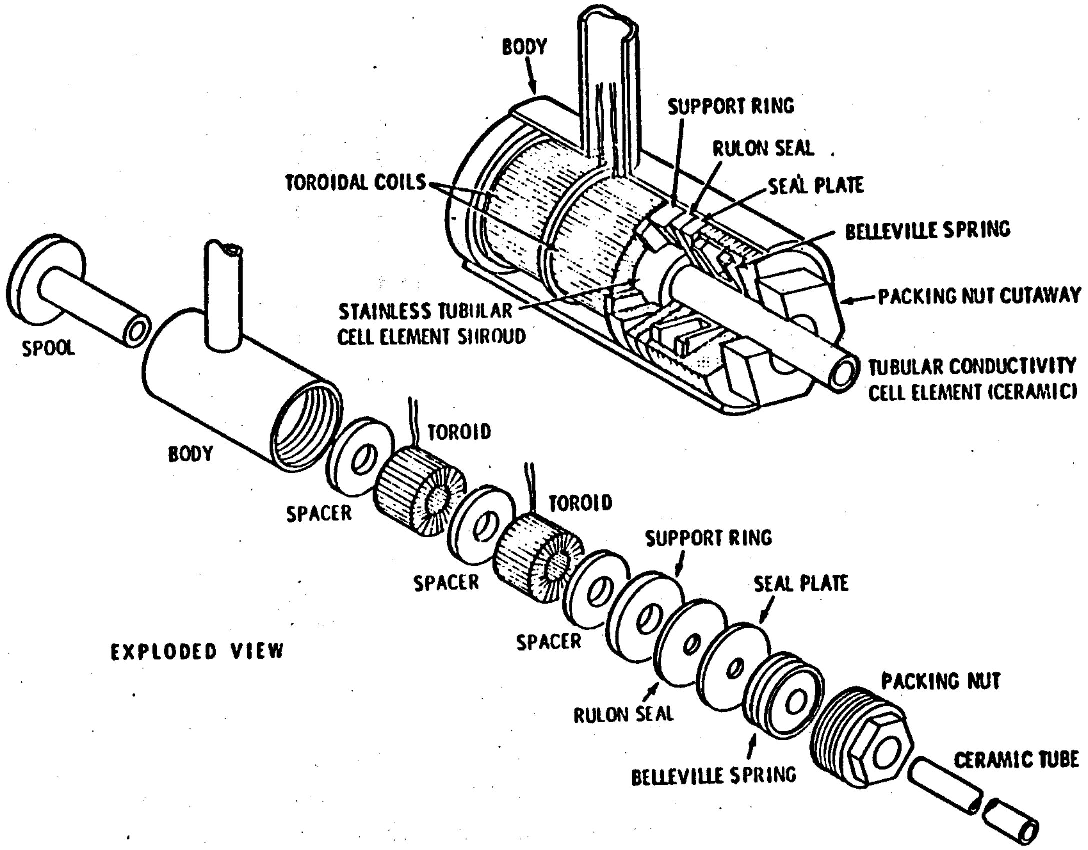

Fig. 15.
Electrodeless conductivity probe.

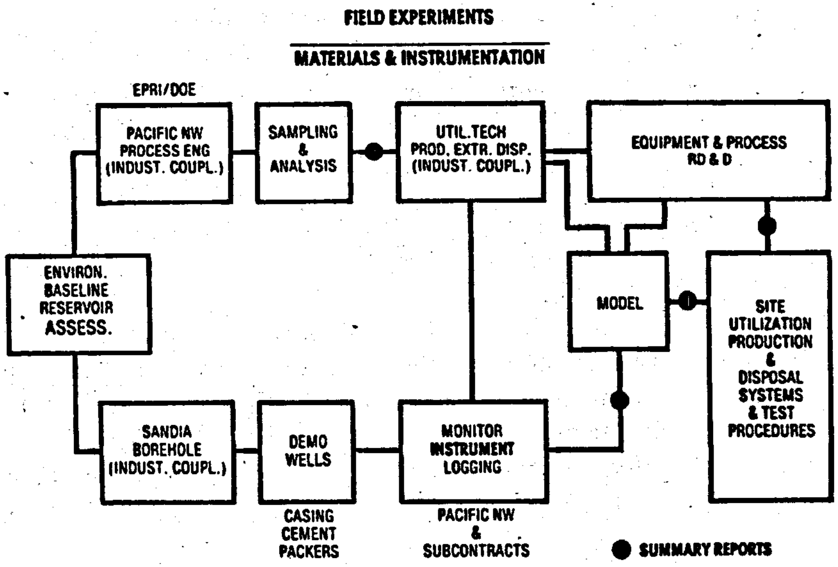

Fig. 16.
Field experiments—materials and instrumentation.

TABLE XII

NATIONAL LABORATORY SUBCONTRACTS NEW EQUIPMENT

Development (PNL):
- Glass Electrode
- Flash Point Indicator

Research (PNL):
- Novel Reference Electrode
- Hydrogen Ion Sensitive Electrode
- Small, Rugged Carbon Dioxide Ion Sensor
- Sulfide-Sensitive Electrode

Logging Program (LASL and Sandia):
- Temperature/Pressure Monitors
- Integrated Thermionic Circuits

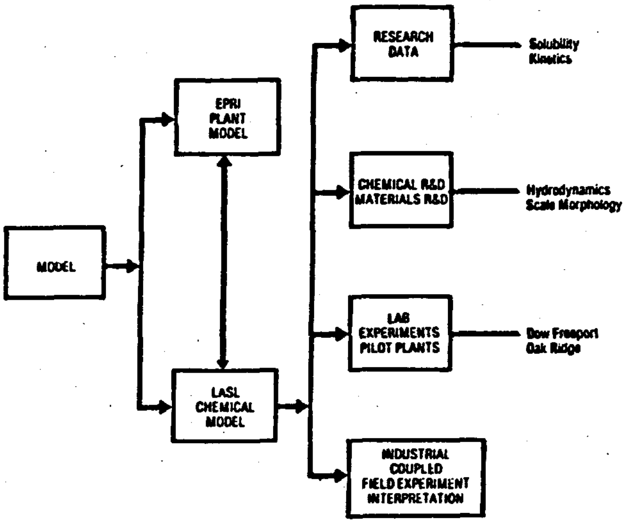

Fig. 17.
"Modeling" flow chart.

The NAS study also recommended transfer of technology for the development of the magnetic flow meter from the chemical industry. This device has recently been successfully tested at East Mesa in a DGE-funded conversion technology project by Aerojet General. Recommendations for increased sampling and analysis work are being implemented at PNL. Because probes are required for the sampler suggested, its development will be delayed until some success with probes has been obtained.

2. **Progress in Developing Monitoring Instrumentation**. The National Academy of Science's definition report was released in February 1978.[20] The Battelle Pacific Northwest Laboratory project has successfully developed a standard reference electrode and conductivity meter. Successful field tests of the conductivity meter were accomplished in FY 1977. The development of a number of other monitoring devices is planned for FY 1978 and 1979 by subcontracts from PNL, and field experiments directed at solving industrial needs have been planned for FY 1979.

3. **Other Uses of Monitored Information**. The input from field tests and monitoring programs will enable us to devise plant models (Fig. 17). These are being developed under contract to the Electric Power Research Institute. Chemical model work in support of EPRI and nonelectric needs for scale control is under way at LASL. This predicts where scale will occur, determines pressure and temperature optimums in the plant, thereby minimizing maintenance and downtime due to scale and scale removal procedures. Evaluations and tests to use the extracted scale as input for polymer concrete pipe are proceeding. Applied R & D is planned that may lead to processes using this waste for insulation or feedstock for other industrial applications. This chemical modeling effort is coordinated between DGE and EPRI, PNL, LASL, and LBL.

C. Modeling

Models indicate directions for the development of alternative approaches and industry-specific hardware options that are applicable to the solution of production, injection, and disposal problems of geothermal fluids.

1. Status of Geothermal Model Development. Specific data on solubility and kinetics of common scale minerals as well as chemical engineering and materials R & D related to hydrodynamics and scale morphology will be identified in the October 1977 Scale Control Workshop as necessary for the modeling effort. This critical information is useful to generate novel and economical waste utilization process development ideas by appropriate applied research. It will be initialized in FY 1978 by LASL subcontracts with universities, nonprofit, and industrial organizations. Additionally, we have laboratory and pilot plant experiments under way at Dow Freeport (a facility we took over from the Office of Saline Water) and Oak Ridge National Laboratory (Fig. 18). These facilities have done iterative experiments with LASL modelers to develop improved models in FY 1978. We will extend these models to include site-specific field experiments, and from the results obtained develop more general models.

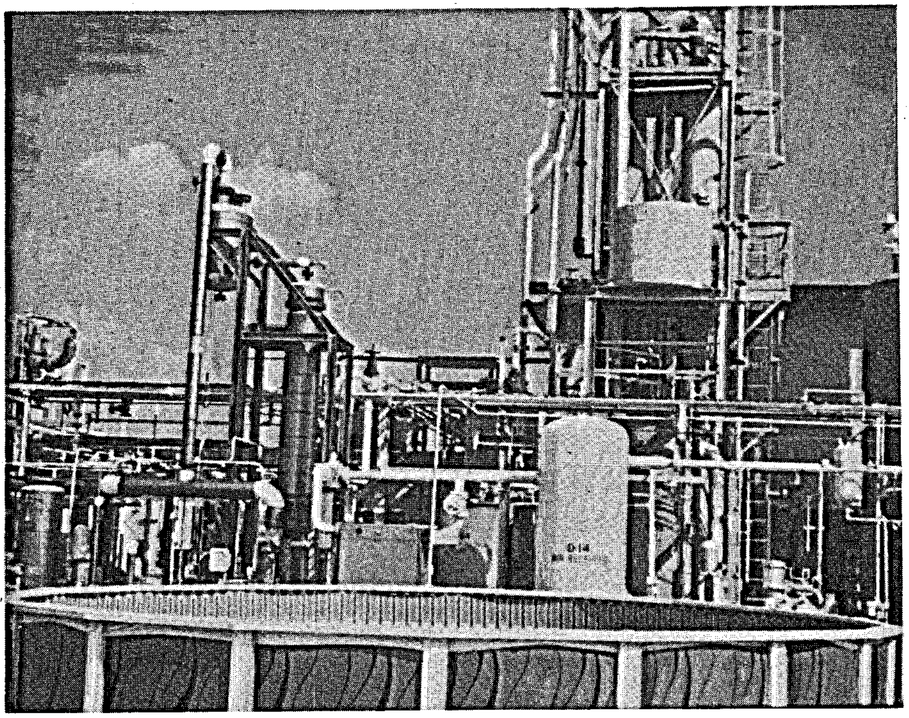

Fig. 18.
Dow Freeport facility.

VIII. DEVELOPMENT OF A SYSTEMS R & D APPROACH TO SOLVING GEOTHERMAL FLUID MANAGEMENT PROBLEMS

Injection has been indicated as an economical and cost-effective method of geothermal fluid disposal. As stated earlier, limited field experience exists outside current experience in oil, gas, and acid mine waste disposal practices. The experience gained from monitoring pilot and demonstration plants will be documented as case studies. These will be invaluable for interpretation of injectivity problems.

The injection process is concerned with large quantities of effluent for continuous disposal over significant periods of time. We must not understress the engineering aspects of the program for the development of site-specific injection procedures (Fig. 19).

The analysis of these engineering aspects may lead to development of pretreatment processes and chemical stimulation methods that will extend the life of the injection wells. Methods of modifying the fluid to increase the life of the production wells and reservoir will be investigated.

A. Importance of a Field-Oriented Fluid Management Project

We must consider well costs. Table XIII indicates the appreciable fraction of total capital costs involved in well costs. This table does not consider the possibility of having a significant number of premature failures due to plugging of formations with scale.

In this project, the plan is to follow R & D through to field procedures and the development of a well-bore model of production-injection wells.

In some cases the geology may not make injection a viable disposal alternative, and the developer will be forced to turn to a less economical method of disposal. For such situations it is necessary to evaluate the nature of the effluent, its chemical composition, and the potential difficulties in disposal. The program will draw from desalination and waste management programs in the chemical and mining industries wherever possible and thereby determine a cost-effective and environmentally acceptable technique for waste treatment and surface disposal.

Another very attractive yet problem-fraught alternative is utilization of the waste water. In many areas of the West and Southwest there is a great demand for water. We would very much like to assist industry in the development of economical processes that use both the geothermal

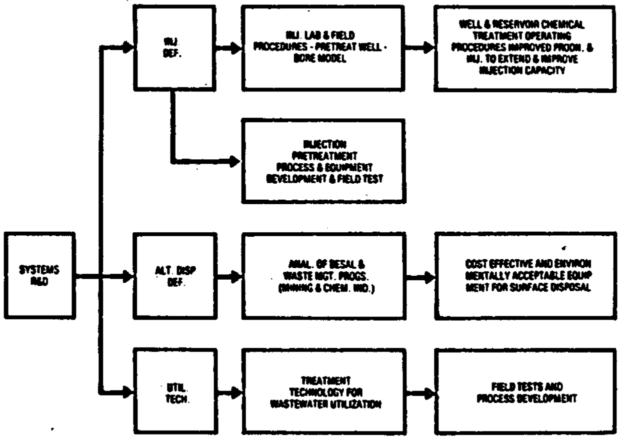

Fig. 19.
"Systems R & D" flow chart.

TABLE XIII

WELL COST FRACTION OF TOTAL CAPITAL COST

MITRE, 1978[21]

Reservoir	Well Cost ($)	Temperature (°C)	Well Fraction (%)
Beowawe, Nevada	984 000	240	55
Puna, Hawaii	2 300 000	356	50
Vale H.S., Oregon	590 000	160	48.5
East Mesa, California	600 000	180	42.9
Brady H.S., Nevada	656 000	214	48.2
Alvord, Oregon	2 437 000	200	67
Safford, Arizona	2 140 000	210	61

energy content and the fluid itself. This would help alleviate those water problems, and thus increase public acceptance of this new technology. In some instances, extraction without injection has caused significant subsidence problems. Our environmental base-line studies are carefully evaluating each site and monitoring field tests to determine if and under what conditions such problems exist.

B. Accomplishments for the Development of Needed Equipment and Chemical Processes

1. A rapid scale-removal system using cavitation has been developed and successfully field tested.
2. Modeling and experimental projects addressing scaling have been coordinated to develop empirical models for surface equipment problems.
3. Field experiments have been carried out at Niland, East Mesa, Raft River, and in the private sector. These indicate that the fluid production from geothermal reservoirs and energy extraction from the fluids are feasible.
4. Some limited injection experiments have been carried out.
5. The overall Fluid Management Program, has been planned and is in the process of implementation. Its emphasis involves significant cooperation with industry.

C. Documentation of Fluid Management Information

The program described, including characterization, monitoring, modeling, and system R & D, is complex. It involves input from the private sector, foreign countries, and several government departments. To focus on what problems are most important, or perhaps even seriously impeding development, it is planned to have an overall coordinating project to provide an ongoing systems analysis of geochemical engineering unit operations. Such a project would document national accomplishments in handbook form.

Thus, all the elements would come together to determine industrial site-specific options and criteria for production, energy extraction, and disposal.

D. Technical and Contractual Implementation of the Program

To implement a program from Headquarters, we must have an adequate dispersion of projects in the field. A significant amount of industrial input is necessary. Figure 20, which shows our currently functioning cement program, illustrates our management methods. Each Technical Implementation Plan proposes to designate a Technical Coordinator, who is associated with a national laboratory or an industrial firm. For cements, the Coordinator is from Brookhaven National Laboratory. The Coordinator will work closely with the technical advisory group, consisting of university and industrial experts. If possible, this group is then affiliated with a national technical society. For example, in our cement program, we have joined the advisory group with the American Petroleum Institute as a geothermal task group of their committee on oil and gas cement standards. Similarly, in the DGE seals program, affiliation is with the American Society for Testing Materials as a D-11 subcommittee for geothermal seals.

These advisory groups and technical societies give input to both the individual projects through the Coordinator and to Headquarters through project review. They also give advice concerning the industry's state of the art, and provide a medium for transfer technology directly to industry.

The Coordinator is also responsible for managing the subcontract R & D phase of the program.

The state-of-the-art evaluation would be performed by someone with hands-on experience and awareness of the proprietary and technical capabilities of the industry (in this case, Dowell, a division of the Dow Chemical Company and a major cement service company).

The first look would be at the current state of the art, and how it could best be adapted to the industry's particular problems. The applied R & D projects carried out in parallel would be short-range (2-3 yr long). Thus parallel paths to state-of-the-art development are carried out because we cannot assume that the problems of geothermal technology can be solved simply by adapting oil or gas technology as a solution. Where data do not exist indicating that positive solutions are available, possible alternatives that have not been commercialized should be developed. These involve current ideas available from the research community.

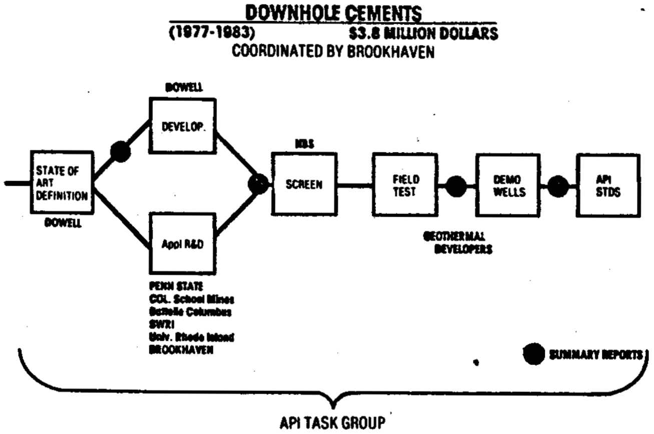

Fig. 20.
Cements program.

As each phase of the Program draws to a close, the Coordinator will present a summary report to be reviewed by the Advisory Committee. If the technology appears to be ready for field testing, testing methods and performance standards would be established, and the field tests begun. This may include downhole testing, demonstration wells, the building of pilot plants, development of maintenance procedures and large-scale chemistry experiments.

After approximately a 5-yr period, a final report would be prepared, including the R & D and field testing results. The technology would be transferred directly to industry through the constant interaction with the technical society committee members.

Figure 21 (the R & D Procurement Implementation Plan) illustrates how Headquarters interacts with both the Coordinator and the Technical Advisory Group to process the various projects through the system and thus accomplish the stated goals.

The Divisional Program Manager identifies a need for a part of the system that has not been well defined. He obtains assistance from a national laboratory or industrial firm and identifies a Coordinator, who initiates the required criteria for writing an RFP (Request for Proposal) for definition or state-of-the-art evaluation. This is usually accomplished by travel, discussing his concept of the need with the DGE Program Manager, meeting with pertinent industries who have input to the problem or related problem areas, and organizing a workshop to define needs of industrial, national laboratory, and university experts. This information is assembled to determine the needs. The procurement specifications are then drawn up for this state-of-the-art evaluation. These specifications are reviewed by the Coordinator and returned to DGE, where it is again reviewed. The final procurement is issued through a Department of Energy regional office in the form of a subcontract for a national laboratory or pertinent industry.

Later stages of the program procurement implementation would occur along these same guidelines. After the state-of-the-art evaluation has been made, and input from the advisory group is obtained, criteria for a competitive procurement are prepared for implementation of R & D phases. The subcontracting procedures are prepared by the Coordinator, and this is reviewed by the DGE Program Manager. It would then go out to the DGE regional office and become a subcontract of the national laboratory or industry.

E. Anticipated Program Benefits

This program should provide us with a number of positive results.

1. Potential means to establish the capacity of specific sites will be defined.
2. Models capable of maximizing the plant availability efficiency and costs will be provided.

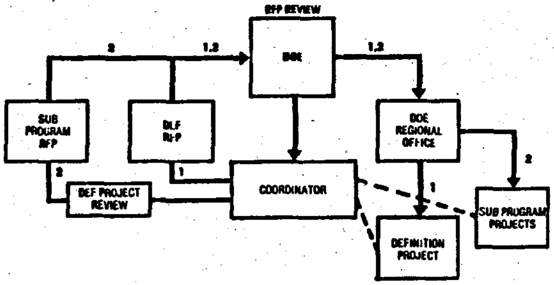

Fig. 21.
R & D procurement implementation plan.

3. Operating procedures that have potential to extend well and reservoir lifetimes will be developed and field data necessary for more efficient use will be obtained.
4. Various options for integrated waste disposal and preinjection treatment systems and their costs on a site-specific basis will be established.
5. Most important, practical data will be obtained from the maximum possible number of reservoirs early in the program. This should help identify R & D barriers preventing the early and efficient use of geothermal energy.

ACKNOWLEDGMENTS

I thank numerous people for input that significantly helped to develop this program. As much as possible they have been referenced in the text. The help of Marianne Melville, J. J. Davis Associates, Inc., with editorial work and manuscript preparation was greatly appreciated.

REFERENCES

1. J. B. Koenig, "Geothermal Exploration in the Western United States," Proc. United Nations Symp. Development and Utilization of Geothermal Resources, Pisa, September 22—October 1, 1970, in *Geothermics*, Special Issue 2 (Int. Inst. Geothermal Research, Pisa, 1971) Vol. 2, Pt. 1, pp. 1-13.

2. S. Mercado and J. Guiza, "Problems of Silica Scaling at Cerro Prieto Geothermal Power Station," Conf. on Scale Management in Geothermal Energy Development, San Diego, California, August 2—4, 1976, ERDA report C00-2607-4 (1976), pp. 59-87.

3. A. Hochrein, Daedalean Associates, Inc., personal communication, 1978.

4. A. R. Hirasuna, G. D. Bilyeu, D. L. Davis, C. A. Stephens, and G. R. Veal, "Geothermal Elastomeric Materials. Twelve-Months Progress Report, October 1, 1976—September 30, 1977," DOE report SAN/1308-1 (December 1977).

5. K. Kubota and K. Aosaki, "Reinjection of Geothermal Hot Water at the Otake Geothermal Field," Proc. 2nd United Nations Symp. Development and Use of Geothermal Resources, San Francisco, California, May 20—29, 1975 (GPO, 1976), Vol. 2, pp. 1379-83.

6. H. P. Rothbaum and B. H. Anderton, "Removal of Silica and Arsenic from Geothermal Discharge Waters by Precipitation of Useful Calcium Silicates," *ibid.*, pp. 1417-25.

7. W. B. Stilwell, W. K. Hall, and J. Tawhai, "Ground Movement in New Zealand Geothermal Fields," *ibid.*, pp. 1427-34.

8. A. J. Chasteen, "Geothermal Steam Condensate Reinjection," *ibid.*, pp. 1335-36.

9. S. S. Einarsson, A. Vides R., and G. Cuéllar, "Disposal of Geothermal Waste Water by Reinjection," *ibid.*, pp. 1349-63.

10. G. Cuéllar, Supt. Geothermal Studies, CEL, San Salvador, El Salvador, personal communication.

11. J. Leigh, A. Cohen, W. Jacobsen, and R. Trehan, "Site Specific Analysis of Geothermal Development Vol. 1," MITRE Corp. report MTR-7586 (October 1977).

12. R. E. Williams, *Waste Production and Disposal in Mining, Milling, and Metallurgical Industries* (Miller Freeman Publ., Inc., 1970).

13. S. R. Cosner and J. A. Apps, "A Compilation of Data on Fluids from Geothermal Resources in the United States," Lawrence Berkeley Laboratory report LBL-5936 (May 1978).

14. O. Vetter, Vetter Research, personal communication.

15. J. M. Thompson, F. E. Goff, and J. M. Donnelly, "Chemical Analyses of Springs and Wells from the Clear Lake Volcanic Area, Northern California," USGS Open-file report 78-425 (1978); R. O. Fournier, J. M. Thompson, and C. F. Austin, "Chemical Analyses and Preliminary Interpretation of Waters Collected from CGEH No. 1 Geothermal Well at Coso, California," USGS Open-file report 78-434 (1978).

16. D. W. Shannon, "Economic Impact of Corrosion and Scaling Problems in Geothermal Energy Systems," Battelle Pacific Northwest Laboratories report BNWL-1866 (January 1975).

17. L. Mink, DOE Idaho Operations Office, Idaho Falls, personal communication.

18. J. A. Apps, "The Definition of Engineering Development and Research Problems Relating to the Use of Geothermal Fluids for Electric Power Generation and Nonelectric Heating," Lawrence Berkeley Laboratory report LBL-7025 (November 1977).

19. H. W. Heath, Jr., "Combined Powdered Activated Carbon-Biological (PACT*) Treatment of 40 MGD Industrial Waste," Preprint, 173rd ACS Meeting, New Orleans, Louisiana, March 20-25, 1977.

20. National Materials Advisory Board (NAS-NAE), "Assessment of the Characterization (in situ-Downhole) of Geothermal Brines," report NMAB-344 (January 1978).

21. R. Trehan, A. Cohen, J. Gupta, W. Jacobsen, J. Leigh, and S. True, "Site Specific Analysis of Geothermal Development-Data Files of Prospective Sites," Vol. II, DOE report HCP/T4014-01/2 (August 1978).

THE EFFECT OF SCALING ON GEOTHERMAL POWER PLANT DESIGN AND ECONOMICS

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I. INTRODUCTION

This paper is divided into three parts. The first summarizes a conceptual design study of a geothermal power plant. The second describes possible reasons for selecting a specific energy conversion process, depending upon the scaling characteristic of the geothermal brine at a particular site. The third part is a discussion of some general chemistry and scaling considerations that affect the design and economics of geothermal power plants.

II. CONCEPTUAL DESIGN

The effects on design, capital cost, and bus-bar electric energy costs caused by an anticipated decline in available geothermal brine temperature over the lifetime of power plants are described in this section. This work is the result of a conceptual design study that was recently completed for the Energy Research and Development Administration.[1,2] A two-stage flash-steam energy conversion process was used for the conceptual design of the power plants, which operate from the liquid-dominated hydrothermal reservoir at Heber, California. Plants with net capacities of 50, 100, and 200 MWe were investigated. The larger plant capacities require increased brine withdrawal rates from the reservoir and result in steeper brine temperature decline curves. The geothermal brine at the Heber site is of the low-salinity, moderate-temperature type and is assumed to have an initial downhole temperature of 360°F. Typically, the total dissolved solids in the brine are 14 000 ppm, and the pH is approximately 6.2.

A. Plant Operating Modes

Geothermal reservoirs are finite sources of thermal energy. If the withdrawal rate of geothermal brine (and the thermal energy it carries) exceeds the replacement rate, the temperature of the brine would be expected to decline with time. Figure 1 shows two possible modes of operation for a power plant under these conditions. The "constant power output" operating mode was considered as one mode for study because constant power is the natural way to rate and specify power plants. As time passes, the net power output is kept constant by increasing the brine flow rate as the brine temperature continuously falls. A contrasting case, the "constant mass flow rate" operating mode, involves holding the brine flow rate constant over the 30-yr period, while producing 50-MWe equivalent. Since the brine is hotter at time zero than at any other time, this

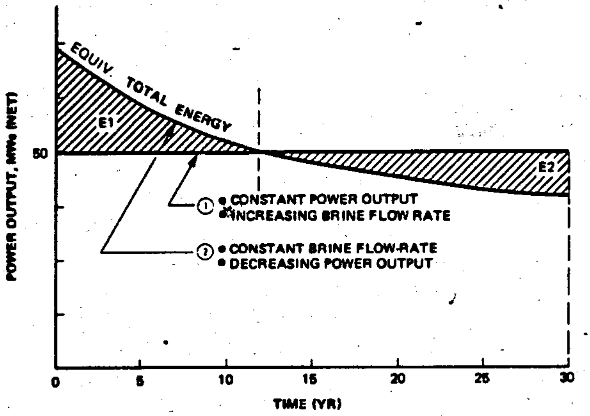

Fig. 1.
Plant capacity vs time.

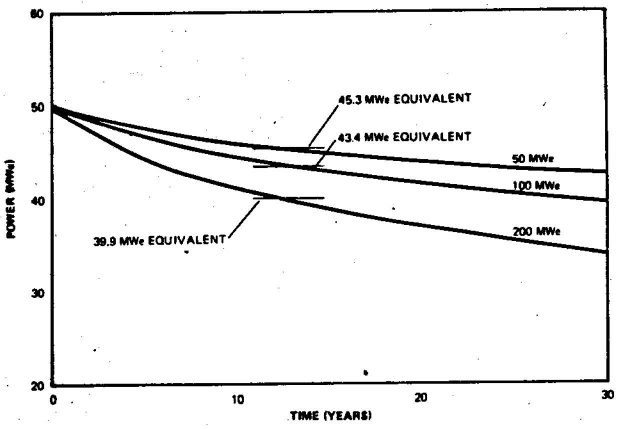

Fig. 2.
Net power output. Base case plants with declining brine. Temperature—50 MWe units.

will be the time of maximum power output. Power output will then decay with time. These two contrasting operating modes represent the envelope conditions that could contain other possible operating modes.

B. Conceptual Design of Power Plant

First, a base case 50-MWe (net) power plant was conceptually designed for constant downhole brine temperature of 360°F. The design incorporated a two-stage flash-steam energy conversion process. The performance and economics of this constant temperature base case design were analyzed for operation under both constant downhole brine temperature and then declining downhole brine temperature. The brine temperature decline data were calculated specifically for the conditions of this study by Chevron Resources, Inc., with their reservoir computer model.[8]

Figure 2 shows the results of subjecting the base case plant, designed assuming constant brine temperature, to a declining temperature. A 50-MWe unit operating in a 200-MWe plant would actually produce the equivalent of 39.9 MWe over the 30-yr plant lifetime.

Next, the base case design was modified to accommodate an anticipated timewise brine temperature decline. Conceptual designs for plants of 50-, 100-, and 200-MWe (net) capacity were developed for each of the two operating modes. The plants consist of one to four 50-MWe units, which are modifications of the 50-MWe base case plant. Figure 3 shows the decline in geothermal fluid temperature over the life of these six plants.

Figure 4 shows that while the two operating modes are very different, the resulting performance in terms of watt-hours per pound of brine is very similar over the lifetime of the power plants.

C. Capital Cost Estimates

Capital cost estimates for the power plants were developed using the high and low ends of turbine-generator prices quoted by several manufacturers. The results are shown in Table I.

Capital costs for the well fields were based on both production and reinjection wells being slant drilled from well islands to a depth of 6000 ft. Production and reinjection well casing diameters

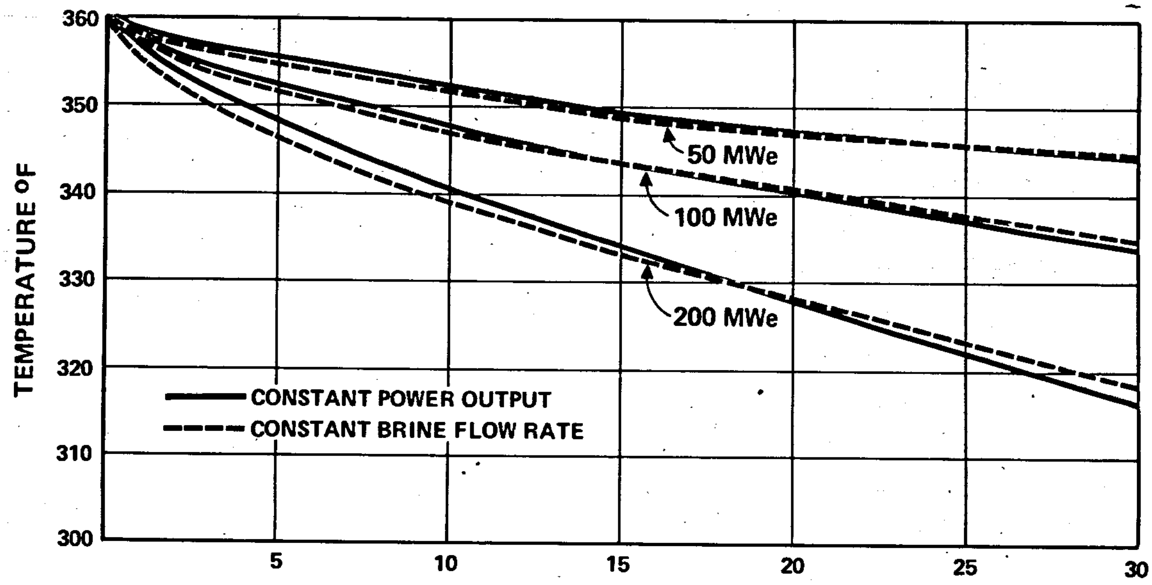

Fig. 3.
Heber geothermal field temperature decline with time.

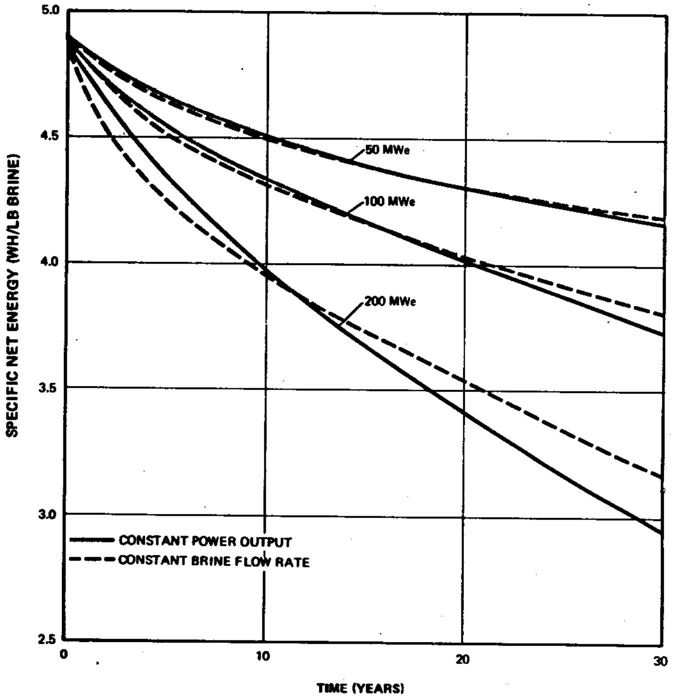

Fig. 4.
Specific net energy with time.

TABLE I

CONCEPTUAL CAPITAL COST ESTIMATE FLASHED-STEAMED POWER PLANT HEBER, CALIFORNIA

	High Turb-Gen Cost		Low Turb-Gen Cost	
	$1 000[a]	$/kWe (net)	$1 000[a]	$/kWe (net)
Base Case	35 000	700	30 400	608
Constant Power				
50-MWe unit for 50-MWe plant	36 000	720	31 400	628
50-MWe unit for 100-MWe plant	36 500	730	31 800	636
50-MWe unit for 200-MWe plant	38 200	764	33 400	668
Constant brine flow rate				
50-MWe unit for 50-MWe plant	37 500	750	32 300	646
50-MWe unit for 100-MWe plant	38 500	770	33 100	662
50-MWe unit for 200-MWe plant	41 400	828	35 400	708

---

[a] Fourth quarter 1976 dollars.

were 10-3/4 in. The production well flow rate is 800 000 pounds per hour, and the reinjection well flow rate is 1 600 000 pounds per hour. Table II shows the conceptual capital cost estimates for the well fields of the various plants.

D. Energy Production Costs

Total bus-bar electric energy production costs were calculated using the plant and well field capital costs described above. A discounted cash flow analysis was employed. The bases for the component of energy costs attributable to the power plant are

- Operating and maintenance, 2% plant capital cost annually.
- Administrative and general, 25% annual operating and maintenance cost.
- Ad valorem taxes, 2.5 %.
- Insurance, 0.1% plant capital cost annually.
- Fixed charge rate, 14%.
- Plant capacity factor, 85%.

The results for the 50-MWe (net) base case plant are shown in Table III.

The base for the well field component of the energy costs are

- Well cost, $425 000/well.
- Annual maintenance
  - Production well, $50 000/well.
  - Reinjection well, $80 000/well.
  - Surface piping, 0.5% of capital cost.
- Annual operating cost, $70 000 + [$250 000 × (#prod. wells/13)$^{0.8}$].
- Royalties, 10% gross field income.
- Ad valorem taxes, 6% field income.
- Exploration, confirmation, and engineering, $2 million + 5% gross field income (low-risk case only).

- Administration and general, 10% annual operating and maintenance cost.
- Income taxes, accelerated depreciation.
- Investment tax credit, 10%.
- Low-risk ROR, 10.8%.
- Risk-adjusted ROR, 20%.

The results for the 50-MWe (net) base case plant are shown in Table IV.

TABLE II

CONCEPTUAL CAPITAL COST ESTIMATE
WELL FIELD
HEBER, CALIFORNIA

	Year 1 ($1 000)[a]	Cumulative Year 30 ($1 000)[a]
Base Case 50-MWe Plant	16 600	16 600
Constant Power Output		
50-MWe plant	17 400	19 500
100-MWe plant	35 400	42 600
200-MWe plant	64 800	106 200
Constant Brine Flow Rate		
50-MWe plant	17 200	18 000
100-MWe plant	36 500	39 000
200-MWe plant	72 700	86 700

---

[a] Fourth quarter 1976 dollars.

TABLE III

POWER PLANT
ENERGY PRODUCTION COSTS DETAIL
50-MWe (NET) BASE CASE PLANT

	Low Turb-Gen Price (mills/kWh)	High Turb-Gen Price (mills/kWh)
Depreciation + return + income taxes	13.8	15.9
Ad valorem taxes	2.5	2.8
Plant insurance	0.1	0.1
Operation and maintenance	2.0	2.3
Administration and general	0.5	0.6
Total power plant costs	18.9[a]	21.7[a]

---

[a] Fourth quarter 1976 dollars.

TABLE IV

WELL FIELD
ENERGY PRODUCTION COSTS DETAIL
50-MWe (NET) BASE CASE PLANT

	Regulated Utility 10.8% Rate of Return (mills/kWh)	Energy Company 20% Rate of Return (mills/kWh)
Book depreciation	1.9	1.8
Return on investment	4.7	8.9
Income taxes	1.8[b]	8.0[c]
Ad valorem taxes	1.0	1.7
Operation	0.9	0.9
Maintenance	3.2	3.2
Administration and general	0.4	0.4
Royalties	1.6	2.8
Reservoir development	0.8	0
Total well field costs	16.3[a]	27.7[a]

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[a] Fourth quarter 1976 dollars.

[b] Includes deduction for bonded debt interest.

[c] 100% equity financed (no interest deduction).

Due to the uncertainty in the price of geothermal brine produced from liquid-dominated hydrothermal resources, an attempt was made to bracket the range. This was accomplished by developing a low limit and a high limit. The low-limit brine price assumes that the well field is financed by a regulated utility at a low-risk 10.8% annual discounted cash flow rate of return. The high limit assumes the well field is financed by an energy company at a risk-adjusted 20% rate of return.

The resulting bus-bar electric energy costs are shown in Fig. 5. For the low-limit rate of return the total bus-bar costs vary from about 36 to 41 mills per kWh. This range includes all of the variables of this study such as turbine generator price, plant capacity, and operating mode. For the risk-adjusted rate of return, the total bus-bar electric energy costs range from about 48 to 53 mills per kWh.

III. ENERGY CONVERSION PROCESSES

There are many possible processes for converting the heat energy in geothermal brine to electric energy. Depending upon the scaling characteristics of the brine at a particular site, potential scaling problems may be mitigated by selecting a specific process. Advantages and disadvantages of several processes are described in the following paragraphs.

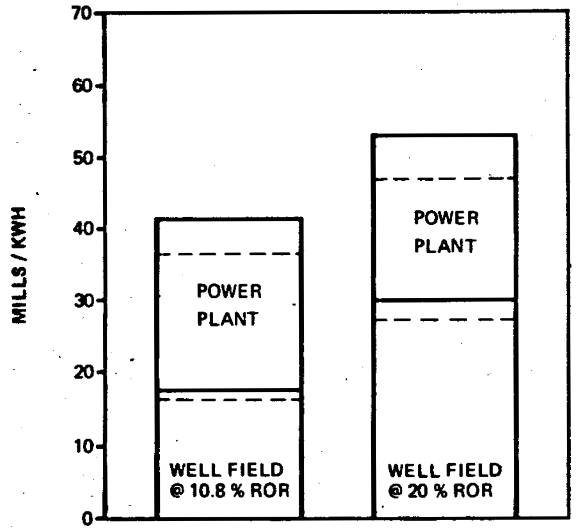

Fig. 5.
Bus-bar electric energy costs, Heber, California (fourth quarter 1976 dollars).

Figure 6 is a schematic diagram of a flashed-steam energy conversion process. Scrubbers are incorporated to remove silica carry-over from steam before it reaches the turbine. Silica deposition on turbine blading may cause excessive maintenance requirements. The release of dissolved noncondensable gases, primarily carbon dioxide, from the brine during the flashing process causes the pH of the brine to increase and may result in the precipitation of calcium carbonate.

If the brine has a high dissolved-solids content, cooling by the flashing process may cause solubility limits to be exceeded. This could result in formidable amounts of silica scale formation or precipitation of various salts in equipment and piping.

A binary process is shown in Fig. 7. It requires a downhole pump to maintain single-phase liquid flow of brine, but the problems of calcium carbonate precipitation caused by the release of carbon dioxide during flashing are avoided. Another advantage is that the turbine is isolated from the geothermal brine. Additionally, the temperature of the brine at the outlet of a binary process is normally higher than that of a comparable flash process. Less scaling would be expected in injection lines and wells, since the scaling components would be farther from their solubility limits. However, scale formation would occur on the surfaces of the brine heat exchangers.

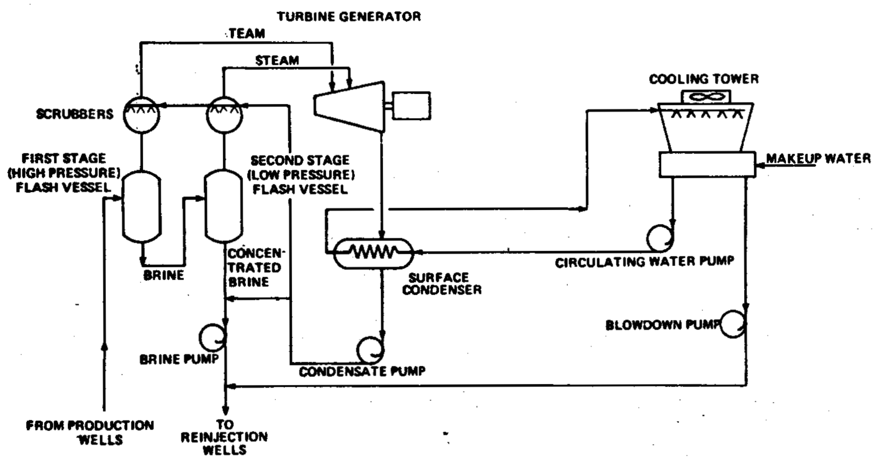

Fig. 6.
Two-stage flashed-steam energy conversion process with scrubbing.

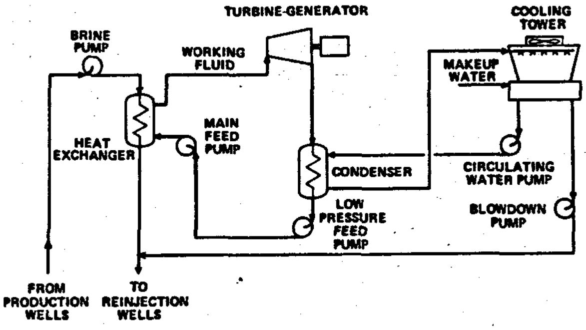

Fig. 7.
Binary energy conversion process.

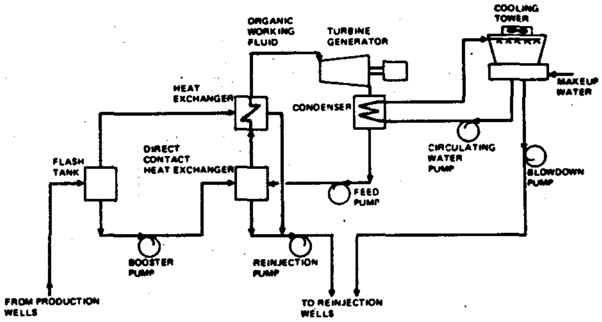

Fig. 8.
Binary energy conversion process with direct contact heat exchangers.

One method of avoiding scale formation on the heat transfer surfaces of brine heat exchangers in a binary process is to eliminate these surfaces by using direct contact heat exchangers, as shown in Fig. 8. The system shown eliminates the need for a downhole pump, but direct contact heat exchangers could be used in place of the surface-type heat exchangers shown in Fig. 7.

Another method of avoiding heat exchanger scaling is to use the flash-binary process, shown in Fig. 9. In this process, the brine is flashed to steam, the steam is cleaned in scrubbers, and the clean steam, rather than the geothermal fluid, goes to the heat exchangers. This process is currently being tested at the Geothermal Loop Experimental Facility, located in California at the Salton Sea. A variation of this process is the multistage flash-binary process, shown in Fig. 10. Additional stages, perhaps 20 to 40, improve performance, and capital cost is not excessive due to the type of construction, which is adapted from desalination technology. In this process, the vapor condenses on the heat exchange tubing and is then recombined with the brine so that the brine is not concentrated. Concentrated brine might cause crystallization of the dissolved salts.

In connection with their development of the total flow process, the Lawrence Livermore Laboratory has been conducting promising experiments in controlling scale formation with the high-temperature, high-salinity brine at the Salton Sea by acid injection.[4] This type of brine modification would also be applicable to other energy conversion processes.

IV. CHEMISTRY AND SCALING CONSIDERATIONS

Scale can occur in every part of the system in contact with the geothermal brine. In the well field, this includes the production wells, the reinjection wells, and the brine piping; and in the power plant, in addition to the brine piping, it includes all contacted components such as flash tanks, heat exchangers, pumps, and valves. Some possible scale control methods are

- Production Wells
  - Downhole injection of scale inhibitors.
  - Downhole pumping to prevent release of CO_2 and consequent $CaCO_3$ precipitation.
- Plant Inlet
  - Slurry seeding for silica scale and coprecipitants such as lead and silver sulfides.
  - Precipitation of $CaCO_3$.
  - Injection of scale inhibitors.
  - Injection of acid for pH control.

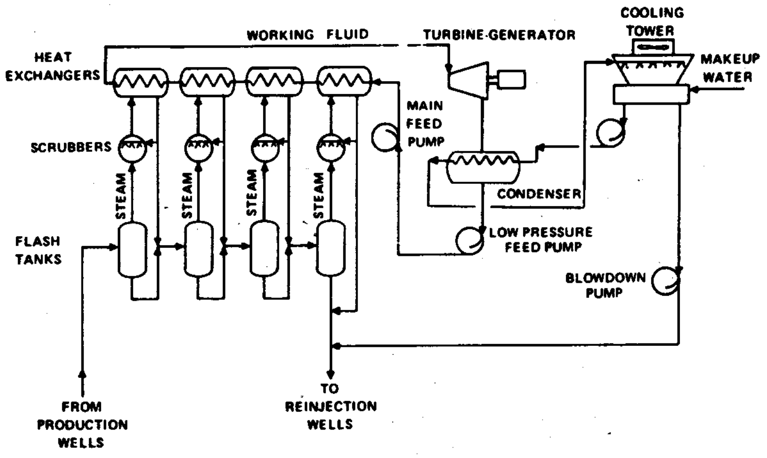

Fig. 9.
Flashed-steam/binary energy conversion process.

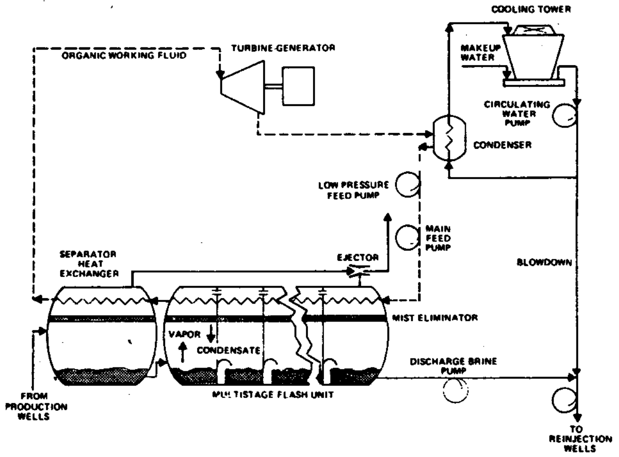

Fig. 10.
Multistage flash/binary energy conversion process.

- Plant
  Selection of conversion process to maintain concentration below solubility limit to prevent crystallization.
  Cleaning of steam by scrubbing before turbine or heat exchangers.
- Before Reinjection
  Settling.
  Contactors (sand, iron filings, etc.).
  Cyclones.
  Centrifuges.
  Filters as last stage.

Some of the costs that would result from scale formation in well fields and power plants include

- Downtime or Reduced Output
  Lost electric energy production.
- Capital Costs
  Special construction materials (if low pH used for scale control).
  Custom-designed equipment.

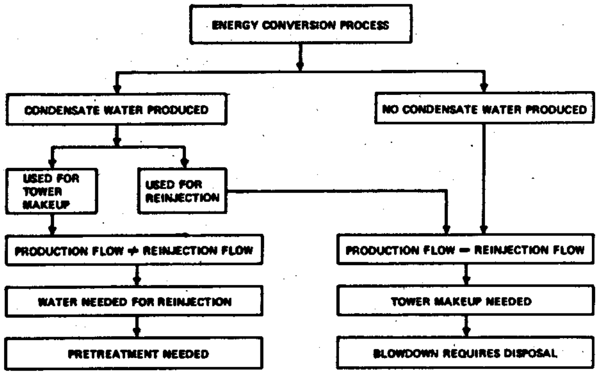

Fig. 11.
Reinjection to prevent subsidence.

  - Duplicate standby equipment.
  - Spare production and reinjection wells.
- Operating and Maintenance Costs
  - Scale removal.
  - Equipment replacement.
  - Chemical inhibitors.
  - Disposal of solids removed from brine.
  - Well rework.
  - Well stimulation.

A very significant potential cost is loss of revenue due to downtime. To reduce downtime, standby equipment, such as duplicate 100% capacity brine reinjection pumps, spare production and reinjection wells, and even complete duplicate sections of the process, should be considered for brines having severe scaling characteristics.

There are many challenging chemistry problems associated with providing cooling water for a geothermal power plant, as shown in Fig. 11. An assumption here is that the reinjection flow rate of fluid into the formation must equal the brine production rate in order to prevent ground surface subsidence. Another assumption is that evaporative cooling towers will be used. Some energy conversion processes produce pure condensate water, which can be used as makeup for the cooling towers, while others do not. Figure 11 illustrates the alternative approaches available for such processes and the resulting water chemistry problems.

REFERENCES

1. Bechtel Corporation, "Conceptual Design of Commercial 50 MWe (net) Geothermal Power Plants at Heber and Niland, California," ERDA report SAN-1124-1 (October 1976).

2. J. W. Hankin, R. A. Hogue, T. A. V. Cassel, and T. R. Fick, "Effect of Reservoir Temperature Decline on Geothermal Power Plant Design and Economics," Proc. 12th Intersociety Energy Conversion Conf., Washington, DC, August 28-September 2, 1977 (Am. Nucl. Soc., La Grange Park, Ill., 1977), Vol. 1, pp. 870-876.

3. A. M. Cooper and L. Mann, Chevron Resources, Inc., San Francisco, California, personal communications, 1976-1977.

4. A. L. Austin, A. W. Lunberg, L. B. Owen, and G. E. Tardiff, "The LLL Geothermal Energy Program Status Report January 1976-January 1977," Lawrence Livermore Laboratory report UCRL-50046-76 (April 1977).

SCALE AND SOLIDS CONTROL AT THE SALTON SEA KGRA

by

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ABSTRACT

The viability of energy conversion processes intended for electric power production at liquid-dominated geothermal resources can be jeopardized by severe scaling, corrosion, and suspended solids problems that arise as a consequence of the high chloride content and trace element composition of geothermal brine. For instance, the Salton Sea KGRA (SSKGRA) is the largest known high-temperature hydrothermal resource in this country, yet all previous attempts, dating back to the 1920s, to produce power economically at the field have been unsuccessful. In 1974, the Laboratory's Geothermal Program began to address the problems related to utilization of high-salinity geothermal resources. Initial emphasis was placed on solving the scale and solids problem since adequate control was recognized as a mandatory requirement for operation of a TOTAL FLOW turbine at the SSKGRA. Furthermore, a totally programmatic approach was adopted insofar as programmatic time frames did not allow for detailed laboratory investigations. A primary virtue of this philosophy was avoidance of the severe difficulties associated with exactly duplicating complex brine systems at elevated temperatures and pressures in the laboratory. Our strategy combined operation of field experimental loops with analysis of scale and solids formation rates, chemical compositions, microstructures, and thermochemistry, coupled with appropriate literature surveys in order to identify potentially effective control measures.

I. NOZZLE TEST RESULTS (TOTAL FLOW IMPULSE TURBINE SYSTEM)

During the summer of 1976, a field experimental loop, located at the ERDA-SDG&E test site in the southwestern part of the SSGF, was used to test acidification for scale and solids control.[1] Experimental results indicated that scaling could be prevented in simulated turbine components when either separated brine or remixed separated brine plus steam was acidified with hydrochloric acid to pH values ≤5 while still at high temperature and pressure. Rates of suspended solids formation were also suppressed in expanded brine effluents cooled to 85°C (at 1 atm pressure) eliminating solids-induced erosion of turbine components.

The economic viability of brine modification with hydrochloric acid is dependent upon the buffering capacity of the geothermal brine. Carbonate was identified as the primary buffer in separated brine. Ammonia becomes an important buffering agent as well when the total wellhead production (liquid plus steam) is acidified. For separated brine, reagent costs add about 1 mill per kWh to the cost of electric power. Reagent cost for remixed brine is about 2 mills per kWh.

The economic impact on materials costs in a TOTAL FLOW system due to acidification is not severe. The only high-temperature components required to process acidified brine are nozzles that can be fabricated from suitable materials without significantly affecting the overall system cost. All other components in the TOTAL FLOW system operate at lower temperatures (60-100°C) where corrosion is less a problem. Finally, ammonia in the steam phase re-equilibrates with brine after passage through the turbine causing an increase in brine effluent pH. This effect minimizes corrosion of piping downstream of the turbine and promotes precipitation of silica, thereby simplifying subsequent effluent pretreatment for injection.

II. LLL BRINE FLASH TEST SYSTEM

A. Objectives

The LLL four-stage brine flash test system is now operational at the Magmamax No. 1 production well in Niland. The objectives are to test alternative scale and solids control methods, effluent injectivity, and materials performance for possible application in the San Diego Gas and Electric Company Geothermal Loop Experimental Facility (GLEF). The results will also be useful in assessing the potential for large-scale, long-term exploitation of the Salton Sea Geothermal Field using conversion methods based on use of steam from brine flashing processes (flash binary or steam turbine).

B. Description

A schematic of the LLL four-stage system is shown in Fig. 1 and current effluent test components are illustrated in Fig. 2. The system was designed as a small-scale simulation of the GLEF for tests of problem solutions prior to larger scale application in the GLEF. This system has now been operated for more than 200 h. Control and stability have been good and target stage temperatures have been achieved. The system is fitted with electrochemical corrosion rate cells and sampling ports (for both brine and steam) at each stage. The system is fitted with an effluent test section to permit evaluation of various solids removal methods and also to test the injectivity of variously treated effluents by core flushing. Corrosion racks containing a variety of materials for tests in modified brine have been prepared for installation in the last three stages of the system. Direct corrosion tests of welded and stressed specimens of minimum one-month duration will be carried out to assess the potential of any given brine handling process for GLEF or larger term applications.

C. Current Results

Highlights of current results are given in the accompanying preliminary report. Near-term plans will be discussed.

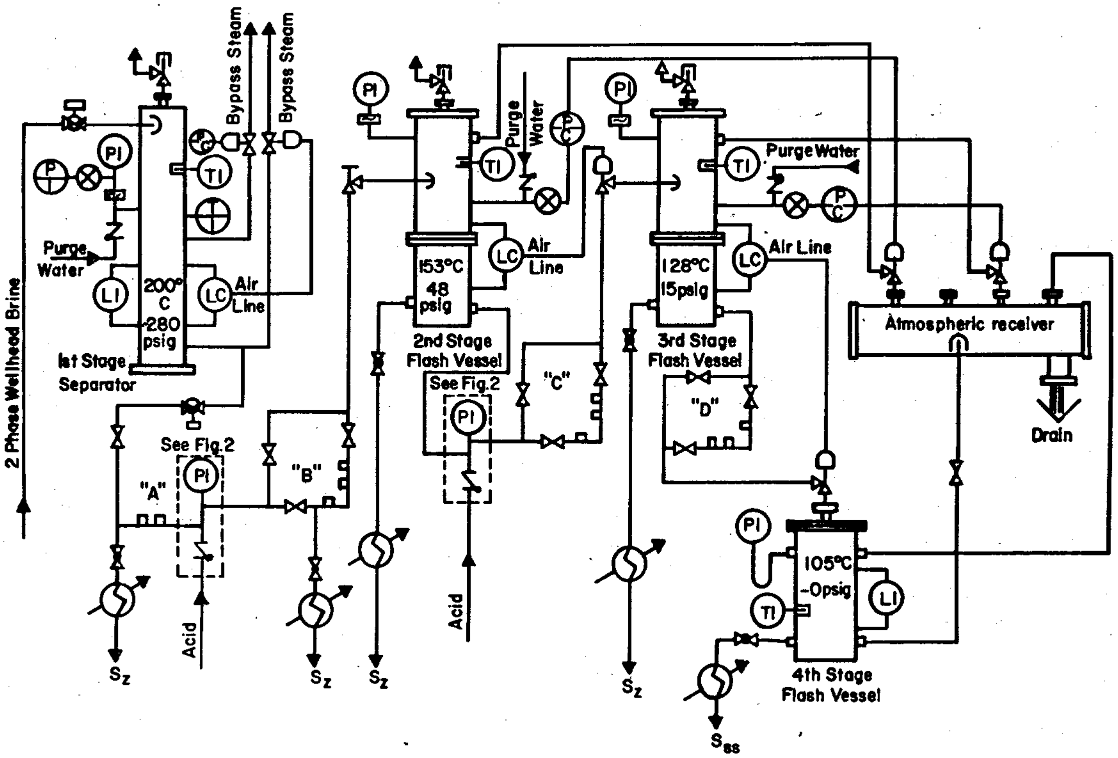

Fig. 1.
LLL brine flash test system.

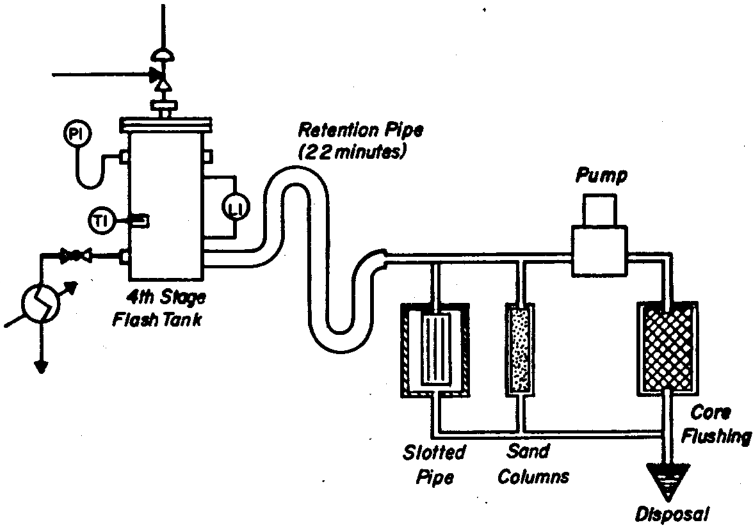

Fig. 2.
Flash system: effluent test section.

REFERENCE

1. A. L. Austin, A. W. Lundberg, L. B. Owen, and G. E. Tardiff, "The LLL Geothermal Energy Program Status Report January 1976—January 1977," Lawrence Livermore Laboratory report UCRL-50046-76 (April 1977).

SUMMARY OF LLL FLASH SYSTEM OPTIMIZATION TESTS PRELIMINARY HIGHLIGHT REPORT

by

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I. RESULTS RELATING TO SHORT-TERM (18-MONTHS) GLEF OPERATION

A. Objective

Determine whether brine acidification can be used for short-term (18-months GLEF operation) solution to GLEF scaling and injection problems with the constraint that corrosion will not be limiting after 18 months of operation (maximum allowable corrosion rate: 0.006 in./month).

B. Conclusion Based on Short Optimization Tests

GLEF brine acidification to pH 4.5 will solve GLEF scaling and injection problems. General corrosion will not be limiting even after 18 months of operation. Final proof requires a 1-month test to assess other forms of corrosion.

C. Summary of Observations Applicable to Short-Term Solution

1. **Test System.** Schematics of the flash test system and downstream test components are shown in Figs. 1 and 2, respectively, in the previous paper. Acid injection is between the first and second stages.

2. **Slot Scaling.** Scaling of slots simulating injection casing slots was eliminated at pH 5 and lower. Slots scaled shut in less than 16 h with unacidified brine (pH 5.7).

3. **Solids Production.** Precipitation of solids greater than 5-μm diam after 1 h incubation at 90°C was decreased by a factor of 8 at pH 5, and 50 at pH 4 (Fig. 1). Precipitation of solids greater than 5-μm diam after more than 100 h incubation at 90°C was dramatically reduced when effluents from acidified brine were diluted with 20% water to simulate neutralized condensate recombination (Fig. 2).

D. Core Flushing

Standard cores exposed to unmodified (pH ≥ 5.2) brine showed rapid loss in permeability after passage of 300 pore volumes of effluent (Fig. 3). Permeability loss can be attributed to buildup of a thick filter cake at the core entry. However, when standard cores were exposed to acidified brine (pH ≤ 4.6) the rate of permeability decline was much lower. The final stabilized value of permeability after passage of about 1500 pore volumes was 20 times greater than the values for unmodified brine. The slotted liner on top of the core flowing acidified brine was clean; all deposition occurred within the core.

Total volume flow was ~7 times greater for acid effluents ($pH < 4.6$) than for normal effluents at the 30-MD permeability level. This indicates that injection of acid effluent should be possible for ~3 months × 7 = 21 months.

E. Corrosion

General corrosion rates (with prescaling) can be maintained below the 75-mpy maximum allowable for short-term GLEF operation at ph 4.5 or greater (Fig. 4). Other forms of corrosion will be evaluated after a 1-month direct corrosion test.

II. TENTATIVE CONCLUSIONS RELATING TO USE OF BRINE ACIDIFICATION FOR LONG-TERM APPLICATION (20- to 30-yr PLANT)

A. Injection

Direct injection of acidified effluent for long times (30 yr) may be possible. Longer term testing is required, and effluent treatment methods need to be investigated.

B. Solids Removal

Technical feasibility of silica removal from both acidified and unacidified brine using sand beds and sand/$CaCO_3$ beds has been demonstrated (Table I). Practical feasibility remains to be demonstrated.

C. Corrosion

Carbon steel cannot be used for long-term operation with acidified brine even with prescaling. Previous data indicate low Cr, Mo alloy steels can be used (at about twice the cost). Direct corrosion testing is planned to further evaluate low-alloy steels and suitable liner materials.

D. Scale Control

Data indicate acidification to pH 4.5 is a long-term solution to scaling problems both in the surface plant and casing slots. Long-term verification test is needed.

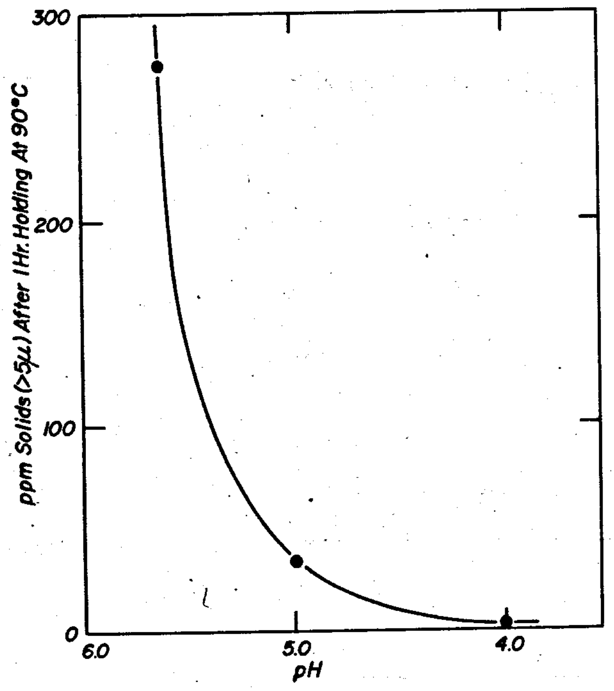

Fig. 1.
Solids precipitation after 1 h holding at 90°C vs pH; short (20-h) flash system optimization tests (September 11-23, 1977).

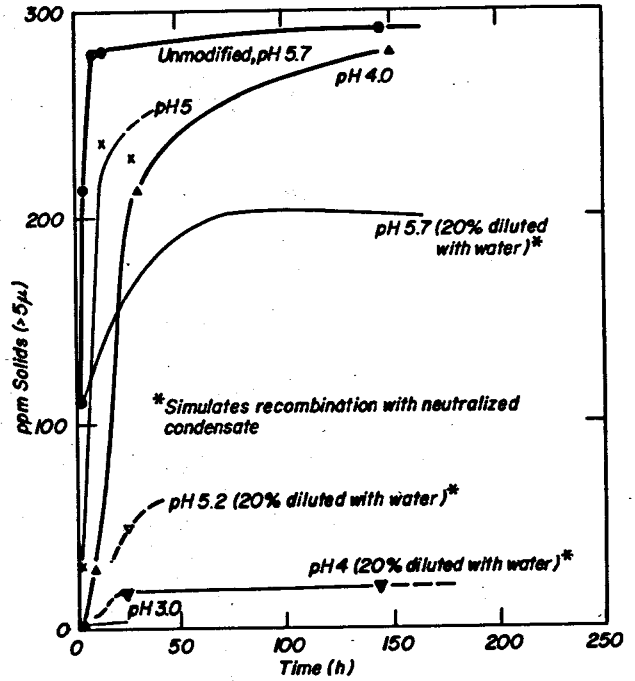

Fig. 2.
Solids precipitation (5-μ filter) vs holding time at 90°C: short (20-h) flash system optimization tests (September 11-23, 1977).

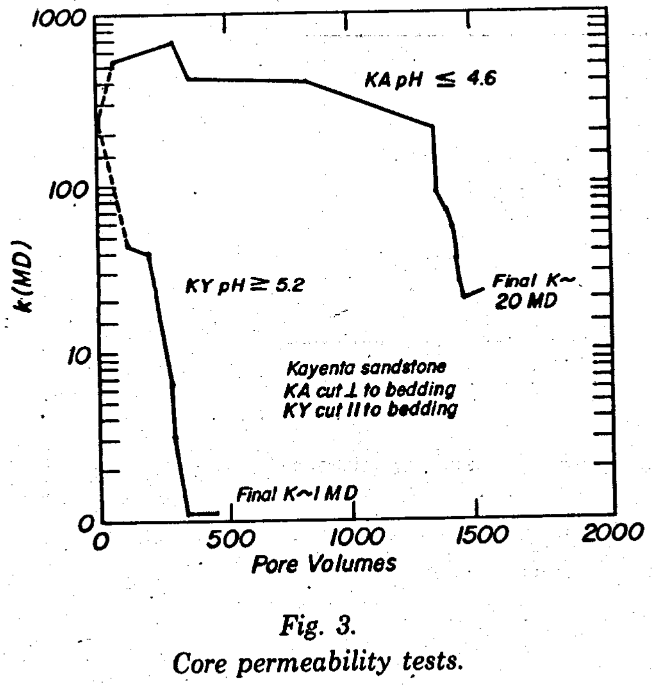

Fig. 3.
Core permeability tests.

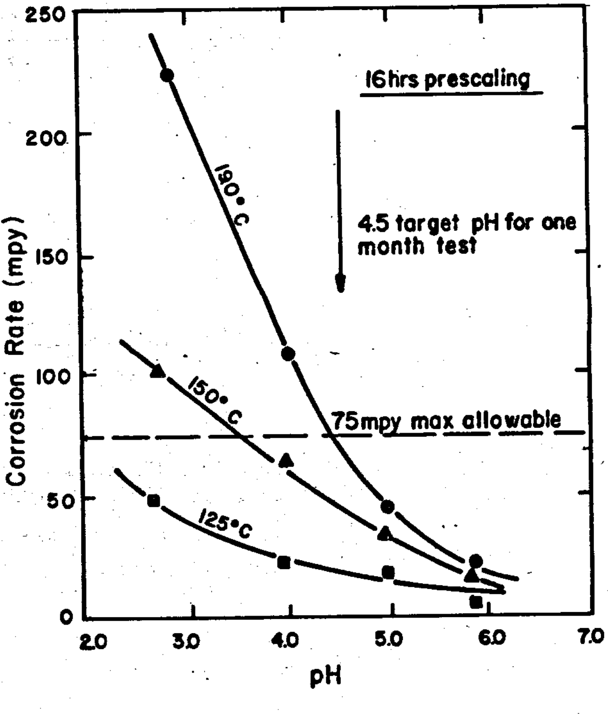

Fig. 4.
Carbon steel electrochemical corrosion rate results: short (20-h) flash system optimization tests (September 11-23, 1977).

TABLE I

SILICA REMOVAL FROM BRINE[a] USING PACKED BEDS[b]

Brine Throughput lb/h-ft^2		350	870	1390
Residence Time min		7.5	3.0	1.9
Temp Brine in °C		85-91	88-91	88-94
Temp Brine out °C		90-97	86-91	88-93
Test No.	**pH Brine in**	**Percent Silica Removed 70 Vol% Sand/30 Vol% Calcite**		
1	3.0	47		
	3.2		28	
	3.2			28
2	3.7	36		
	4.0		16	
3	4.2			33
	4.6	54(c)		
	4.7		38	
4	5.1			0
	5.2		17	
	5.2	17		
5	5.8	44		
	5.8		44	
		Percent Silica Removed 100% Sand		
6	4.1		14 @ 520 lb/h-ft^2	
	4.2			0
	4.4	9 @ 175 lb/h-ft^2		
7	5.8	46		
	5.8		42	

---

[a] Magmamax No 1: Effluent brine from 4-stage flash system plus injection pipe simulator located at LLL test facility.

[b] 4 in. diam by 18 in. deep: Fine silica sand and coarse limestone particles.

[c] 50-55% silica removal lowers concentration to saturation value.

SCALE FORMATION AND SUPPRESSION IN HEAT EXCHANGE SYSTEMS FOR SIMULATED GEOTHERMAL BRINES

by

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I. INTRODUCTION

The utilization of the geothermal resource is accomplished either by nonelectrical or by electric power generation. Both processes use the heat stored in the geothermal brines. Herein lies one of the main problems of using geothermal resources, that is, scale formation on the heat transfer surfaces. Depending on the resource, scale formation can range from very severe, as in the Niland case, to minor, as in the East Mesa case.

The experimental loop at the Texas Division of the Dow Chemical Company is set up to simulate a wide variety of geothermal brines. Figure 1 is a simplified flow sheet of the experimental loop and this demonstrates the flexibility of the system. For example, the salinity of the simulated brine may vary from 0 to 26%, any cations or anions can be added, the pH may be varied from 1 to 12, the flow rate can be varied from 1 gpm to 5 gpm, and the temperature may be controlled up to 350°F.

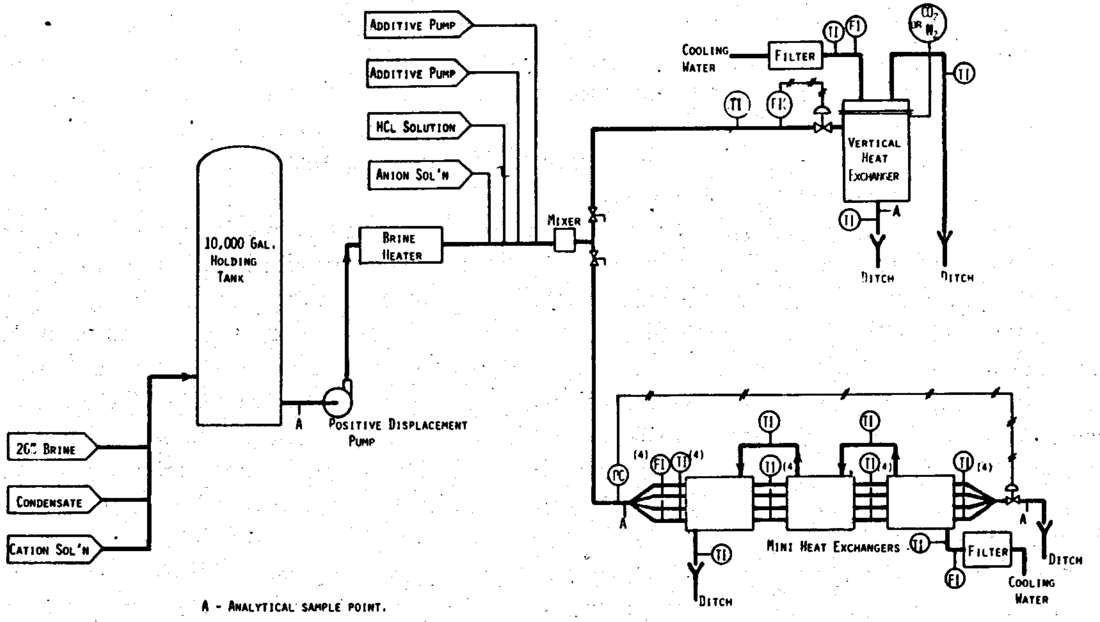

Fig. 1.
Simplified experimental loop.

II. APPROACH

Our emphasis is to evaluate various commercial and experimental scale control systems. A list of the various additives tried so far follows: Betz Chemicals, Betz 403; Hercules Chemical Corporation, AF-504; Ciba-Giegy, Belgard E. V.; Calgon Corporation, CL-165; an experimental Dow Corning substance, B-2083-78; two experimental Dow polymers, PEI-Itaconic acid and XFS-4029-Methylene sulfonic acid; and ammonium bifluoride. Other scale control methods have been evaluated, such as a high-pressure (150-psig) carbon dioxide pad on the main exchanger, and the injection of sulfate ion to form calcium sulfate crystals for nucleating sites in the simulated geothermal brines.

Other methods to be evaluated include scale control by electrical phenomena with the use of a Progressive Water Treater made by Progressive Equipment Company, and scale control by magnetic phenomena with the use of a Water Wizard made by Electronic Water Conditioners, Inc. Also further evaluation of any promising results from previous runs will be done.

A cooperative program with the Los Alamos Scientific Laboratory (LASL) will be initiated in which we will provide experimental data to LASL to support their development of a computer model to predict the formation of scale in our mini-exchange system (Fig. 1).

III. RESULTS

The first problem in operating a test loop is defining a base of "standard" scaling solution as a basis for comparison of the various scale control methods. A base scaling solution was established that reduced the overall heat transfer coefficients over 50% in less than 20 h, as shown in Figs. 2-5 (line 1). The composition of this "base" scaling solution was 25 ppm calcium, 400 ppm silica, 800 ppm carbonate, 3% salinity, and a pH of 6.8-7.0.

The scale was analyzed semiquantitatively with the energy dispersive x-ray method, and the results, shown in Fig. 6, showed the composition to be essentially all silica with small amounts of iron, calcium, and residual sodium chloride.

The first scale control methods evaluated were commercial additives. Of those, only the Calgon Corporation agent CL-165 has shown any promise. The other additives did not alter the scaling characteristics of the simulated geothermal brines. The CL-165 levels evaluated ranged from 12 ppm to 25 ppm, with the rest of the constituents of the solution being the same as the "standard" solution. The effects of the additive were the prolongation of the run by over 100% before a high-pressure shutdown occurred, and a reduction in the amount of scale formed on the heat transfer surfaces, even though the run was longer.

In conflict with these results are the overall heat transfer coefficients seen in Figs. 2-5 (line 3). The overall heat transfer coefficients for the Calgon run and the standard scaling solution run are not different. Further work will be done to resolve this discrepancy.

Another method evaluated was a high-pressure carbon dioxide pad on the main exchanger. This method did not increase the length of the run, as did the Calgon CL-165, but did give the same discrepancy in the heat transfer curves and the visual inspection of scale: There was little scale formation seen on the heat transfer surface in the main exchanger. The mini-exchangers, where no CO_2 pad existed, had a typical amount of scale formation. Even though there was little scale formation on the heat transfer surface of the main exchanger, the overall heat transfer coefficients followed the same pattern as a "standard" scaling run, as shown in Figs. 2-5 (line 2). Another characteristic of this run was the lowering of the pH of the brine. The pH dropped from the 6-7 range to the 5.0-5.5 range, indicating CO_2 adsorption, which was verified by CO_2 consumption; thus the pH drop.

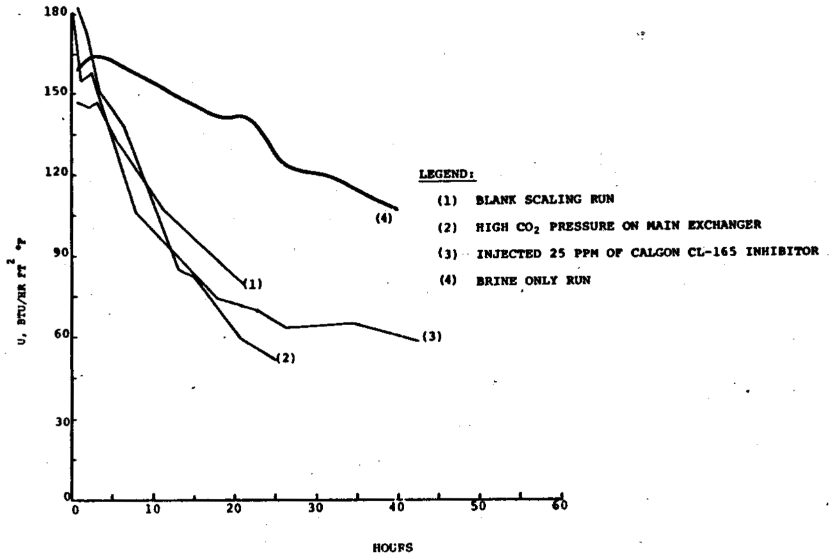

Fig. 2.
Overall heat transfer coefficients. Main exchanger.

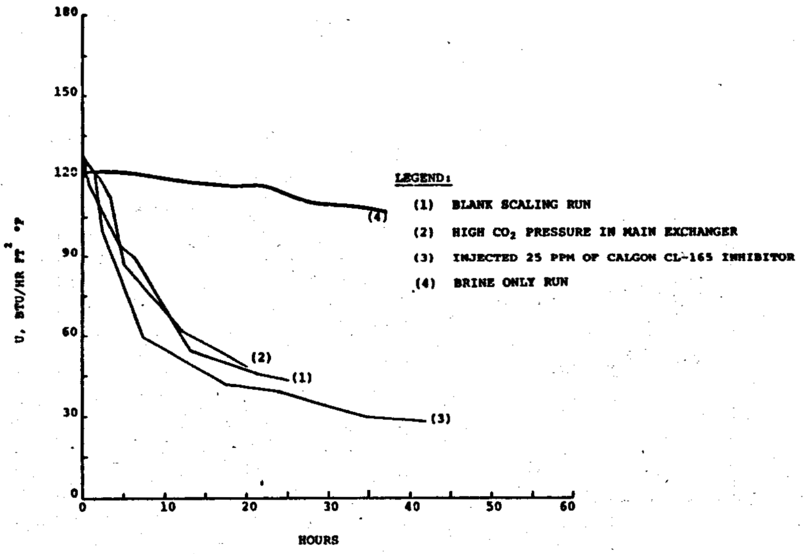

Fig. 3.
Overall heat transfer coefficients. Mini-exchanger No. 1.

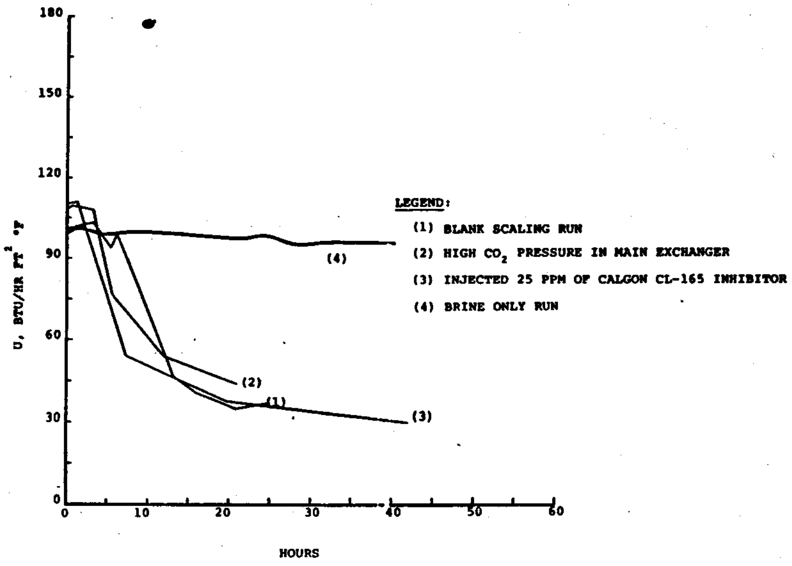

Fig. 4.
Overall heat transfer coefficients. Mini-exchanger No. 2.

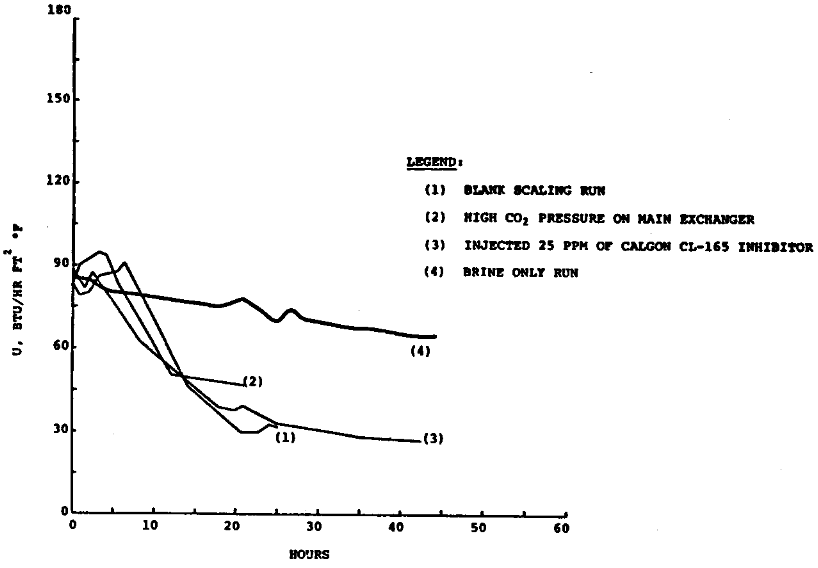

Fig. 5.
Overall heat transfer coefficients. Mini-exchanger No. 3.

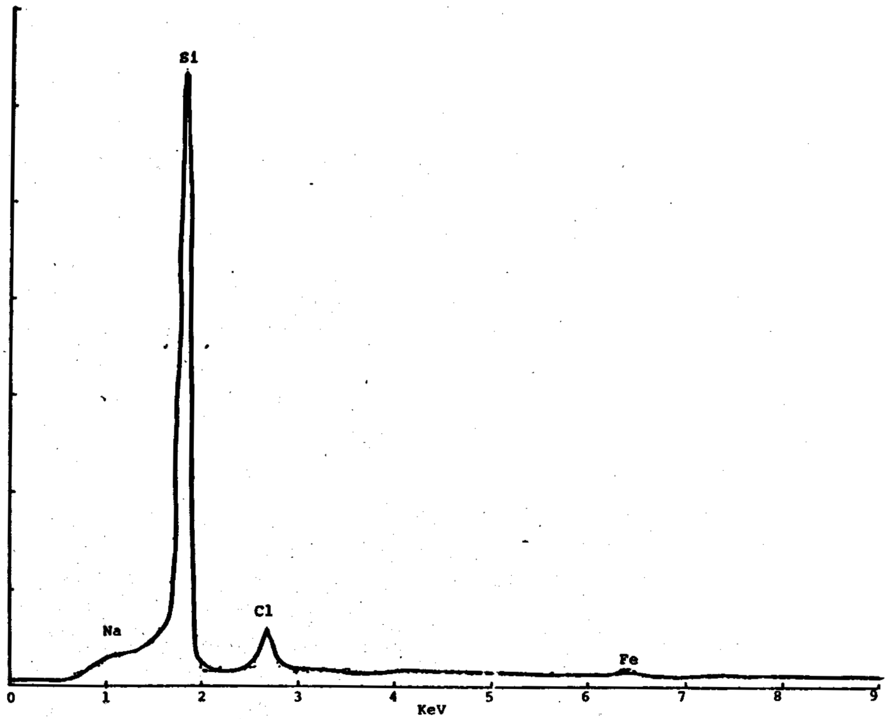

Fig. 6.
Energy dispersive x-ray scan. Typical scale analysis.

IV. CONCLUSIONS

At a pH of less than 6 the system will not scale. Also, at a calcium level less than 10 ppm the system will not scale. This suggests that the pH and the calcium level are the critical parameters of this system. This should be verified by LASL.

Of the methods evaluated, none has shown a marked effect on the overall heat transfer coefficients. The only two methods that have shown any promise are high carbon dioxide partial pressure and Calgon CL-165, which have reduced the scale formation that can be seen. This is probably due to the effect on the pH in the first case and the calcium carbonate seeding in the second case. The carbon dioxide run lowered the pH and the Calgon CL-165 affected the calcium carbonate in the solution.

SILICA PRECIPITATION AND SCALING IN DYNAMIC GEOTHERMAL SYSTEMS

by

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Oak Ridge National Laboratory, TN 37830

SUMMARY

An existing 100-gpm titanium loop was modified to provide a facility for studying the formation of silica precipitates, their properties and fates, as a function of brine composition, temperature, and flow conditions. Simulated silica saturated geothermal waters are prepared by circulating part of the loop flow (~1 gpm) through a bypass column filled with amorphous silica powder. A second ~1-gpm stream is circulated through a heat exchanger in which dynamic scaling studies are conducted. Design variables include overall $\triangle T$ to 125°C, linear flow rate of 3-7 fps, Reynolds number of 10^4 to 10^5. The heat exchanger was divided into five consecutive segments so successive temperature intervals could be instrumented to monitor changes in heat transfer characteristics; selective destructive examination when desired is also facilitated. Blind end flanges on each segment permit borescope examination of scales *in situ* and sampling access. The stream leaving the heat exchanger is reheated by an electrical reheat system to replace the 40-kW heat equivalent removed at maximum $\triangle T$, and recycled.

Five runs have been carried out in this system and the results are summarized in Table I. Run 2 was directed at silica scale formation from 1 M sodium chloride at pH 6. Spontaneous nucleation did not occur in 143 h operation, so the system was shut down and restarted twice in an effort to seed the heat transfer surfaces, but without success. Similar operations in a low-flow (~1-fpm) Pyrex pipe system seeded during shutdowns of several hours with subsequent rapid scaling in continued operation. A subsequent 141-h shutdown of the titanium loop also seeded that system and scaling rates ranging from 0.3 to 1 $mg/cm^2 \cdot h$ were observed. The relatively high silica concentrations were resorted to in an effort to induce spontaneous nucleation.

Run 3 was operated under the same conditions as Run 2 to demonstrate that our cleaning procedures had adequately removed all the silica scale formed in Run 2. It further demonstrated that spontaneous nucleation was not easily initiated under these conditions.

The remaining three runs showed that spontaneous nucleation was relatively rapidly initiated from 4 M NaCl at pH 7 and 650 ppm silica. Much higher growth rates were observed at the higher temperatures, but the rates were comparable to those in Run 2 at the lower temperatures.

As in the Pyrex system studies, the scales deposited at the high temperatures are much harder and more refractory (to dissolution by 4 M NaOH at 75°C) than those formed at lower temperatures. However, all require hours of the hydroxide treatment for complete removal.

Run 5 was aborted by loop heater relay failures shortly after scaling was indicated to have begun by heat transfer changes.

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*Research sponsored by Department of Energy, Division of Geothermal Energy, under contract with Union Carbide Corporation.

A somewhat surprising result was the observation of scale deposits in the reheat portion of the system. Total amounts deposited were comparable to those found in the heat exchangers as shown in Table II. The results indicate serious problems for reinjection if silica is not removed beforehand.

The possibility of seeding during shutdowns with subsequent rapid scale growth suggests special flushing or treatment measures would be very beneficial in connection with shutdowns.

TABLE I

SILICA DEPOSITION IN DYNAMIC LOOP STUDIES

					Segment 1			Segment 2			Segment 3			Segment 4			Segment 5		
Run No.	Time (h)	pH	SiO_2 (ppm)	NaCl (M)	ΔT (°C)	mg/cm² Total	mg/cm² per h	ΔT (°C)	mg/cm² Total	mg/cm² per h	ΔT (°C)	mg/cm² Total	mg/cm² per h	ΔT (°C)	mg/cm² Total	mg/cm² per h	ΔT (°C)	mg/cm² Total	mg/cm² per h
2A	143 (30)[a]	6.0	850-950	1	220-155	---	---	155-95	---	---	95-65	---	---	65-58	---	---	58-49	---	---
2B	46 (98)[a]	6.0	700-900	1	220-160	---	---	160-96	---	---	96-67	---	---	67-58	---	---	58-50	---	---
2C	29 (141)[a]	6.0	700-1000	1	215-160	---	---	160-106	---	---	106-75	---	---	75-65	---	---	65-57	---	---
2D	29	6.0	800-900	1	240-170	29.4	1.0	170-110	31.4	1.1	110-75	17.4	0.6	75-60	10.0	0.3	60-55	17.7	0.6
3	94	6.0	725	1	173-138	---	---	138-107	---	---	107-76	---	---	76-51	---	---	51-36	---	---
4	44	7.0	700	1	165-134	---	---	134-100	---	---	100-72	---	---	72-49	---	---	49-35	---	---
5	29	7.1	650	4	180-140	10.6	0.37	140-105	9.4	0.32	105-72	5.7	0.2	72-50	5.7	0.2	50-37	2.5	0.1
6	13	7.0	650	4	198-161	60[b]	4.6[b]	161-127	42[b]	3.2[b]	127-79	6.5[b]	0.5[b]	79-49	2.6[b]	0.2[b]	49-32	2.6[b]	0.2[b]

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[a] ( ) Shutdown periods to permit seeding.

[b] Cleanups were not quite complete when sodium hydroxide solutions were lost.

TABLE II

HEAT EXCHANGER BYPASS SILICA DEPOSITION

		Composition			Total Silica Deposited (g)	
Run	Time (h)	NaCl (M)	SiO_2 (ppm)	pH	Cooldown	Reheat
2D	29	1	850	6	62	48
5	29	4	650	7.1	20	25
6	13	4	650	7.0	75	83

MODELING OF GEOTHERMAL POWER SYSTEMS

by

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I. INTRODUCTION

This work is sponsored at Battelle Northwest by the Electric Power Research Institute. The program objectives are to

- develop a data base on the chemical factors affecting scaling,
- develop computer models to estimate scaling rates in plant components, and
- develop computer models of the impact of scaling on long-term plant electric output and maintenance requirements.

There have been a number of studies trying to optimize a geothermal power plant cycle (such as multistage flash vs binary fluid) for various geothermal reservoirs. So far these studies have not taken into consideration that the power cycle chosen and the engineering details of temperatures, pressures, and flows can profoundly alter the extent of scaling and corrosion, and the potential for plugging the waste injection wells. *Scaling is not an inherent characteristic of a geothermal fluid; it results from the process used to extract the energy.*

We recognize that the computer models being developed have limitations and can only give back what has been programmed. Obviously, at the present state of the art, our understanding is incomplete; therefore, our models will be incomplete. We must accept that these are first generation models.

However, computer models can be useful.

- The massive memory allows consideration of many facts simultaneously. An important fact is less likely to be overlooked.
- The models will be useful educational tools to scientists and engineers new to geothermal technology.
- The models provide a framework within which to plan field work and define test data to be gathered.
- The models will permit comparison of one reservoir with another and with various power cycle concepts.

Our program centers on the development of four computer codes.

EQUILIB	- an equilibrium chemistry code that takes a brine model and calculates what minerals would become insoluble and how much would precipitate with changed temperatures, pressures, and volumes in a power cycle.
FLOSCAL	- a code to estimate the build-up rate of scale on pipes and components.
PLANT	- an extensive thermohydraulics code that optimizes a typical multistage flash plant or binary cycle plant for a reservoir and then calculates plant degradation due to scale buildup.

GEOSCALE - a time-dependent code to combine the above codes to assess when and how the performance of a geothermal power plant will degrade with time as a result of scale buildup.

II. EQUILIB

A. Why Does Scale Form?

When a geothermal brine flashes, the gases fractionate to the steam phase (Fig. 1). This process causes pH changes that affect calcite solubility (Fig. 2) and sulfide solubility. As temperatures drop, the solubility of quartz, cristobalite, or amorphous silica can be exceeded, and one or more forms of silica can be precipitated (Fig. 3). Other factors are shown in Table I.

B. What Process Parameters Affect Scaling?

Many factors affect scaling, as shown in Table II. Precipitation of a mineral does not necessarily lead to scale formation because mass transport must take place toward a pipe wall, and sticking must occur for a scale growth to form. Thus, it is the interplay of chemical and thermohydraulic factors that controls scale growth.

The code EQUILIB only looks at part of the problem—the chemical driving forces affecting precipitation. This is very important to assess what minerals are thermodynamically possible. The concept of EQUILIB is illustrated in Fig. 4. Some of the important chemical factors are considered in Table III.

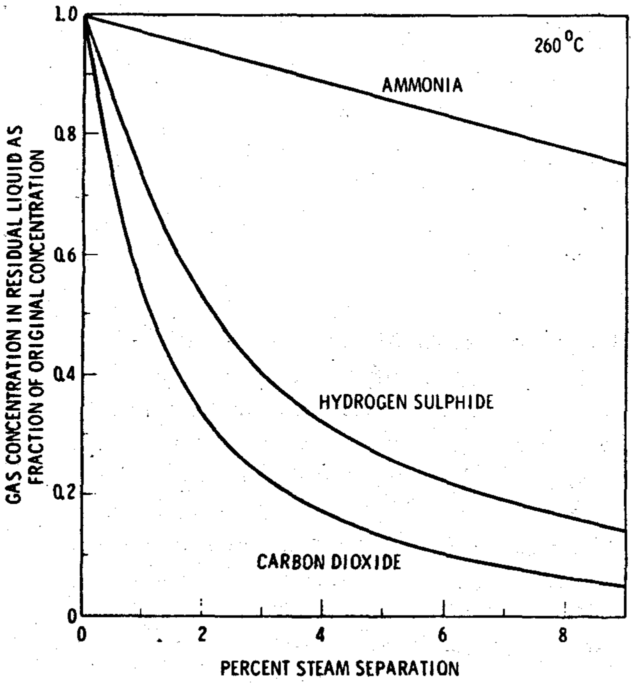


Fig. 1.
The concentration of gases in the water phase remaining after the equilibrium separation of steam (Ref. 1).

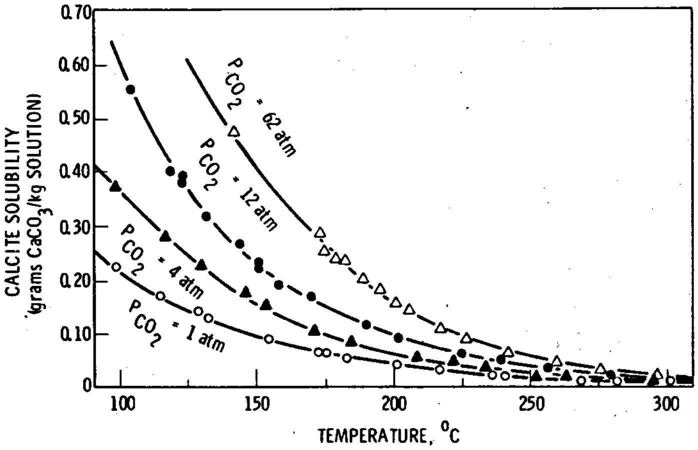


Fig. 2.
The solubility of calcite in water up to 300°C at various partial pressures of carbon dioxide (Ref. 2).

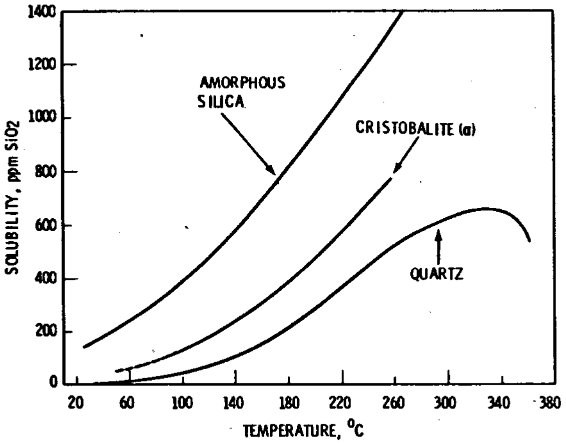


Fig. 3.
Silica solubility in water (Ref. 3).

C. Status and Some Results

EQUILIB has its origin in code work at LASL (Herrick) and LLL (Miller). It is operational using a data base originally developed by H. C. Helgeson for another purpose. The EQUILIB code was developed at BNW by J. R. Morrey. We have used the code to verify a mineral solubility diagram (Fig. 5). The code correctly identified the stability fields of siderite, pyrite, and hematite. We used EQUILIB to calculate what corrosion products would form on carbon steel and compared the result with actual experimental results (Table IV). The code has also been used to compare scaling in a Heber heat exchange tube where sulfides and silica were predicted to deposit (Table V). When the same brine was flashed in a code calculation, calcite, silica, and iron silicate were predicted to deposit. We are expanding the data base to include more species of interest to geothermal power plants, including Ba, Sr, Sb, F, and NH_3.

TABLE I

WHY DOES SCALE FORM?

TYPE	CAUSES
Silica and silicates	Temperature drop decreases solubility, steam loss concentrates brine, and pH changes affect kinetics.
Calcite	CO_2 loss increases pH and steam loss concentrates brine.
Sulfides	Temperature drop decreases solubility and CO_2 loss increases pH.
Iron deposits from corrosion	Fe^{+2} ion precipitates on surfaces and in other scale deposits.
Carry-over	Incomplete steam separation results in aerosol carry-over of salts.
Sulfates	Temperature or pressure changes decrease solubility, and Mixing different fluids—barium in one stream and sulfate in another = $BaSO_4$ scale.

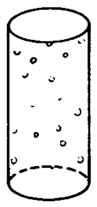
TABLE II

IMPORTANT FACTORS AFFECTING GEOTHERMAL SCALING

- Brine composition
- Gases present and pH − CO_2, H_2S, NH_3, HCl, H_2, O_2
- Temperature in reservoir
- Fluid produced single-phase or 2-phase
- Degree of flashing and steam fraction
- Distribution of gases between liquid and vapor
- T and P
- Oxidation-reduction potential
- Brine concentration from steam loss
- Nucleation-growth phenomena
- Deposition surface
- Velocity, Reynolds number, and other flow effects

III. FLOSCAL

FLOSCAL is a code in its beginning stages of development. It will take the output of EQUILIB (which predicts what minerals will precipitate) and estimate how fast scale will build up on walls. The FLOSCAL data base is the most inadequate because we need equations to describe scaling kinetics mathematically. We are concentrating on the species in Table VI and recognize that more species must be added at some future time (sulfides, silicates, sulfates, etc.).



CONCEPT OF EQUILIB

- CALCULATIONS ARE DONE ON 1 kg OF BRINE AT ANY TEMPERATURE 25 TO 300°C
- GAS VOLUME CAN BE ANY VALUE - ZERO TO X EXPRESSED AS LITERS OF GAS VOLUME/kg OF BRINE
- THE GASES CO_2, H_2S, HCl WILL DISTRIBUTE BETWEEN GAS PHASE AND LIQUID AS FUNCTIONS OF T, pH, SALT CONTENT
- TWO PHASE MIXTURES SIMULATED BY INSERTING PROPER VALUE OF V TO SIMULATE STEAM VOLUME
- DURING A FLASHER CALCULATION BRINE PHASE CONCENTRATIONS ARE CORRECTED FOR WATER LOSS
- IF ALL WATER FLASHES CODE STOPS AND TELLS YOU
- CODE CALCULATES AQUEOUS PHASE CONCENTRATIONS, ACTIVITIES, pH AT TEMPERATURE, GAS PARTIAL PRESSURE, AND IDENTIFIES TYPE AND QUANTITY OF INSOLUBLE MINERALS AT CHEMICAL EQUILIBRIUM

Fig. 4.
Concept of EQUILIB.

TABLE III

FACTORS TO BE INCLUDED IN AN EQUILIBRIUM CHEMISTRY MODEL

- Temperature
- Concentrations of all brine cations and anions
- pH
- Partial pressures of gases
- Activity coefficients
- Ionic strength, which affects chemical activities
- Components that control oxidation potential
- Solubilities of solid minerals that could form
- Aqueous phase equilibria that distribute components among many species and complexes
- Total mass balance between aqueous and gas phases

Part of our effort is devoted to laboratory experiments on the kinetics of calcite and silica precipitation in two-phase flow (Tables VII and VIII).

IV. PLANT

A computer model has been developed to simulate two types of geothermal power plants: the flashed-steam plant and the binary cycle plant. This computer model not only establishes a baseline description of the power plants, but also simulates the performance of these power plants as scale buildup occurs.

The inputs to the code, general process information provided by the user to the code, and output are given in Tables IX through XII.

We have the code PLANT running with manual input of scale thicknesses. Two such cases are given in Table XIII and Figs. 6 and 7, where the impact of scale buildup on power output is illustrated.

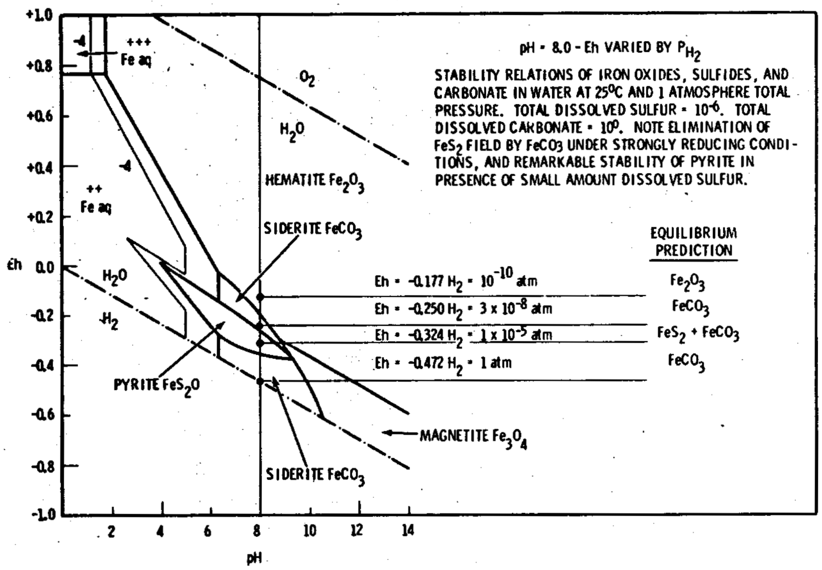


Fig. 5.

EQUILIB calculations compared with experimental stability fields of Fe phases at 25° C (Eh-pH diagram from Ref. 4).

TABLE IV

EQUILIB CODE PREDICTIONS OF CORROSION PRODUCTS ON CARBON STEEL

	1% NaCl, pH 7.5		1% NaCl, pH 4.8		1% NaCl, pH 4.8 + H_2S	
T(°C)	**EQUILIB**	**Experimental**	**EQUILIB**	**Experimental**	**EQUILIB**	**Experimental**
50	$FeCO_3$	None detected	Fe^{++}	85% Fe 10% $FeCO_3$	FeS_2	FeS
150	Fe_3O_4	Fe_3O_4	$FeCO_3$	$FeCO_3$	$FeCO_3$ FeS_2	80% $FeCO_3$ 10% FeS 5% FeS_2
250	Fe_3O_4	Fe_3O_4	Fe_3O_4	70% Fe_3O_4 + 30% $FeCO_3$	Fe_3O_4	Not run

V. GEOSCALE

All of the above material will be integrated into a large code called GEOSCALE, which will permit assessing the time-dependent performance of a geothermal power plant. The general flow logic of GEOSCALE is illustrated in Fig. 8.

TABLE V

ATOMIC PERCENTAGE OF MAJOR CONSTITUENTS OF THE SCALE DEPOSITS IN HEBER TUBES

ELEMENT	E1-IN (173°C)	E2-OUT (116°C)	E2-OUT (84°C)	E3-OUT (66°C)	E4-OUT (56°C)
S	19.8	31.7	42.7	46.4	67.0
Sb	7.0	3.8	27.5	7.7	23.8
Fe	44.3	27.8	2.1	17.7	0.4
Si	5.4	10.5	9.0	23.1	4.4
As	8.9	1.9	3.2	0.6	1.2
Zn	5.1	9.3	0.7	0.9	0.2
Ca	4.6	8.8	0.7	0.2	0.3
Pb	0.1	0.8	2.2	0.2	0.3
Tl	-	-	-	0.4	1.3

TABLE VI

DEPOSITION FORMULATIONS

Calcium carbonate
- Attenuation length model
- Correlation for attenuation length to be developed

Quartz
- Reaction rate model (H. L. Barnes)

Amorphous Silica
- Deposition only if amorphous silica solubility exceeded
- Attenuation length or mixed kinetics model to be developed for scale correlations

TABLE VII

KINETIC EXPERIMENTS

Test Objective
- Define the interactions of temperature, salinity, chemistry, and hydraulics on scaling rates during flashing in 2-phase flow

Test Parameters

• RESERVOIR TEMP	FLASH TEMP	% STEAM
290°C (554 F)	171°C	28
235°C (455 F)	143°C	19
180°C (356 F)	116°C	13

- Salinity 0.58% and 5.8%
- Chemistry Saturated with $CaCO_3$, SiO_2 at reservoir temperature and 1 atm CO_2 overpressure

TABLE VIII

INITIAL OBSERVATIONS FROM SCALING KINETICS TESTS

- $CaCO_3$ deposits in both calcite and aragonite forms
- $CaCO_3$ deposits very rapidly and is in chemical equilibrium in a few cm downstream from flash point
- $CaCO_3$ scaling increases as reservoir temperature drops
- $CaCO_3$ scaling decreases as salinity increases
- SiO_2 scaling is much slower—20-30 h to equilibrium
- SiO_2 scaling occurred only in 290°C test
- SiO_2 scaling increases as salinity increases

TABLE IX

INPUT TO PLANT CODE

Reservoir Properties
- Thermodynamic properties
- Composition
- Well flow rates

Plant Parameters
- Binary or flash steam
- Size
- Plant component options

Meteorological Conditions

TABLE X

GENERAL PROCESS INFORMATION

Geometry of Specific Plant Components
- Diameter
- Length
- Cross-sectional area
- Description of internal configuration

Degradation of component efficiencies due to scaling
Pressure and heat losses in system
Heat transfer coefficients where appropriate
Scaling conditions at key plant locations
Descriptions of flow streams other than brine
Alterations in plant base-line operating conditions due to deposition
Internal plant electrical consumption
Power output
Brine conditions at over 90 locations in plant

Temperature
Pressure
Enthalpy
Density
Wt% of dissolved solids (and species)

Velocity
Thermodynamic phase
Flow rate
Viscosity
Reynolds number

TABLE XI

LIST OF MODELS FOR FLASHED-STEAM SYSTEM COMPONENTS IN CONTACT WITH GEOTHERMAL FLUID

- Production wells (reservoir not included)
- Brine pump
- Transmission lines
- Flasher separator
- Steam scrubber
- Turbine
- Condenser
- Gas ejector

TABLE XII

LIST OF COMPONENT MODELS FOR BINARY SYSTEM IN CONTACT WITH THE GEOTHERMAL FLUID

- Production wells (reservoir not included)
- Brine pumps
- Transmission system
- Geothermal/working fluid heat exchanger(s)

TABLE XIII

EFFECT OF SCALE ON POWER OUTPUT

INPUT CONDITIONS:

Flashed-Steam Plant

- 200°C brine, compressed liquid at wellhead, with 7% dissolved solids
- Double-flash system with flashing at the plant
- 44 MWe gross power output

Binary Cycle Plant

- 205°C brine, compressed liquid at wellhead, with 7% dissolved solids
- Subcritical cycle using isobutane as the working fluid
- 55 MWe gross power output

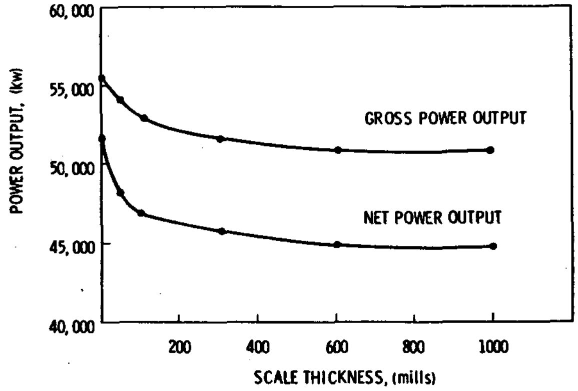


Fig. 6.
Plant power output flashed steam plant.

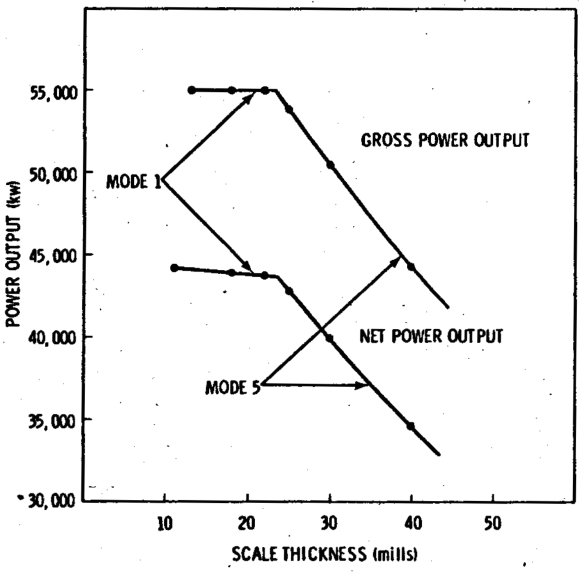


Fig. 7.
Power output binary cycle plant.

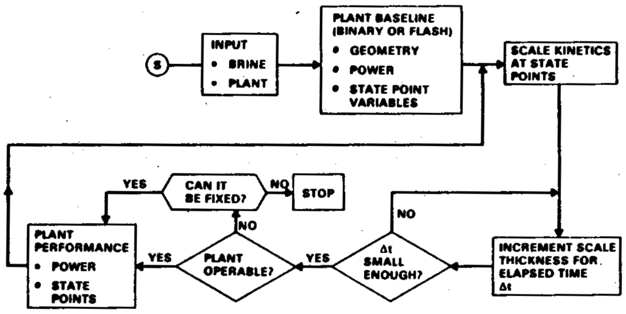


Fig. 8.
GEOSCALE calculation flow.

REFERENCES

1. A. J. Ellis, "Interpretation of Gas Analyses from the Wairakei Hydrothermal Area," New Zealand J. Sci. 5, 434-452 (1962).

2. A. J. Ellis, "The Solubility of Calcite in Sodium Chloride Solutions of High Temperatures," Am. J. Sci. **261**, 259-267 (1963).

3. H. L. Barnes, "Chemistry of Silica Scale Formation," Proc. 2nd Workshop Materials Problems Associated with Development of Geothermal Energy Systems," El Centro, California, May 16-18, 1975.

4. R. M. Garrels and C. L. Christ, *Solutions, Minerals and Equilibria* (Freeman, Cooper & Co., San Fransisco, 1965).

LASL'S RELATIONSHIP TO THE MODELING OF GEOCHEMICAL SYSTEMS

by

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Figure 1 presents the basic relationship of LASL modeling and coordination tasks to other activities described in contributions to this workshop. The previous paper discussed the Plant System Economics and Performance Models being developed at BNWL (GEOSCALE)[1] and LBL (GEOTHM).[2] These models are large codes that, in considering all the factors influencing economics of geothermal plant design and cycle choices, become relatively inconvenient to use as vehicles for studying design problems of specific components (i.e., heat exchangers, piping, fittings, valves, flashers, etc.). It is perhaps more efficient of computer resources to study that class of problems using small-component models. This is the LASL approach to the computer modeling of geothermal geochemical problems. To accomplish this, one has to consider input from several other tasks and areas of research. For example, the previous discussion of the subroutine FLOSCAL illustrates the need for better understanding in the area of scaling mechanisms and theory. Other areas expected to provide input to the modeling capability are expansions of the thermodynamic/kinetic property data base and the incorporation of advanced numerical techniques.

The "component-size" computer models can fill three specific needs in the design of geothermal plants.

- Use can be made of small models to check out and fit parameters for simplified design equations to be used for components in the larger codes (GEOSCALE AND GEOTHM).
- Small codes can better be used to interact with experimental programs to accomplish such things as checking various proposed scaling mechanisms and hydrodynamic effects.

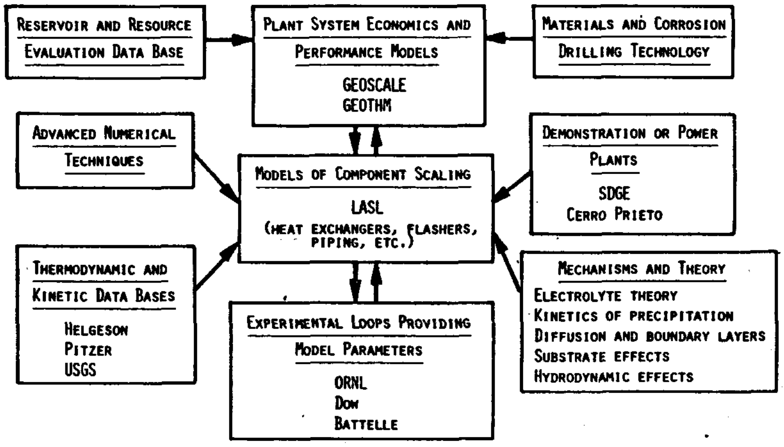

Fig. 1.
Relationships of LASL tasks to other geochemical activities.

TABLE I

COMPONENT MODELING APPROACH

- DEFINE SYSTEM TO BE MODELED
  - Type of heat exchanger
  - Connecting pipes
  - Other plant components
- ENGINEERING CALCULATIONS
  - Define geometry
  - Calculate temperatures (bulk, wall, etc.)
  - Pressures
  - Other variables
  - Point values
- CHEMISTRY CALCULATIONS
  - Takes temperatures and pressures from ENGR
  - Given fluid feed composition
  - Calculates precipitates
- SCALE DEPOSITION
  - Present code uses a "modified infinite rate model"
- LOOP BACK TO OBTAIN SCALE EFFECT ON ENGR CALCULATIONS
  - Time rate of change of U
  - Spatial definition of scale rates
  - Changes in wall temperatures
  - Changes in velocities of fluid

- Considerable potential exists for use of small component models in trouble-shooting actual plant operation problems.

In pursuing this concept a little further, we have taken upon ourselves the task of modeling a few components and incorporating some of these advantages.

Table I is an outline of the calculational approach used to model the "mini-exchanger" of the Dow Chemical loop described earlier in this meeting. In this simple modeling approach, we decide what is to be modeled. In this example, we have chosen the heat exchanger No. 1 and the associated inlet piping. First, we do some engineering calculations; define geometry, calculate temperatures, pressures, heat fluxes, and any other engineering parameters that the particular scaling model would need for predicting scale formation. There are a number of engineering parameters that can be calculated, such as boundary layer thicknesses, wall temperatures, and static pressures. These can be used to fit scale deposition theories and experimental observations. We then proceed in our calculational model to a chemistry calculation that will be discussed in more detail later. The chemistry calculation takes the fluid chemistry and the engineering parameters of temperature and pressure and calculates a potential for scaling. This information is then fed to another subroutine, where a scale deposition model is applied and a scale thickness buildup rate is calculated. At present, our model of scale deposition assumes a "modified infinite rate model," where an arbitrary fraction of the chemically permitted scale is assumed to appear as scale on the tube wall. The code then loops back to the engineering calculations to calculate the time rate of change in the overall heat transfer coefficient and the effect on such parameters as temperature changes caused by the scale deposition and velocity changes caused by tube plugging. In this model, we break the tube spatially into increments (5 to 10 being the numbers used

TABLE II

CHEMICAL CALCULATIONAL FEATURES

- REALLY KINETIC PROBLEM
- BASED ON MA-SHIPMAN CODE
  - Existing code
  - Equilibrium method
  - Uses activity coefficient formulation
  - Added aqueous solutions
  - Automatically redefines components
  - Uses two-step solution
  - Can now handle
    - Gas phase
    - Solution phase
    - Multiple solids
- ADDITIONAL DATA BASES AND CODE MODIFICATIONS ANTICIPATED
- CHEMISTRY ROUTINE "BLACK BOX" TO LARGER CODE

TABLE III

ENGINEERING METHODS

Valves—Pressure loss based on flow coefficients
Fittings—Equivalent length
Pipes—Moody friction

$$f = 0.005 \left[1 + \left(2 \frac{\varepsilon}{D} \times 10^4 + \frac{10^6}{R_E}\right)^{0.33}\right]$$

Heat Exchanger—
Tube Side (Turbulent) McAdams

$$N_U = 0.027 \; Re^{0.8} \; P_r^{\;0.33} \left(\frac{\mu_B}{\mu_W}\right)^{0.14}$$

Tube Side (Laminar) McAdams

$$N_U = 1.86 \left(R_e \; P_r \; \frac{De}{L}\right)^{0.33} \left(\frac{\mu_B}{\mu_W}\right)^{0.14}$$

Shell Side Kern

$$N_U = (\text{Const}) \; (Re)^{0.55} \; P_r^{\;0.33} \left(\frac{\mu_B}{\mu_W}\right)^{0.14}$$

$$\frac{1}{U} = \frac{1}{H_O} + \frac{1}{H_I} + R_s + R_W + R_F$$

to model the 4-ft-long tube in the Dow mini-exchanger), which allows the model to predict local scale deposition based either on local conditions or conditions that were present upstream.

The features of the chemical calculations are outlined in Table II. The scaling mechanisms are dominated by kinetics. We have chosen to start the modeling task by using a modified version of the Ma-Shipman code.[3] This is basically an "equilibrium" code, but since it was already in existence, it provided a place to start. The code uses an activity coefficient formulation based on data of Helgeson and others. We have added aqueous solution capability to the code. One feature is that the code automatically redefines components to speed up the calculation. Convergence is based on a two-step procedure of an initial "steepest descent" estimation, followed by a Newton-Raphson solution. We have modified the code so that it now can handle gas phase, solution phase, and multiple solids.

Plans for the near term are to expand the chemical data base and improve the convergence methods used in the chemistry calculations. Because this calculation must operate as a "black box" to the engineering model, the opportunity to "fiddle with the tolerance" on the convergence scheme is not allowed. We have had trouble with this, but are optimistic that the problem can be solved.

Table III provides an indication of the level of engineering calculational sophistication that we have in the Dow heat exchanger model. These are standard engineering calculations with correlations taken from Kern[4] and McAdams.[5] The Moody friction factor correlation is based on a paper published in 1947.[8] This expression allows a direct calculation of friction factor as a function of roughness and Reynolds number without iteration.

The constant multiplier in the shell-side heat transfer correlation was modified from that presented in Kern to provide a better fit of the Dow data. This is justified because the Dow mini-exchanger has only four tubes and the correlation is based on data from larger exchangers.

Resistances of the scale, pipe wall, and shell-side fouling are included in the calculation of the overall heat transfer coefficient.

One point that should be made is that these engineering parameters can easily be calculated to any level of sophistication by just changing a subroutine. The simple approach seems to be adequate at this stage.

Property data are needed for engineering calculations both for transport properties of the fluid and physical properties of the scale. Table IV lists the common properties used in the component model. Viscosity[7] and density[8] data used are from the LBL GRID data base. Heat capacity[9] and thermal conductivity data[10] were recommended by Dow personnel. Solid property data of the scales are, in general, scarce. To properly model the thermal resistance of scale, one needs to know an effective density (thickness) and a thermal conductivity (in the wet condition). The morphology of the scale will affect the thermal conductivity and density, and hence the thermal resistance. It is tempting to model this as one unknown parameter incorporating the fraction of the material that sticks to the wall, but we have resisted, and each factor is estimated separately in our current model. There is very little discussion in the literature of these parameters, even when chemical composition is included in scale description.

Some results of our calculations are illustrated in Fig. 2. Here, one can see the effect of varying some of the calculational parameters superimposed on a set of Dow data. FRACT is the fractional percentage of the scale allowed to deposit in each tube increment compared to the total available based on the equilibrium chemistry calculation. For example, if we assume FRACT = 0.01, then we are saying that 1% of the available scale is actually deposited to the walls in that increment, and the other 99% is put back into the chemistry calculations at the next increment. This is a very simple approach, and it illustrates that a very small fraction of the material available to cause scale actually is seen on the wall. Also included in Fig. 2 is one case where the effective density of the scale was changed, which, compared to the same FRACT case, shows the effect of different scale thicknesses. This is to emphasize the point made earlier that chemical composition of the scale alone does not define it in enough detail to allow modeling in the engineering sense.

To illustrate the magnitude of scale thickness to significantly affect the heat transfer, we have plotted scale thickness in Fig. 3. This is a plot of scale thickness as both a function of position in

TABLE IV

ENGINEERING PROPERTY DATA USED IN MODEL

TRANSPORT PROPERTIES OF FLUID
- Viscosity
- Heat capacity
- Density
- Thermal conductivity

SOLID PROPERTY DATA
- Density of scale
- Effective thermal conductivity of scale

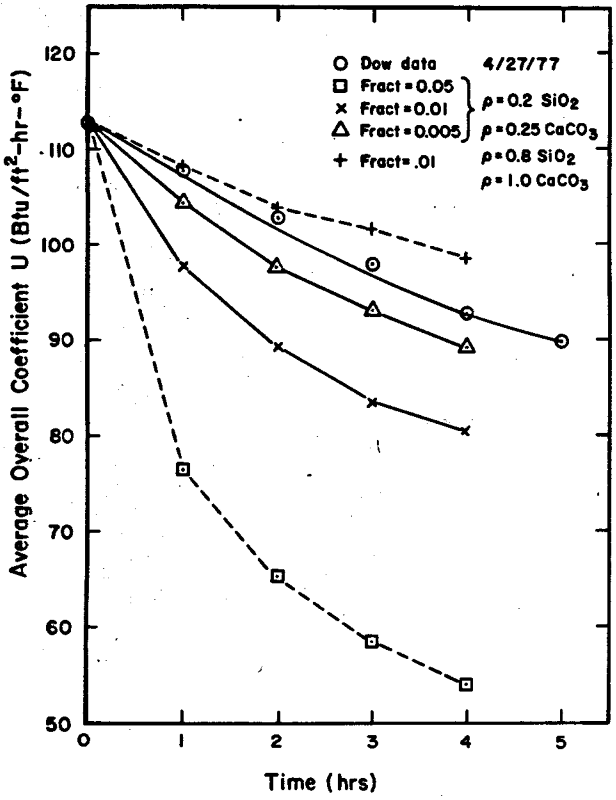

Fig. 2.
Comparison of calculations with experiment.

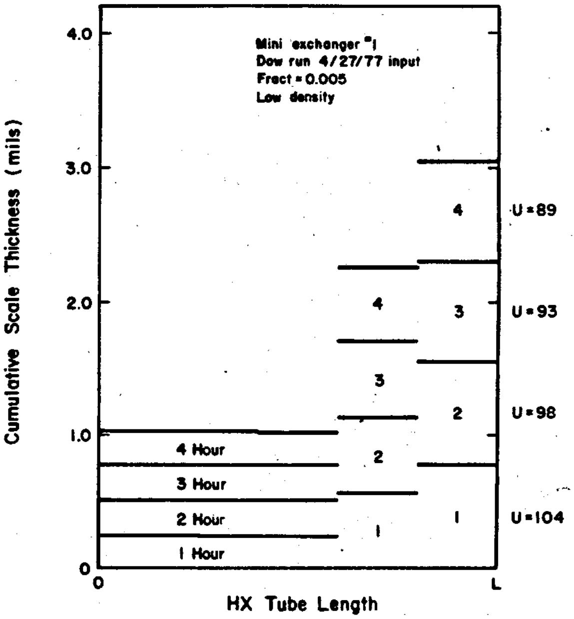

Fig. 3.
Cumulative scale thicknesses with length.

the tube and time that the scale has been accumulating. Note that only a couple of mils of scale will reduce the heat transfer coefficient by nearly 20% from the clean condition. Another interesting feature of the scale calculated in this example is that the temperatures and brine composition were such that the chemistry code predicted carbonate scale in the forward end of the tube and silica scale at the aft end. We have not analyzed the spatial distribution of the scale observed in the Dow experiments to see if this is true.

Table V shows future plans for the modeling project at LASL. Our initial effort is to continue the interaction with the Dow experimental loop to try to develop test data that can be used to support various modeling assumptions. A run is planned with a turbulance promoter in one of the tubes; the other three tubes are unaffected to see if turbulence changes the scaling rates. We intend to run with different chemical feeds and obtain more data on the actual scale that is formed.

LASL will be preparing and evaluating some requests for proposals to fill needs in the area of brine chemistry and modeling. We hope to extend our modeling to other components of interest in plant design. These can be suggested either by plant economics studies or field experience. As experimental data become available from other loops we probably will attempt to model the results. This will require expansion of the chemistry code to include sulfides and sulfates.

TABLE V

FUTURE PLANS

DOW
- Suggest runs to develop FRACT models
- Turbulence promoter in tube
- Different chemical feeds

RFP
- Hydrodynamic effects

OTHER COMPONENTS
- Flashing units
- Plant economics suggested
- Field experience suggested

OTHER LOOPS

DATA COLLECTION
- Thermodynamic chemistry
- Experimental results from plants and loops elsewhere

EXTEND TO MORE COMPLEX CHEMISTRY
- Sulfides
- Sulfates

REFERENCES

1. R. A. Walter, D. L. Lessor, and D. W. Shannon, "The GEOSCALE Computer Model for Geothermal Plant Scaling and Corrosion Analysis," Battelle Pacific Northwest Laboratories report BN-SA-709 (March 1977).

2. M. A. Green, H. S. Pines, W. L. Pope, and J. D. Williams, "Thermodynamic and Cost Optimization Using Program GEOTHM," in *Geothermal: State of the Art*, Trans. Geothermal Resources Council Annual Meeting, San Diego, California, May 9-11, 1977 (Geothermal Resources Council, Davis, California, 1977), Vol. 1, pp. 115-118.

3. Y. H. Ma and C. W. Shipman, "On the Computation of Complex Equilibrium," AIChE J. 18(2), 299-304 (1972).

4. D. Q. Kern, *Process Heat Transfer* (McGraw-Hill Book Co., New York, 1950).

5. W. H. McAdams, *Heat Transmission* (McGraw-Hill Book Co., New York, 1954).

6. L. F. Moody, "An Approximate Formula for Pipe Friction Factors," Mech. Eng. **12**, 1005-1006 (1947).

7. H. Ozbek, J. A. Fair, and S. L. Phillips, "Viscosity of Aqueous Sodium Chloride Solutions from 0 to 150°C," Lawrence Berkeley Laboratory report LBL-5931 (1977).

8. S. L. Phillips, Lawrence Berkeley Laboratory, personal communication.

9. L. A. Bromley, "Further Studies of Properties of Sea Water and Its Concentrates to 200°C," NTIS report PB-109 994 (1970).

10. J. E. King, Jr., Dow Chemical Company, personal communication.

THERMODYNAMICS AND KINETICS OF SCALE FORMATION

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I. SCALE INVENTORY

A. Scale Types

It is generally agreed that the four major classes of scales are
(a) silica and silicates,
(b) carbonates,
(c) sulfates, and
(d) sulfides.

Silica seems to be exclusively in the form of amorphous silica, such as opal. Silicates are also amorphous to near-amorphous. Their abundance is not clear because detection must depend essentially on compositional data, but they are probably much more common than generally assumed. Skinner et al.[1] mention that the Salton Sea opal scale has a high refractive index and that substantial amounts of iron are present. Arnorsson[2] found silicate scales with up to 18% Al_2O_3 as well as considerable amounts of Mg-silicates of unknown chemistry (see also Barnes et al.[3]).

Carbonate scales are predominantly low-magnesium calcites although some high magnesium contents are listed by Mercado and Guiza,[4] and aragonite has also been reported. The phases seem to be well crystallized, though probably cation-disordered.

Sulfates are mainly the calcium sulfates (anhydrite, bassanite, and gypsum) and barite. Anhydrite dominates at the higher temperatures. Sulfates are formed from sulfate-rich geothermal fluids or when such fluids are contaminated with sulfate-rich ground waters. They could also form by addition of oxygen to sulfide-bearing geothermal fluids.

Sulfides occur in the form of many phases, usually well crystallized. Predominant are Pb, Zn, Fe, and Cu sulfides such as galena, sphalerite, pyrrhotite, pyrite, chalcocite, chalcopyrite, and others.

B. Scale Characterization

Reports that carefully characterize individual scales are surprisingly scarce. The 10-yr-old paper by Skinner et al.[1] is still the most rigorous treatment of scales using modern mineralogic techniques. They found the Salton Sea scales to consist of disseminated euhedral Cu-Fe-Ag sulfide crystals embedded in an iron-rich opaline matrix. They paid particular attention to the textures, but were unable to relate the depositional events reflected in the scales to the P-T regime of the well.

Quong[5] and Mercado and Guiza[4] have contributed valuable scale studies for the Niland, California, experimental facility and the Cerro Prieto, Mexico, field, respectively.* Quong[5] found galena to be the major precipitate before steam separation and an iron-rich amorphous silicate after that event. Sulfates and carbonates were encountered also, but are related to contamination. The scales are distinctly layered, indicating a complex depositional history, but are not further characterized texturally. X rays and a few bulk chemical analyses are given, but often not on the same samples. The summary by Mercado and Guiza[4] is particularly valuable, because they show actual scale cross sections within pipes. Scales are principally silica and calcite, which seem to vary antithetically in abundance (Figs. 1-3).

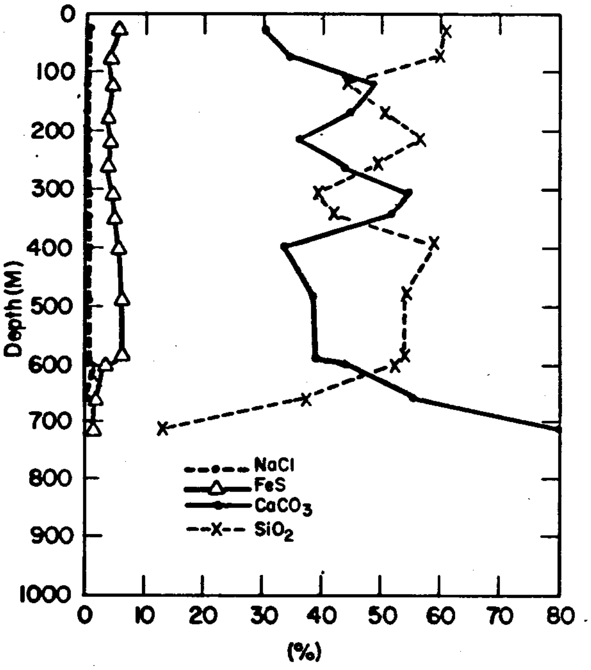

Fig. 1.
Deposits in Well M-11. Chemical variations vs depth (Ref. 4).

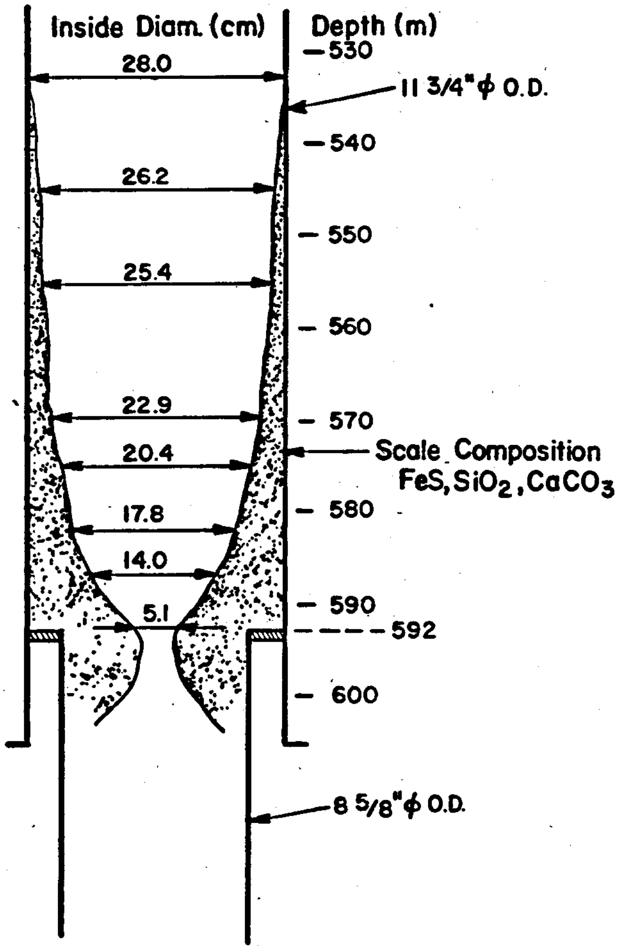

Fig. 2.
Profile of scale in Well M-13 (Ref. 4).

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*Excellent scale descriptions are also contained in Ref. 6.

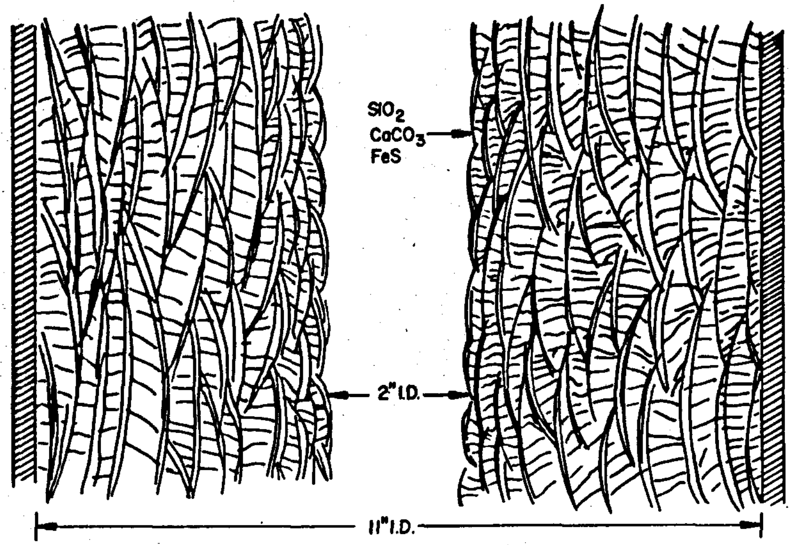

Fig. 3.
Deposits of Well M-13 at 591-m depth (Ref. 4).

C. Needed Data

Modeling of scale formation depends critically on the nature of scales, where they form, and yet such information is essentially nonexistent. Every natural scale encountered is an experiment from which we could extract valuable information. Prerequisites are mineralogic characterization of the scale and detailed records of the well history. In addition to the usual x-ray studies and bulk chemistry, we need detailed textural information (thin sections!) combined with chemical traverses done by microprobe analysis. The hope would be to eventually correlate individual scale layers with particular P-T regimes, and thus more quantitatively define scaling conditions.

II. MECHANISMS OF SCALE FORMATION

Little is known of the precise mechanisms leading to scale formation, but many suggestions have been made. It may be useful to distinguish three main environments of scale formation:

1. deposition from a single-phase fluid,
2. deposition from flashing fluids, and
3. deposition by steam carry-over.

Of these, 1 and 3 are easiest to understand, and yet probably most scales form by process 2.

Precipitation of solids from a single-phase fluid has been studied for many years. The fluid obviously must be supersaturated with respect to that phase. Nucleation and the kinetics of deposition depend strongly on the degree of supersaturation, P, T, and additional catalytic or inhibitory effects, such as the presence of minor elements, the nature of the substrate.

Geothermal fluids from which silica and silicates precipitate must all be supersaturated with respect to amorphous silica since quartz has not been reported in scales. As Harder and Fleming[7] have pointed out, quartz can only crystallize from solutions undersaturated with respect to amorphous silica. Flörke[8] found the deposition of silica glass and opal-CT to be favored by low substrate temperatures (high supersaturation) and high depositional rates, but the relationships have not been quantified.

Deposition from flashing fluids is little understood, though it appears to be a major cause of scaling. Flashing is initiated by pressure drops or by cavitation in turbulent flow. The only experiment we know of that relates flashing to scaling is the Niland experiment. Flashing is thought to be responsible for the calcite scales of Icelandic wells.[9] Flashing greatly enhances supersaturation through one of three mechanisms: (a) loss of steam from the liquid phase increases concentrations of the remaining solutes, (b) temperature drop associated with the expansion process, and (c) loss of stable gases such as CO_2 or H_2S increases pH.

Deposition by steam carry-over is responsible for scales on turbines and other components exposed to steam only. This is caused by water droplets carried along and then evaporated on a substrate. Because they are based on complete evaporation, such scales also may contain some of the soluble minerals, such as borates and halites.

A. Information Needed

Reasonably good information is available on the kinetics of silica precipitation (see Van Lier et al.[10] and Cordurier et al.[11] for basic data, and the summary reports by Owen,[12] Apps,[13] Bohlmann et al.,[14] Downs et al.,[15] Harvey et al.,[16] and Barnes et al.,[8] for more recent treatment), but much less is known about the kinetics of carbonate, sulfate, and sulfide precipitation.

The most urgent need, however, is for a better understanding of the relationship between flashing and scale formation. This involves hydrodynamics, to be discussed in a later section.

III. SOLUBILITY DATA

Degree of supersaturation with respect to a given precipitate can be determined by comparing the analysis of a particular geothermal fluid with solubility data. The advantage of this method lies in the fact that ideally no extrapolations are necessary, and the disadvantage that the solubility data must refer to a fluid composition close to that of the geothermal fluid.

A. Solubility Data for Quartz and Amorphous Silica

Data for pure water along the L + V curve have been summarized by Fournier[17] and are shown in Fig. 4. Since silica solubility is a direct function of fluid density (Kennedy[18]), the older data on amorphous silica of Hitchen[19] are probably too high. It is interesting to note that while at room temperature, amorphous silica is 20 times as soluble as quartz, at 300°C the difference is only twofold. The solubility C of amorphous silica along the L + V curve can be computed from

$$\log C \text{ (in ppm)} = \frac{-731}{T,\ K} + 4.52 \quad .$$

The solubility in superpressured fluids is given in Fig. 5. An excellent summary of silica solubility is that of Volosov et al.[20]

The effects of added solutes on silica solubility are not clear.* The most direct influence comes from the lowering of a_{H_2O} due to the salts, since precipitation is a dehydration reaction.

$$4(H_4SiO_4)_{aq} \rightarrow (SiO_2)_s + 2H_2O \quad .$$

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*W. L. Marshall (personal communication) found a decrease in amorphous silica solubility in $NaNO_3$ solutions.

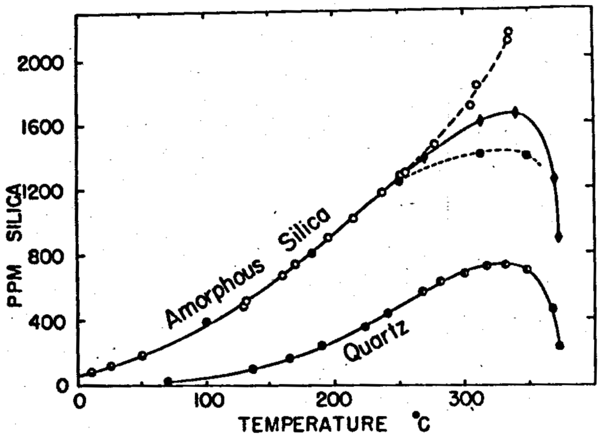
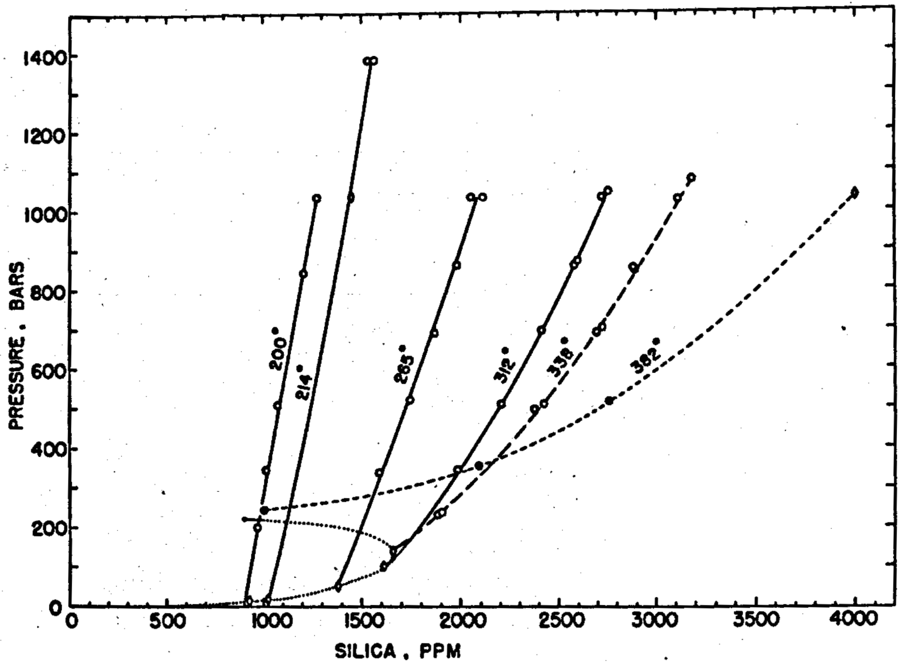


Fig. 4.
Solubility in water of amorphous silica compared to quartz at the vapor pressure of the solution (Ref. 17).

Fig. 5.
The solubility of amorphous silica (colorimetrically reactive silica in solution) at various constant temperatures and variable pressure (Ref. 17).



Barnes[70] has calculated this effect, which is not very large and is shown in Fig. 6. Additional changes may come from complexing in the solution. Evidence is inconclusive, but Anderson and Burnham[21] have found little influence of high concentrations of KCl and NaCl on quartz solubility at higher temperatures.

B. Solubility of Calcite

The solubility of calcite is very strongly dependent upon P_{CO_2} and temperature. At constant P_{CO_2}, the solubility decreases rapidly with T. Solubilities in pure water were given by Ellis[22] and are shown in Fig. 7. Effects of higher fluid pressures and addition of electrolytes are, we think, not known.

C. Sulfate Solubilities

The solubility of anhydrite decreases rapidly with temperature. Values along the L + V curve for pure water are shown in Fig. 8 from Dickson et al.[23]

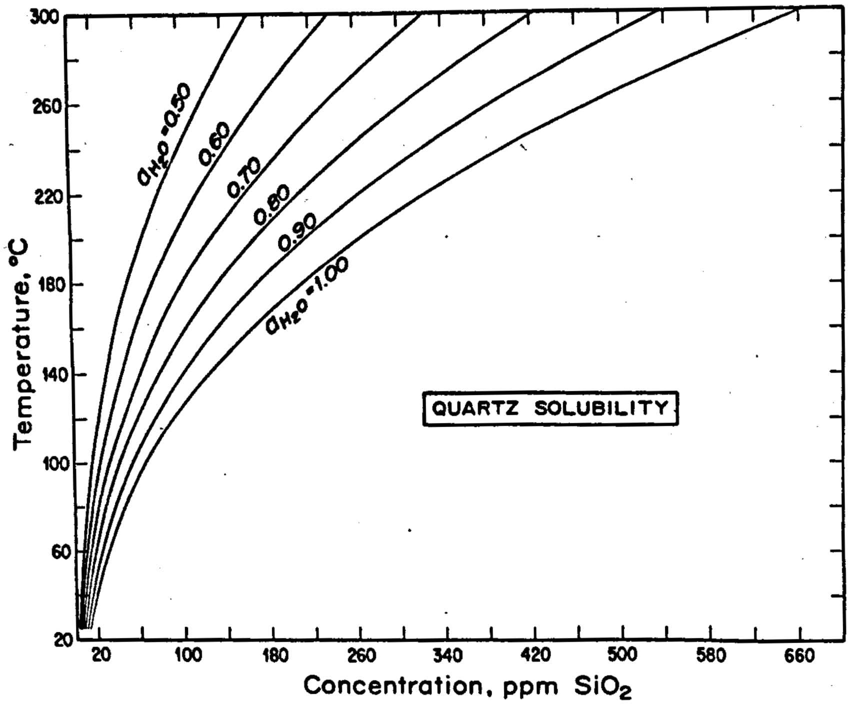


Fig. 6.
Quartz solubility at various temperatures and activities of water (Ref. 70). The activity of water varies with salt concentrations typically as follows:

	Concentrations				
a_{H_2O}	**NaCl**			**CaCl$_2$**	
	m	%		m	%
0.90	2.8	14		1.6	15
0.75	6.2	27	(sat. at 25°C)	---	
0.70	---			3.4	22
0.50	---			5.0	36
0.30	---		(sat. at 25°C)	7.2	44

These values are exact for temperatures near 25°C and approximately correct to 350°C.

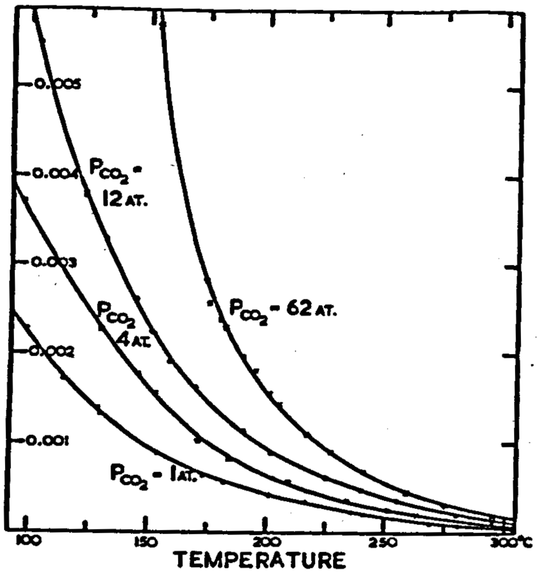


Fig. 7.
The solubility of calcite in water up to 300°C at various partial pressures of carbon dioxide (Ref. 22).

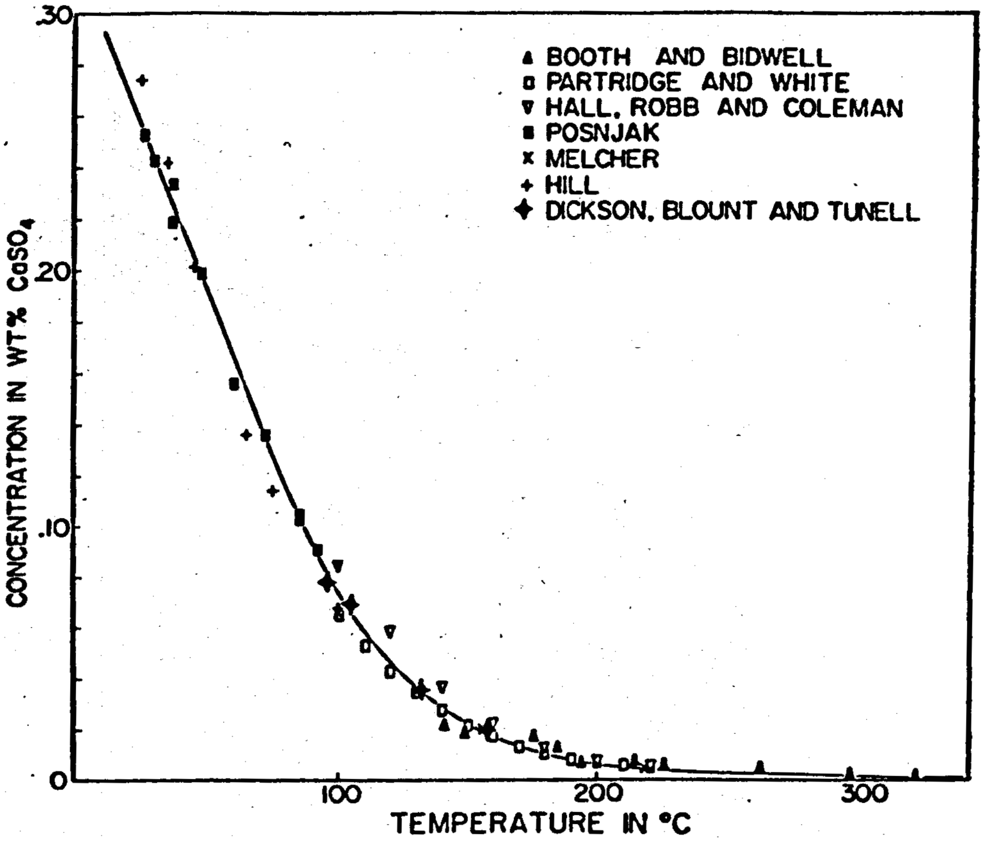


Fig. 8.

Comparison of work on the solubility of anhydrite at 1 atm below 100°C and at the vapor pressure of the system above 100°C (Ref. 23).

The effect of adding NaCl and $CaCl_2$ was determined by Templeton and Rodgers[24] and by Marshall et al.[25] Marshall and Slusher[26] also measured anhydrite solubility in sea water and other brines. Figure 9 shows the effect of NaCl as reported by Templeton and Rodgers.[24]

Barite solubility in water was reported by Strübel[27] along the L + V curve and is reproduced in Fig. 10. The solubility seems to increase to 200°C and then reverse above that temperature. The effect of adding other electrolytes was measured by Templeton[28] and Gundlach et al.,[29] and the data have been analyzed by Malinin et al.[30]*

D. Sulfides

There is a vast literature on the solubility of sulfides. In general, sulfides are quite insoluble in water, but the presence of electrolytes, particularly chloride, enhances the solubilities considerably. Sinclair[32] measured the solubility of copper sulfides in aqueous chloride solutions, and Crerar and Barnes[33] reported values for chalcopyrite and chalcocite. Crerar[34] has measured the solubility of pyrrhotite and pyrite in NaCl solutions in the presence of magnetite (Fig. 11).

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*For more recent data on barite see Ref. 31.

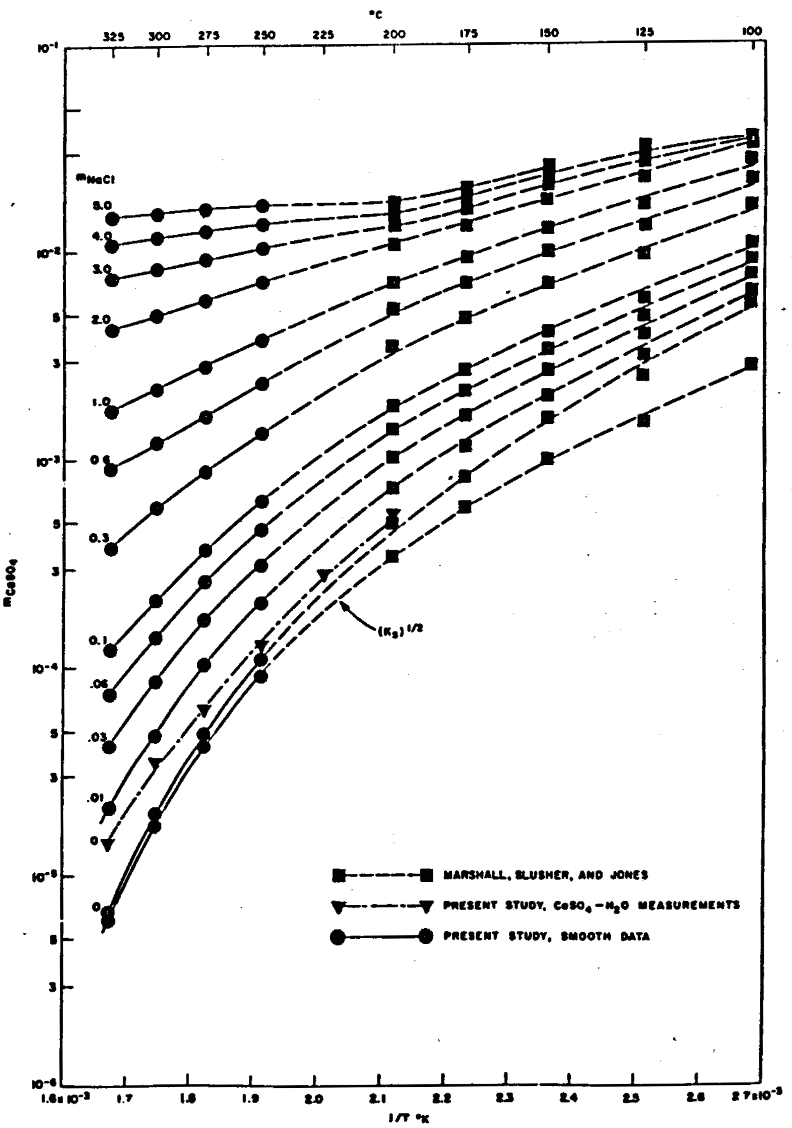

Fig. 9.
Solubility of anhydrite in NaCl-H_2O solutions from 100°C to 325°C (Ref. 24).

E. Data Needed

Solubility data in solutions approximating geothermal fluids are needed for almost all scale phases. Most solubilities refer to water or H_2O-NaCl mixtures. Particularly necessary are data on amorphous silicates, calcite, and sulfides.

IV. SOLUBILITIES CALCULATED FROM THERMODYNAMIC DATA

Ideally, solubility constants can be calculated from changes of the standard Gibbs free-energy changes of the precipitation reactions, such as

$$Ca^{++} + CO_3^{--} \rightarrow CaCO_{3\,(s)} ,$$

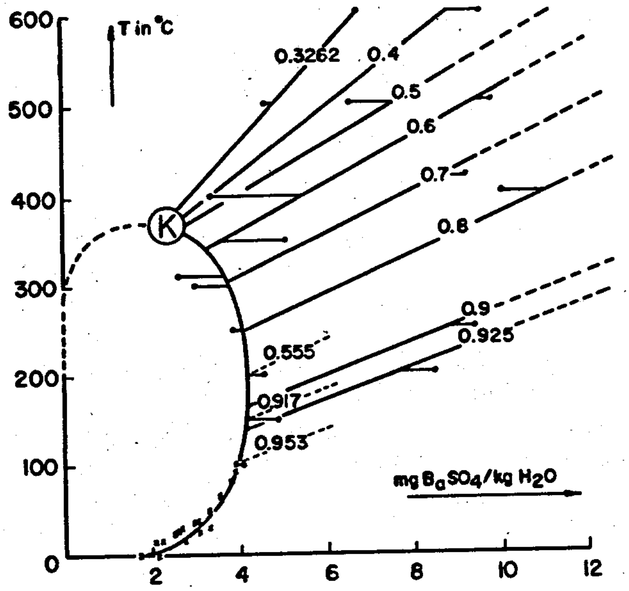

Fig. 10.
Solubility isochores of barite in water and the solubility along the boundary of the three-phase region in the temperature solubility diagram (Ref. 27).

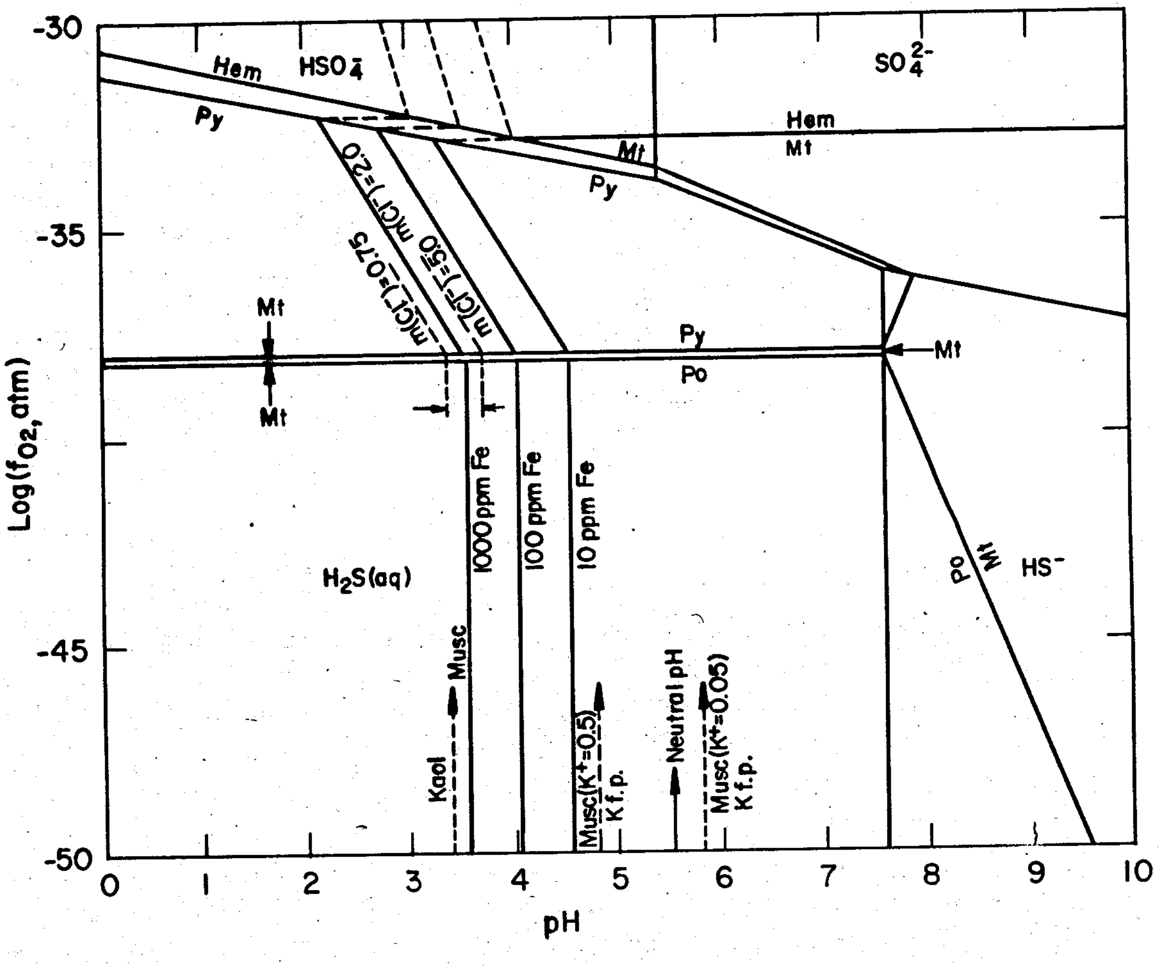

Fig. 11.
Solubility of pyrrhotite and pyrite in NaCl solutions in presence of magnetite (Ref. 34).

using the relation

$$\Delta G^\circ_r = -RT\ln K \quad ,$$

where

$$K = \frac{a_{CaCO_3}}{a_{Ca^{++}} \cdot a_{CO_3^{--}}} \quad .$$

This approach is very flexible because it can take into account variations in P, T, and the compositions of the solids and fluids, provided the necessary information on free energies and activities exists. Of particular concern when working with thermodynamics data is their reliability. Some numbers are very well known, while others have large uncertainties. Because reactions are additive their errors are also, and those can be very large indeed.

A. Mineral Data

It is beyond the scope of this brief report to summarize the mineral data banks available, from the classic works of Robie and Walbaum[35] and Helgeson[36] to the updated, unpublished versions of Robie, Hemingway, and Fisher (in preparation) and of Helgeson, Delany, and Nesbitt (in preparation). The USGS compilations emphasize values established by calorimetry, whereas Helgeson used many other sources of information, as well as extrapolation procedures to fill in the gaps. Because of their direct applicability to geothermal systems, Helgeson's compilations are extensively used in the geothermal literature, but often by people who are unaware of the pitfalls. This has led to some mineralogically ridiculous conclusions.

Of particular importance for scales are the effects of degree of crystallinity and of composition on free energies. It is probably safe to assume that all silica and silicate phases will be essentially amorphous, while carbonates, sulfates, and sulfides will be largely crystalline, although crystal size does have an effect. On the other hand, it will not be safe to use values for amorphous silica in case of the amorphous silicates. For the case of crystalline solid solutions, a vast literature on solution models exists, and compositional effects are known or can be estimated.

B. Solution Data

The thermodynamic properties of electrolyte solutions have been studied as extensively as those of minerals. For our purposes this information is important because it provides the activity coefficients necessary to make the connection between the brine analysis and the solubility constant of the scale in question, through the relation

$$a_i = m_i \gamma_i \quad ,$$

where m_i is the molality of species i in the brine, a_i its activity as it appears in the solubility constant, and γ_i its activity coefficient. The activity coefficients depend on P, T, and composition of the phase, and this dependency must be known. There are many methods for measuring activity coefficients (see for instance Robinson and Stokes[37]). Important studies are those of Silvester and Pitzer,[38] Lindsay and Liu,[39] and Liu[40] (Figs. 12 and 13). The latter study was specifically concerned with thermodynamic properties of simulated geothermal brines.

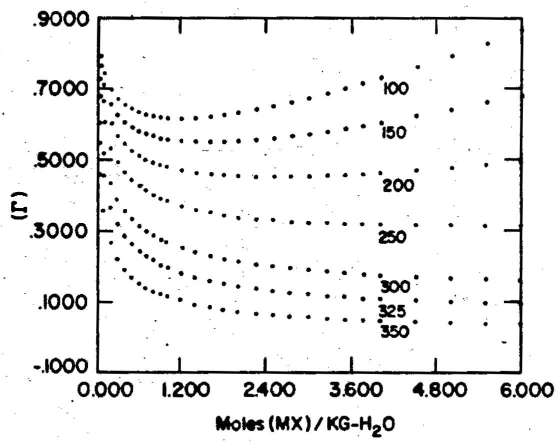

Fig. 12.
Activity coefficient of NaCl (Ref. 38).

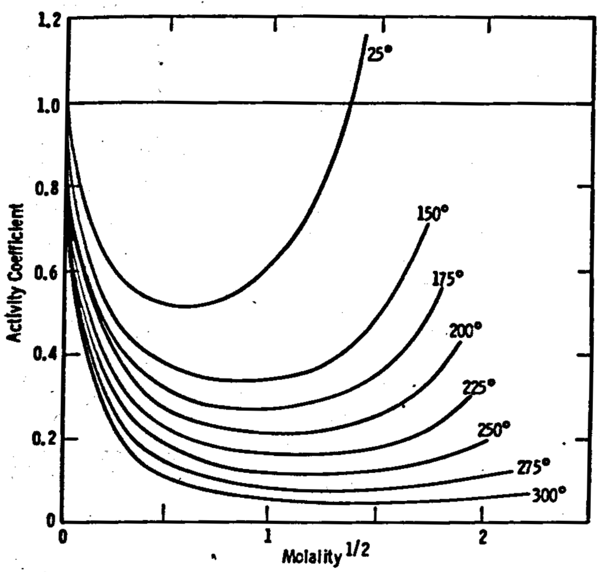

Fig. 13.
Activity coefficients for $MgCl_2$ solutions at high temperatures (Ref. 39).

Activity coefficients can also be calculated, at least in dilute solutions, from the Debye-Hückel relation, particularly in its expanded form.

$$\log \gamma_{\pm i} = - \frac{|Z_+ \; Z_-| A\sqrt{I}}{1 + a^\circ B\sqrt{I}} + \dot{B}_i I \quad .$$

Helgeson and Kirkham[41] have given values for A and B along the L + V curve (their Table 17). a° is an ion-specific parameter and $\dot{B}_i$ is the Scatchard deviation function. The Debye-Hückel relation can be extended still further to calculate solubilities in very concentrated solutions (Wood[42,43]).

Recently, Helgeson and Kirkham[44] have evaluated molal volumes of electrolytes to derive equations of state at infinite dilution. Potter and Brown[45,46] summarized bulk densities of electrolyte solutions as a function of P and T.

C. Calculated Solubility Constants

Helgeson[36] has calculated solubility products of many scale-forming minerals in an aqueous phase up to 300°C (his Table 11). This includes chalcopyrite, galena, sphalerite, chalcocite, pyrrhotite, pyrite, anhydrite, barite, calcite, and dolomite, as shown in Fig. 14. He has also evaluated the effect of a 3 m NaCl solution particularly on sulfide solubilities (Fig. 15).

Any solubility calculation depends on knowing the principal species present in solution. This is best done by a computer program such as WATEQ of Truesdell and Jones.[47] This program has been adapted by Arnorrson[9] to investigate calcite scales in Iceland.

More ambitious programs also consider the changes in the fluid as minerals precipitate and dissolve. This is achieved by solving simultaneously mass action and mass balance constraints. The prototype is Helgeson's PATHCALC program,[48] and various adaptations for scaling problems have been discussed by Shannon et al.,[49] and Jackson et al.[50]

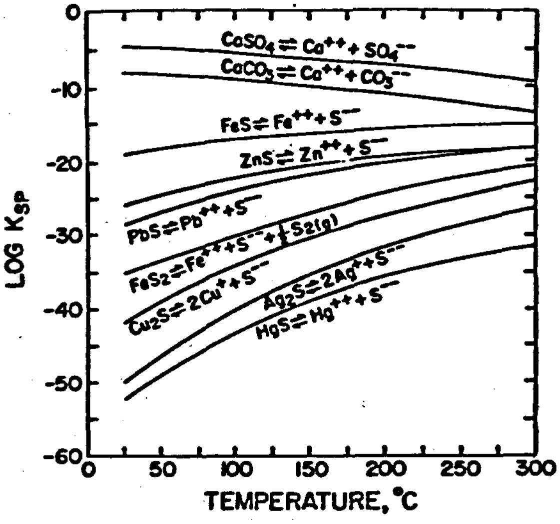

Fig. 14.
Activity product constants for anhydrite, calcite, and various sulfides (Ref. 36).

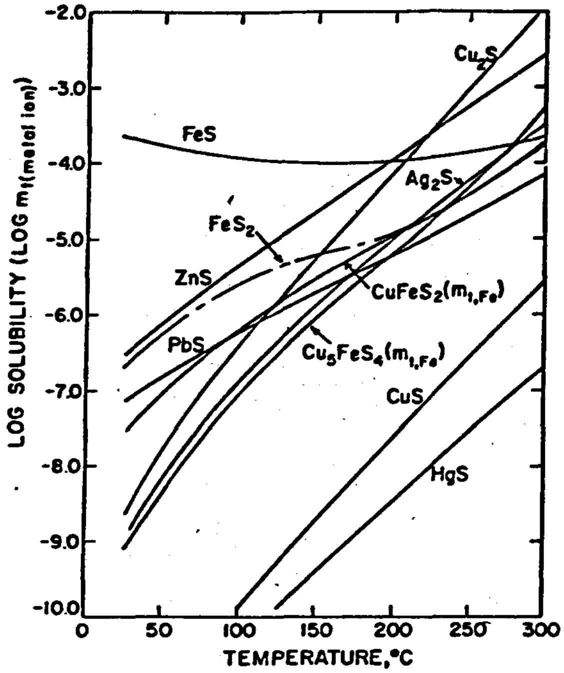

Fig. 15.
Calculated stoichiometric solubilities (in terms of the total molality of the metal ion) of various individual sulfides in a 3 molal sodium chloride solution with a pH of 5 (Ref. 36).

D. Need for New Information

Thermodynamic data on minerals and electrolytes need to be continuously updated and expanded. This is a major and absolutely essential effort because no calculations and predictions are meaningful without a reliable data bank. There are many glaring holes and untested assumptions. Most obvious is the absence of data on amorphous silicates, but such data cannot be collected until scales are better characterized. Next, we need to test by direct measurements the relevant solubility constants listed in Helgeson,[36] both in pure water and in electrolyte solutions. A better knowledge of activity coefficients for scale-forming ions is essential for using those solubility constants. This applies particularly to Ca, Ba, Fe, and some of the other cations, as well as $SO_4^=$, HCO_3^-, and $CO_3^=$.

V. EXAMPLES OF SOLUBILITY TESTS

A. Silica Saturation

It is normally assumed that the geothermal fluid of the reservoir is in chemical equilibrium with the minerals with which it is in contact. This assumption is supported by surprisingly reliable estimates of reservoir temperatures based on the SiO_2 and Na-K-Ca thermometers (Fournier and Rowe,[51] Arnorsson,[52] Fournier and Truesdell,[53] and Fournier,[54,55]). As an example, the Cerro Prieto estimate by Fournier[55] is shown in Fig. 16. Arnorsson[52] has shown that best fits

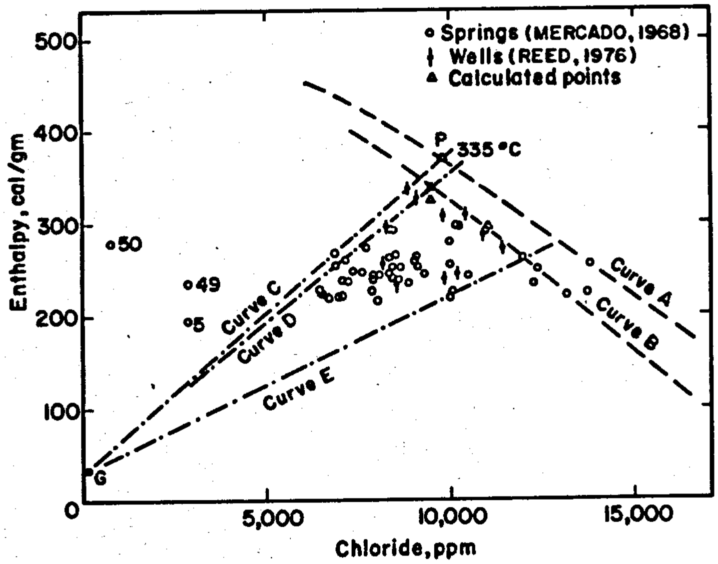

Fig. 16.
Enthalpy-chloride graph of data from wells at Cerro Prieto, Mexico (Ref. 55).

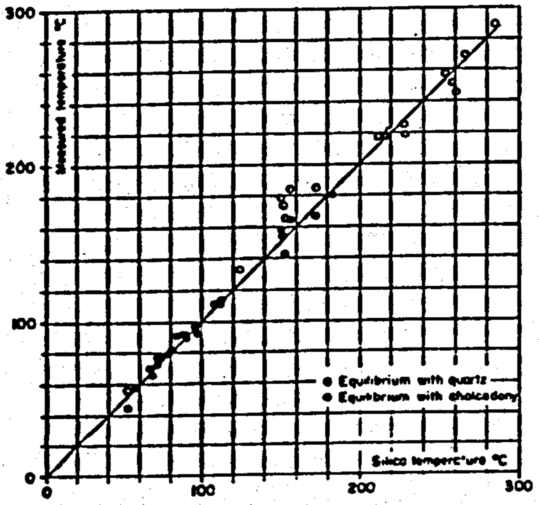

Fig. 17.
Comparison between measured temperatures and silica temperatures in deep drillholes (Ref. 52).

are obtained if it is assumed that reservoir brines are equilibrated with chalcedony below 100°C and quartz above 180°C (Fig. 17).

B. Calcite Saturation

A detailed check with respect to calcite scaling has been carried out by Arnorsson.[9] Using a computer program, the effects of adiabatic flashing were evaluated in steps of 20°C for eight Icelandic wells with aquifer temperatures of 127-290°C and total CO_2 contents of 50-2000 ppm. Upon flashing, very rapid loss of CO_2 occurs, especially initially (Fig. 18), and by the time the waters have reached 100°C, 60-99% of the carbonate is lost. This causes a pH increase of 1-2 units

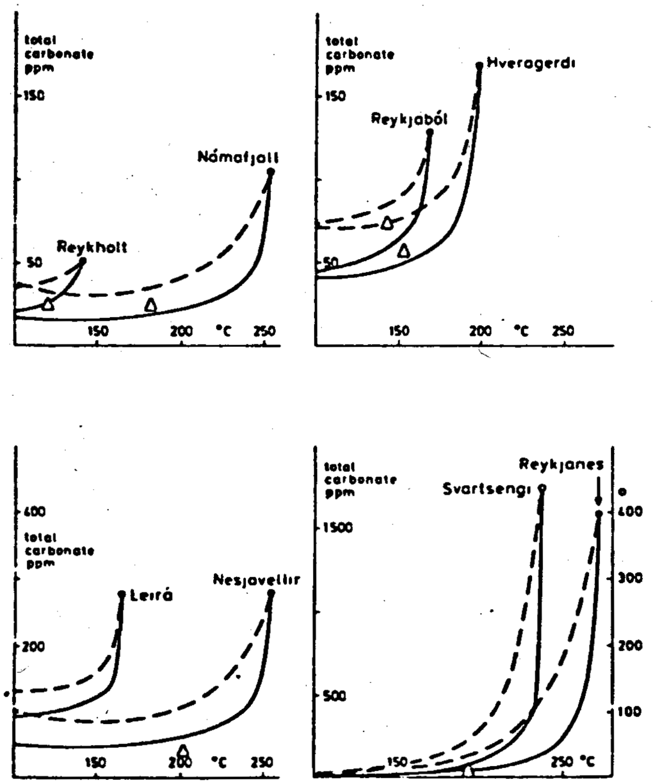

Fig. 18.
The variation in the total carbonate of the geothermal water during one-step adiabatic flashing. The solid lines assume maximum, i.e., equilibrium degassing. The dashed lines assume 1/5 of maximum degassing. The triangles correspond to the analyzed total carbonate in the water sample of the discharge, which was collected at the respective temperatures (Ref. 9).

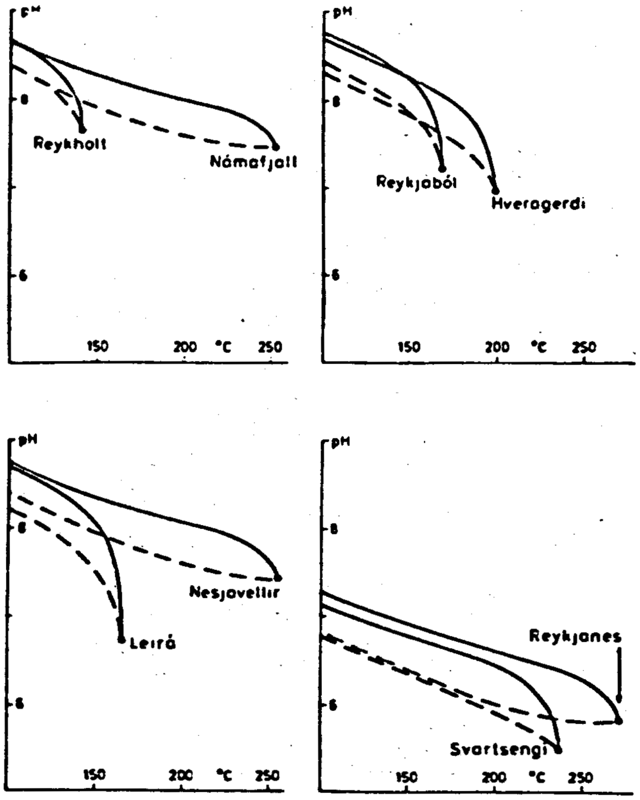

Fig. 19.
The variation in the pH of the geothermal water during one-step adiabatic flashing. The solid lines assume maximum degassing, but the dashed lines 1/5 of maximum degassing (Ref. 9).

(Fig. 19). The activity of Ca ions increases partly because of steam loss and partly because of decreased complexing at low temperatures (Fig. 20), and CO_3^{--} activity also increases because of pH (Fig. 21). Most waters are near calcite saturation in the reservoir, or somewhat supersaturated, but upon flashing, all immediately become highly supersaturated. Those initially low in total carbonate may actually become undersaturated at lower temperatures (Fig. 22). Arnorsson concluded that calcite scaling is important only in wells and when flashing is substantial. This can be controlled. Correlation of the calculations with actual scaling experience is not straightforward. All calculations used the solubility constants of Helgeson.[86]

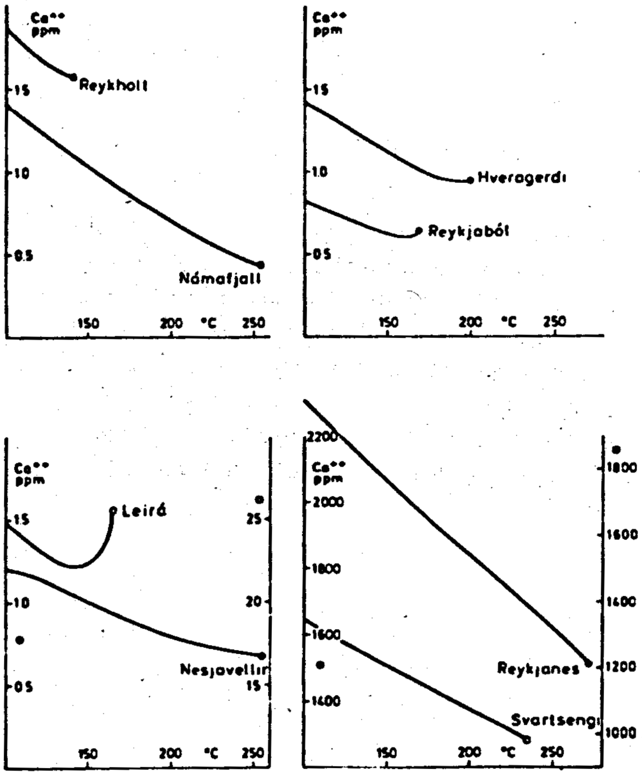

Fig. 20.
The variation in the concentration of free Ca++ ions in the geothermal water during one-step adiabatic flashing. Maximum degassing is assumed (Ref. 9).

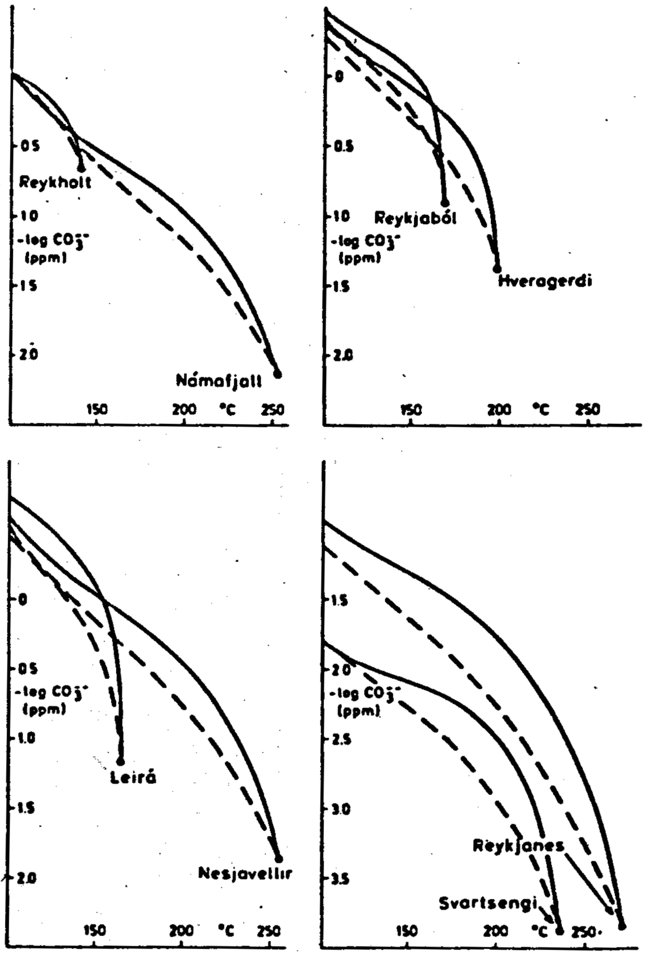

Fig. 21.
The variation in the CO_3^{--} content of the geothermal water during one-step adiabatic flashing. The solid lines assume maximum degassing, but the dashed lines 1/5 of maximum degassing (Ref. 9).

C. Saturation with Soluble Salts

Scaling with soluble salts is not important except in steam carry-over. However, a method was developed recently to calculate solubilities in very concentrated solutions that could have application to the more common scales as well. This method (Wood[42]) is based on adding a Harned coefficient term to the extended form of the Debye-Hückel expression

$$\log \gamma_{\pm i} = - \frac{|Z_+ Z_-| A\sqrt{I}}{1 + a^\circ B\sqrt{I}} + 2\,\frac{\nu_+ \nu_-}{\nu}\left(B_i^\bullet + \sum_1^n \alpha_{ij} y_j\right) I \quad (j \neq i) \quad ,$$

where α_{ij} is the Harned coefficient of salt j of ionic strength fraction y, j being added to salt i.

These parameters are empirical mixing parameters that can be obtained from isopiestic measurements or from solubility data. They are salt specific and independent of concentration.

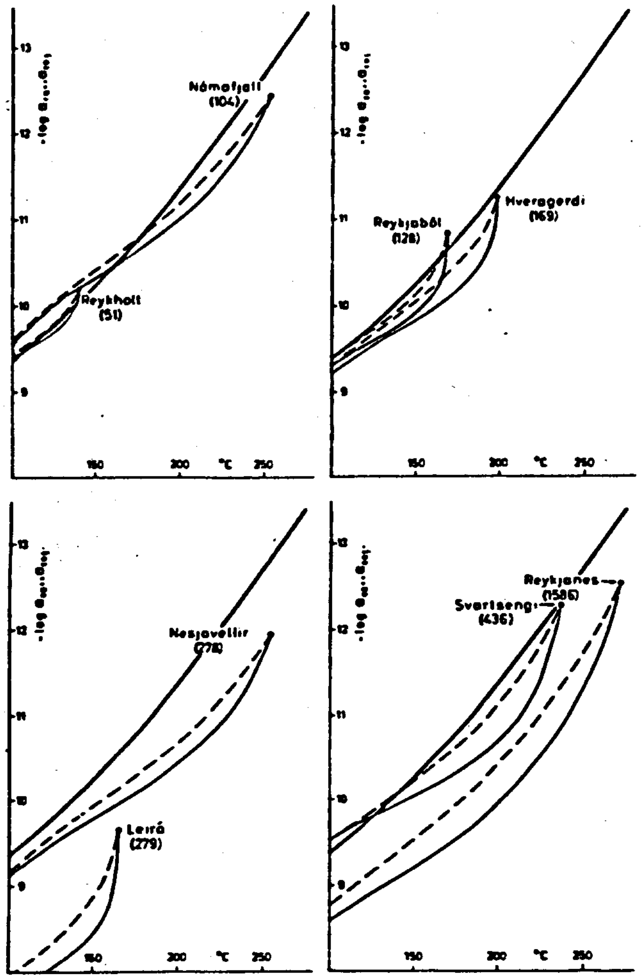

Fig. 22.
The computer activity product of Ca^{++} and CO_3^{--} in the geothermal water during one-step adiabatic flashing in relation to the calcite solubility curve (thick solid line). The solid lines assume maximum degassing, but the dashed lines 1/5 of maximum degassing. The figures in the brackets indicate total carbonate in the reservoir water calculated in ppm as CO_2 (Ref. 9).

and hence can be extrapolated to saturation. Figure 23 shows the effect of ionic strength on B, and Figs. 24-26 give various applications to solubilities calculated at 25°C.

This approach has been extended to 200°C for the system NaCl-KCl-HCl (Wood[43]). The temperature sensitive parameters are A, B, a°, B', and α_{ij}. Helgeson and Kirkham[41] have given A and B. Osmotic coefficients and isopiestic measurements give values for a° and B'. Next, solubility constants are calculated and compared with measured solubilities to obtain α_{ij} values. For mixtures, Zdanovskii's rule can be used, which states that if two salt solutions with the same a_{H_2O} values are mixed, a_{H_2O} does not change. Because of greater association at higher temperatures, Harned coefficients tend toward zero (Fig. 27). Results of calculations in mixed electrolytes agree very well with measurements (Fig. 28). At the present time, calculations cannot be extended beyond 200°C for lack of KCl activity coefficient data.

VI. KINETICS OF SCALE PRECIPITATION

Because of its industrial importance, the process of precipitate formation has received a great deal of attention in recent years. The thrust of this research has been toward the control and understanding of crystal production under carefully controlled conditions. There has been relatively little research on precipitation in natural environments of direct interest to geothermal

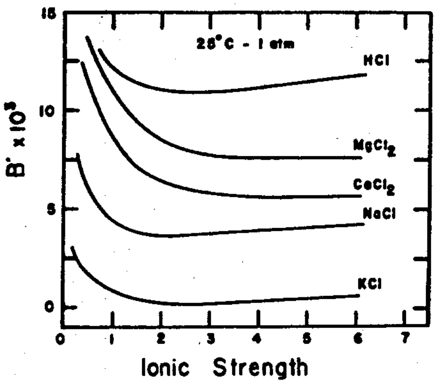

Fig. 23.
Variation of B' with stoichiometric ionic strength for some alkali and alkaline earth chlorides (Ref. 42).

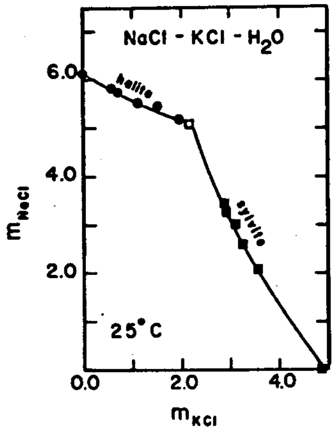

Fig. 24.
Phase diagram of the NaCl-KCl-H_2O system at 25°C. Full circles calculated (Ref. 42).

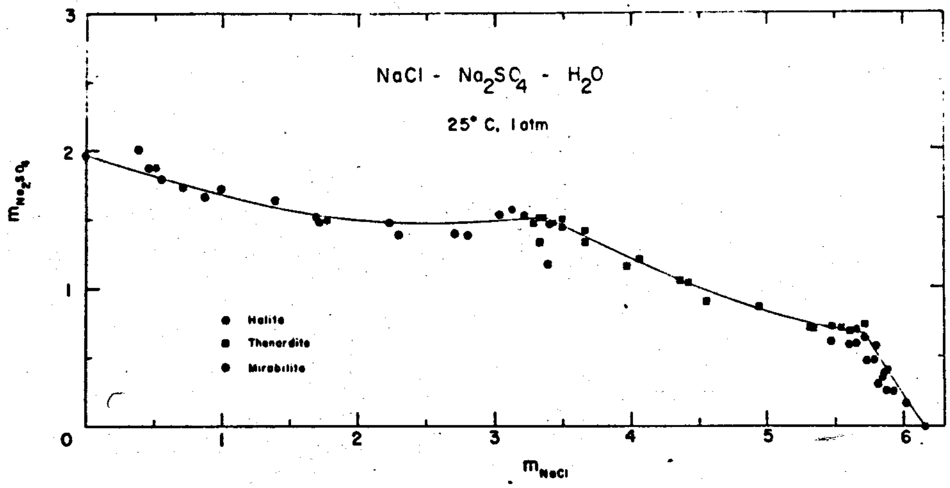

Fig. 25.
Phase diagram of NaCl-Na_2 SO_4-H_2O system at 25°C. Full circles calculated (Ref. 42).

chemistry. In this survey we will first briefly review the very limited data on silica directly relevant to geothermal fluids. Although little is known about scaling reactions, there is considerable literature on the process of crystallization of various inorganic electrolytes, and we will discuss those parts of that literature that appear to be relevant to the understanding of scale formation. We will conclude by suggesting research areas where we feel particular emphasis is needed.

We have found very few precipitation studies of geothermal systems other than the equilibrium calculations of supersaturation of Arnorsson[9] already discussed. All the work deals with precipitation of silica under conditions somewhat different from those expected in geothermal wells. The direct application of these measurements is therefore speculative. As is implied in the

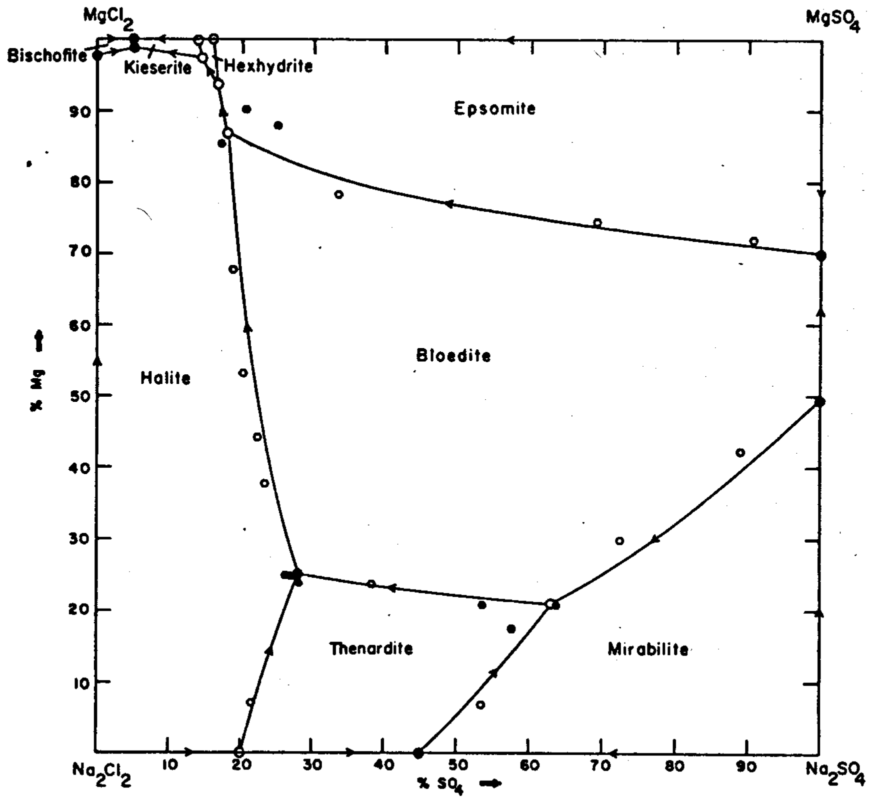

Fig. 26.
Janecke diagram of NaCl-$MgSO_4$-H_2O reciprocal system at 25°C. Full circles represent invariant points, open circles, reaction points. Arrows show direction of changing solution composition during evaporation (Ref. 43).

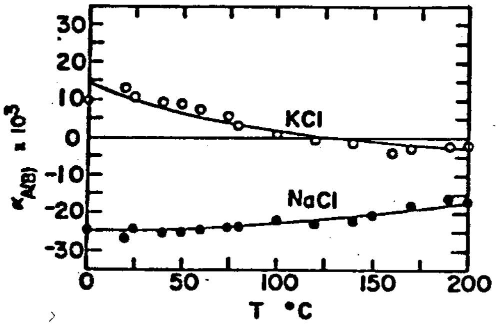

Fig. 27.
Temperature variation of Harned coefficients for NaCl and KCl in aqueous mixtures (Ref. 43).

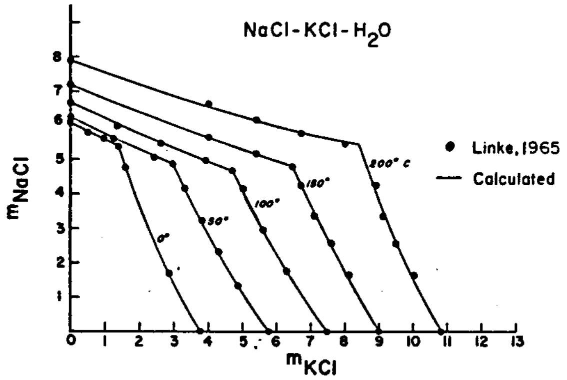

Fig. 28.
Solubility diagram for NaCl-KCl-H_2O system from 0 to 200°C (Ref. 43).

solubility data (Fournier[17]), metastable amorphous silica precipitates from highly concentrated solution (~400 ppm), while the stable form, quartz, precipitates directly only from lower concentrations (~150 ppm). The amorphous silica precipitation data of Harvey et al.[16] are given in Figs. 29 and 30. In these experiments supersaturated solutions were prepared and the subsequent precipitation measured. The effect of changing salinity and pH was investigated. As shown in Fig. 30, there is a breeding time from 15 to 90 min before precipitation occurs.

Care was taken to avoid contamination by foreign ions. The authors feel that the data are consistent with the homogeneous nucleation theories of Volmer, Becker, and Doering (Nielsen[56]). However, there is no direct evidence that this is the case. It would be unusual for this mechanism to be controlling at such low supersaturations (Nielson[56]). No effort was made to extract kinetic information.

Figure 31 shows data of Downs, Rimstidt, and Barnes.[15] These data were taken at substantially lower initial salinations (~100 ppm) and the equilibrium values are consistent with those of quartz. The data are plotted in terms of the variables t and $\ell n\ [\ (S_t + 1)/S_o + 1)]$, where S_t is the supersaturation $[H_4SiO_4]_t/[H_4SiO_4\ ]_{eq}$ at time t. The authors have made an effort to describe the data in terms of a first-order reaction rate scheme which leads to the rate equation

$$\frac{\partial [H_4SiO_4]}{\partial t} = \frac{A}{V}\ [k_+ a_{SiO_2}\ a^2_{H_2O} - k_- a_{H_4SiO_4}] \ ,$$

which has the solution

$$t = -\frac{V}{A}\ \frac{1}{k_-}\ \ell n \left(\frac{S_t - 1}{S_o - 1}\right) .$$

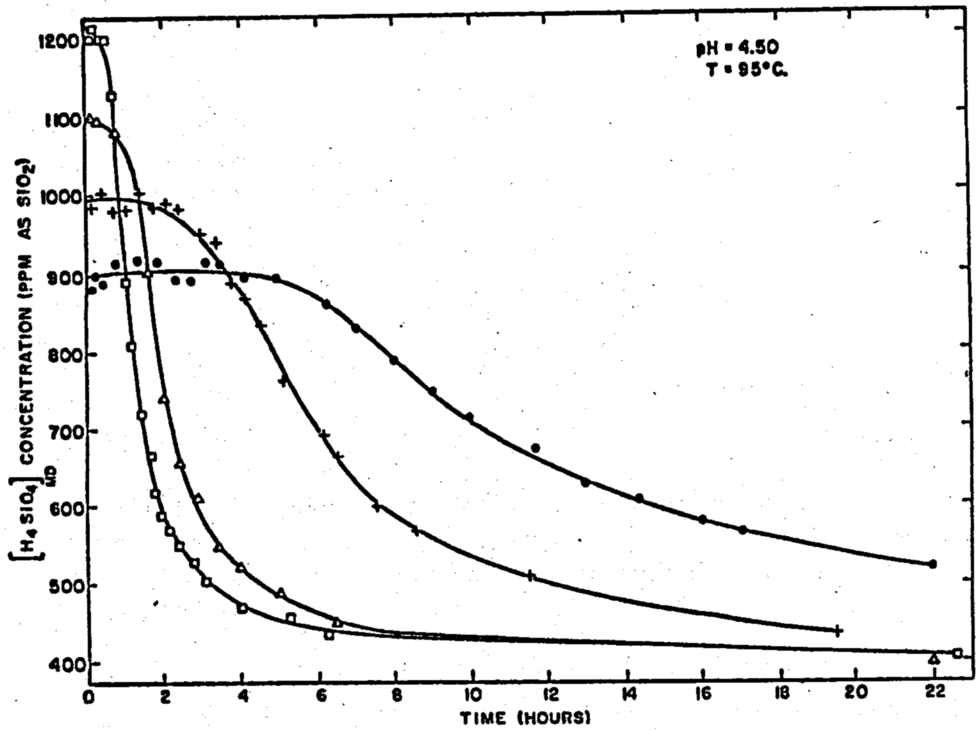

Fig. 29.
Silica condensation as a function of time for a series of initial silicic acid concentrations (Ref. 16).

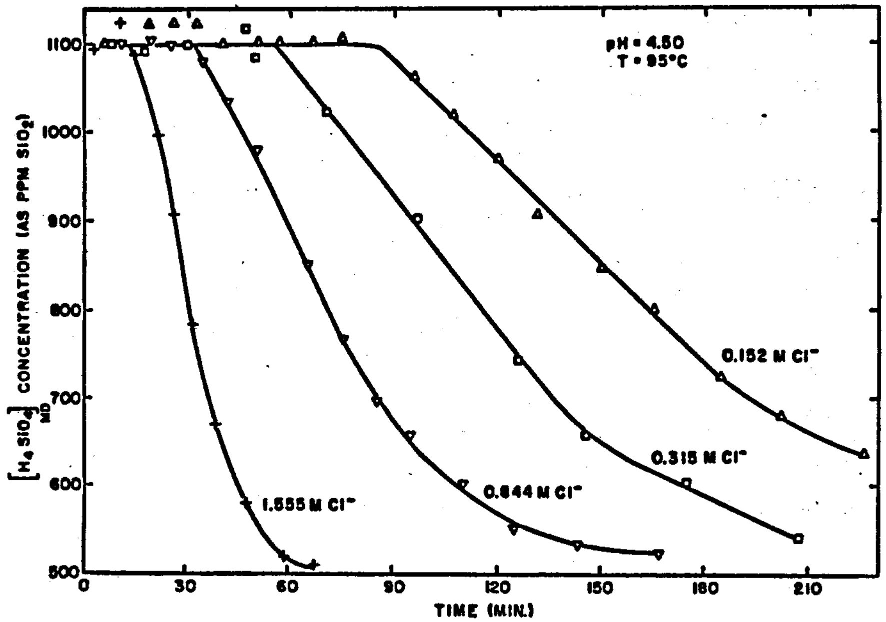

Fig. 30.
Silica condensation from a solution of 1100 ppm (as SiO_2) as a function of time at various salinities (Ref. 16).

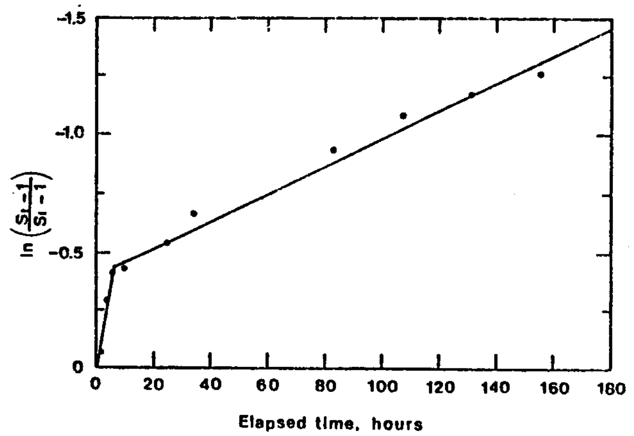

Fig. 31.
The change in the degree of saturation of silica at 105°C with respect to time. Deposition of silica in air-saturated, distilled water (Ref. 15).

If the assumptions are correct, the data should fall on a straight line. The agreement with the data is not very satisfactory. We have no explanation other than the questionable assumption of first-order kinetics. Precipitating systems often do not satisfy first-order rate equations.[57]

Quartz precipitation kinetics has also been studied by Van Lier et al.,[10] and their results are plotted in Fig. 32. Apps,[13] using essentially the same kind of kinetics, has achieved a more successful fit. To compare the work of Downs et al.[15] with that of Apps,[13] we have plotted both sets of data on Fig. 33. The two sets do not agree. Aside from the small differences in temperature we have no explanation for the difference. Figure 34 is an Arrhenius plot of literature data collected by Apps.[13] From this we can obtain an activation energy of approximately 11 kcal/mol. This is to be contrasted to the activation energy found by Barnes et al.[3] of 22 kcal/mol (Fig. 35). There is not sufficient experimental information to locate the problem.

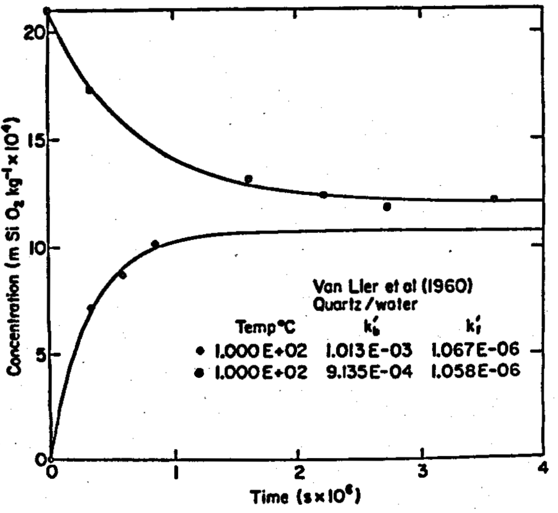

Fig. 32.
The dissolution and precipitation of quartz in water at 100°C (Ref. 13).

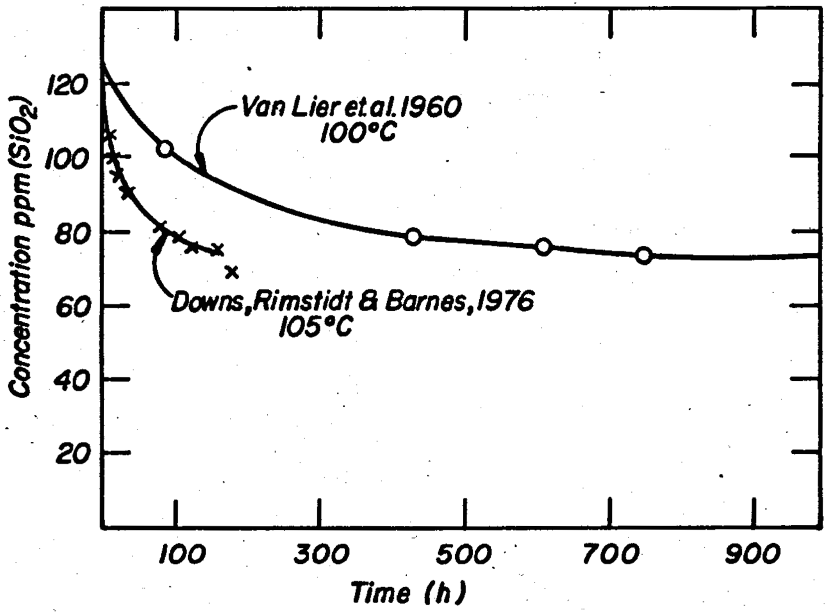

Fig. 33.
The precipitation kinetics of quartz.

We have not found any data on other scale mineral precipitations. There are data on calcite dissolution and precipitation under conditions quite different from geothermal systems. For example, Lund et al.[58] studied the solution kinetics of calcite in HCl solutions at room temperature. Berner and Morse[59] have made similar studies in less acid environments but still at relatively low temperatures.

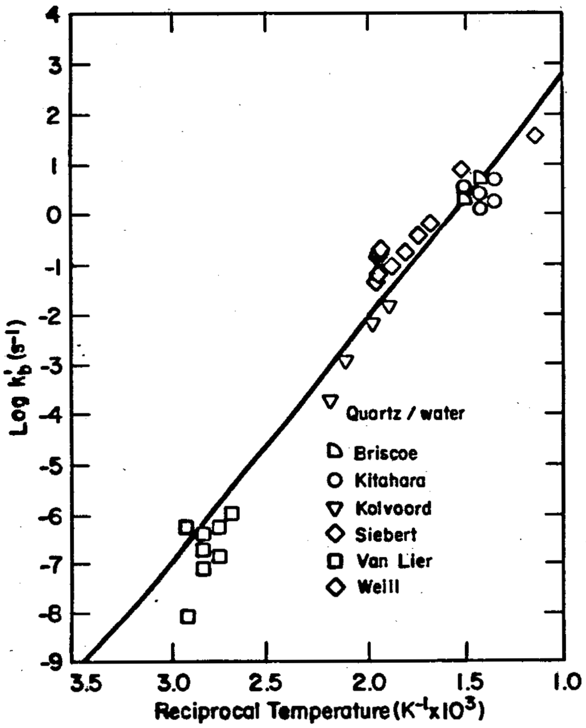

Fig. 34.
The specific back rate constant, k_b', for the dissolution of quartz in water plotted against the reciprocal of the absolute temperature. Values of k_b' are calculated from literature data (Ref. 13).

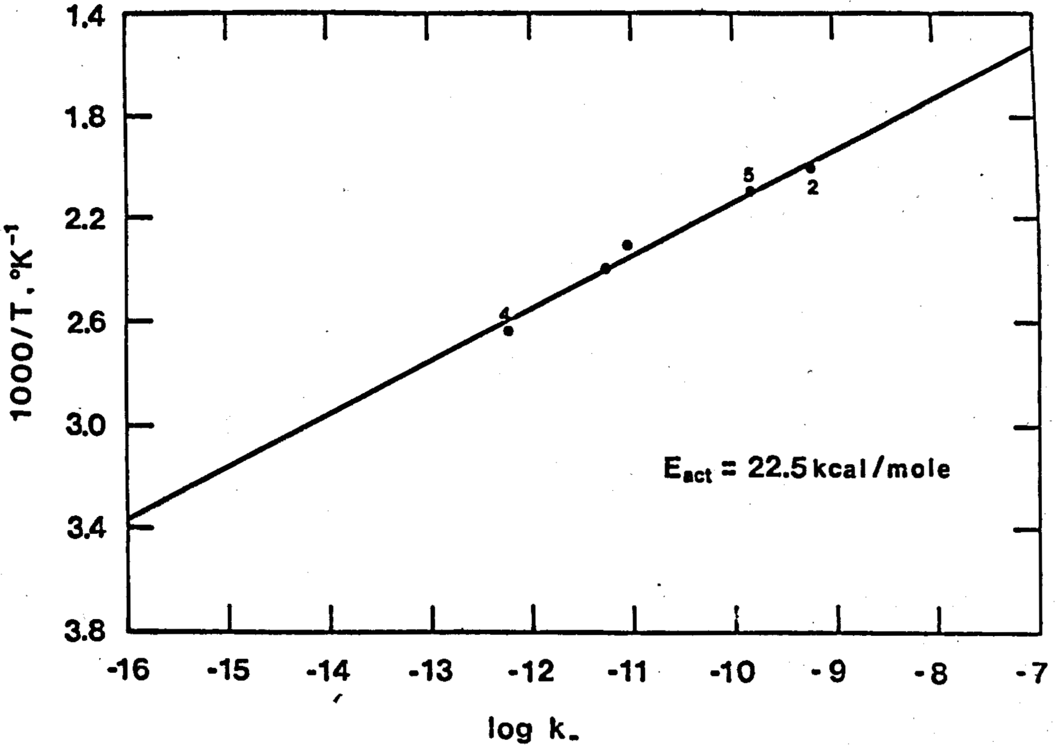

Fig. 35.
Arrhenius plot of k_- for the quartz-water reaction (Ref. 3).

VII. PRECIPITATION KINETICS

Next we discuss some of the general features of the nucleation process and briefly refer to experimental data that illustrate these results. It is convenient to divide crystallization phenomena into three processes:

(a) supersaturation,
(b) nucleation, and
(c) crystal growth.

In a natural environment these three complicated processes are proceeding simultaneously. A great deal of effort has been devoted to separating the processes experimentally, although they may strongly affect one another in a real environment.

A. Supersaturation

Basically this is a measure of the distance of the system from equilibrium. Obviously a system must reach supersaturation, S, before precipitation sets in. For a single component system, the most popular definition is $S = c/c^*$, where c^* is the equilibrium concentration and c the concentration in the fluid. Others have suggested that a more accurate estimate of departure from equilibrium would be given by the ratio of activities as in irreversible thermodynamics. For inorganic salts, where the precipitation reaction is of the form $C^+_{(aq)} + A^-_{(aq)} \rightarrow CA_{(s)}$, the supersaturation may be associated with the nonequilibrium solubility product. For example, Nielsen[56] chooses $\sqrt{a_{C+}a_{A-}/K_{eq}}$ as a measure of the supersaturation. For the Icelandic geothermal systems, Arnorsson[9] calculates this ratio to be ~3. In principle, one can calculate the supersaturation from equilibrium extrapolations as in Arnorsson.[9] However, geothermal fluids may initiate precipitation at lower supersaturation levels. Since supersaturation is a requirement for precipitation, such calculations are useful for prediction of when supersaturation will occur. It seems better, however, to rely on experimental data such as those of Downs et al.[15] and van Lier et al.[10] to determine supersaturation.

Degree of supersaturation is a way to classify what is likely to happen in a system. We can use the diagram of Mullin[57] to illustrate the situation (Fig. 36). In the stable region no nucleation occurs, while in the metastable region crystallization is possible but not without introducing an impurity. In the labile region, the high supersaturation region, spontaneous nucleation is possible. It is unlikely that geothermal systems are ever in the labile region.

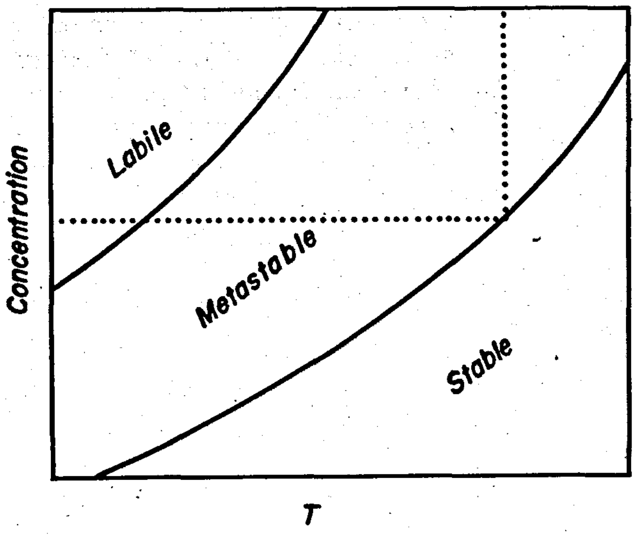

Fig. 36.
Regions of stability for solutions.

B. Nucleation

The phenomenon of nucleation, or the formation of stably growing crystals, is probably the most difficult to understand theoretically. It is convenient to divide this process into three categories:

(a) homogeneous or spontaneous nucleation,
(b) secondary nucleation, and
(c) heterogeneous nucleation.

The only commonly accepted theory of nucleation refers to homogeneous nucleation. This theory, developed 50 years ago, is known as the Volmer-Becker-Doering theory, and has been updated by many authors. While this approach is conceptually useful, there is little evidence that nucleation processes ever satisfy this theory except at extraordinarily high supersaturations. This is shown in the $BaSO_4$ data of Nielsen[60] given in Fig. 37. The interesting part of this figure is the uppermost graph, which shows that the number of nuclei that form in the precipitation is not a function of concentration until rather high supersaturations are reached ($\ell nS > 3$). Nielsen[56] did some calculations to show that at these high supersaturations the kinetics did in fact satisfy the homogeneous nucleation theory. Note that for low supersaturation there is an incubation time as in the silica data of Harvey et al.[16] We emphasize that without some morphological data it is difficult to assess the agreement with classical theory.

Both secondary and heterogeneous nucleation rely on crystal growth on existing particles suspended in the solution. The term heterogeneous nucleation is reserved for growth on particles already existing in the solution, whereas secondary nucleation relies on particles formed by some mechanical process from already existing growing crystals. This may be responsible for the effect noted by Barnes et al.,[3] where considerable precipitation in liquid saturated around 300°C occurred when it reached a temperature of ~280°C. This corresponds to a supersaturation of 1.4, and a

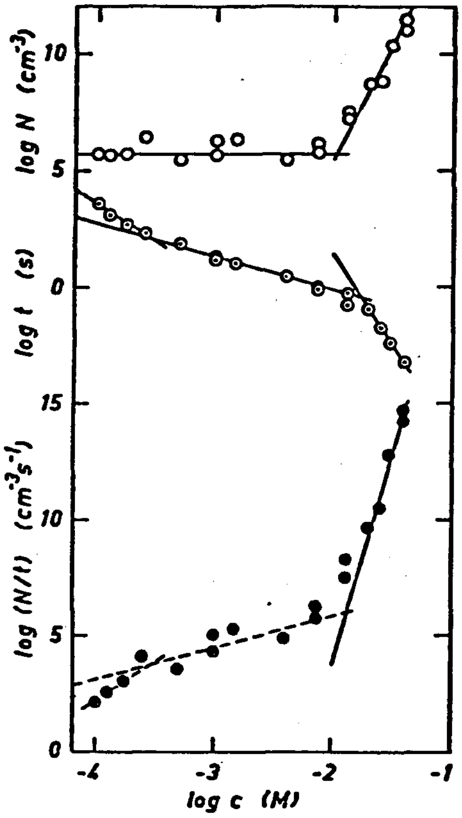

Fig. 37.
Kinetics of $BaSO_4$ precipitation. The following quantities are shown as functions of the initial concentration c of $BaSO_4$. From above: 1, number concentration of crystals formed; 2, induction period; 3, quotient of the former two. For c 0.01 M (log c > -2) this is assumed to equal the rate of homogeneous nucleation (Ref. 60).

secondary nucleation process is probably responsible for this result. At low supersaturation growth seems to be controlled by a form of secondary nucleation termed contact nucleation, which results from crystal breakage by contact with other crystals or container walls. This is illustrated in Fig. 38 (Clontz and McCabe[61]). In strongly agitated geothermal systems, secondary growth mechanisms are likely candidates for growth, since growing crystals are likely to be present in geothermal fluids.

There is strong evidence that additions of foreign ions affect growth rates. For example, in the data of Harvey et al.[16] there is a correlation between higher chloride ion concentrations, faster precipitation and shorter incubation periods (Fig. 30). This was explained in terms of increased supersaturation caused by increasing ionic strength. Similar results were found for KNO_3 by Shor and Larson[62] (Fig. 39). However, these authors also noted that the nucleation rate also decreases with the additions of Cr^{+++}.

For pure systems the experimental results for rate laws from a number of systems have been summarized schematically in Fig. 40 (Randolph[63]). B° is the nucleation rate and $G = dL/dt$ (L = radius of crystal) is the growth rate, assumed to be a measure of supersaturation. We see that in regions of low supersaturation the log of the nucleation rate is linearly related to the log of the supersaturation. At very high supersaturations nucleation is a much stronger function of supersaturation. An example of this behavior was given in the $BaSO_4$ data of Nielsen.[56]

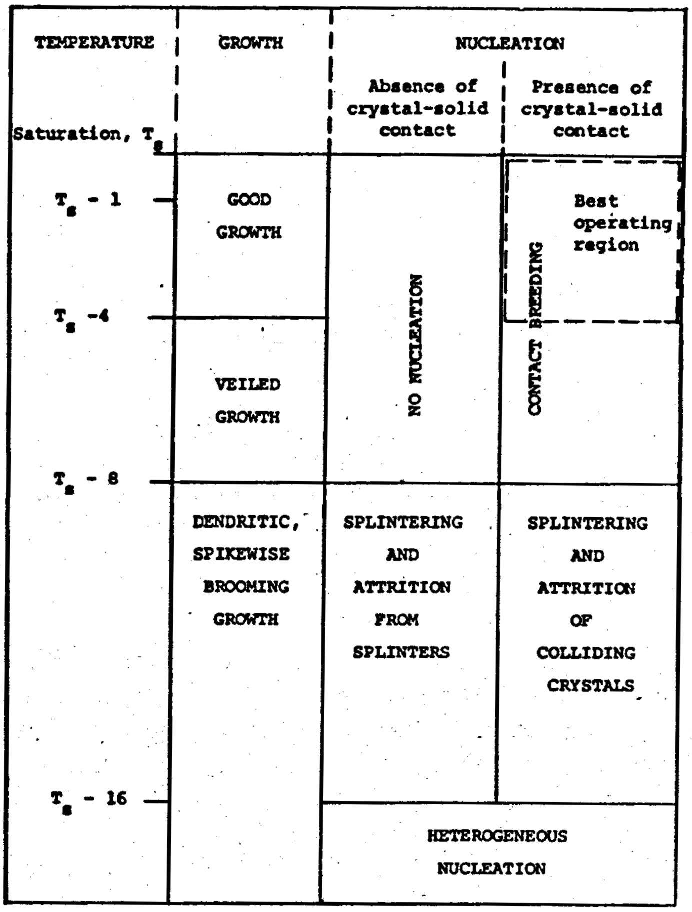

Fig. 38.

Effect of supersaturation on crystal growth quality and type of nucleation for magnesium sulfate heptahydrate (Ref. 61).

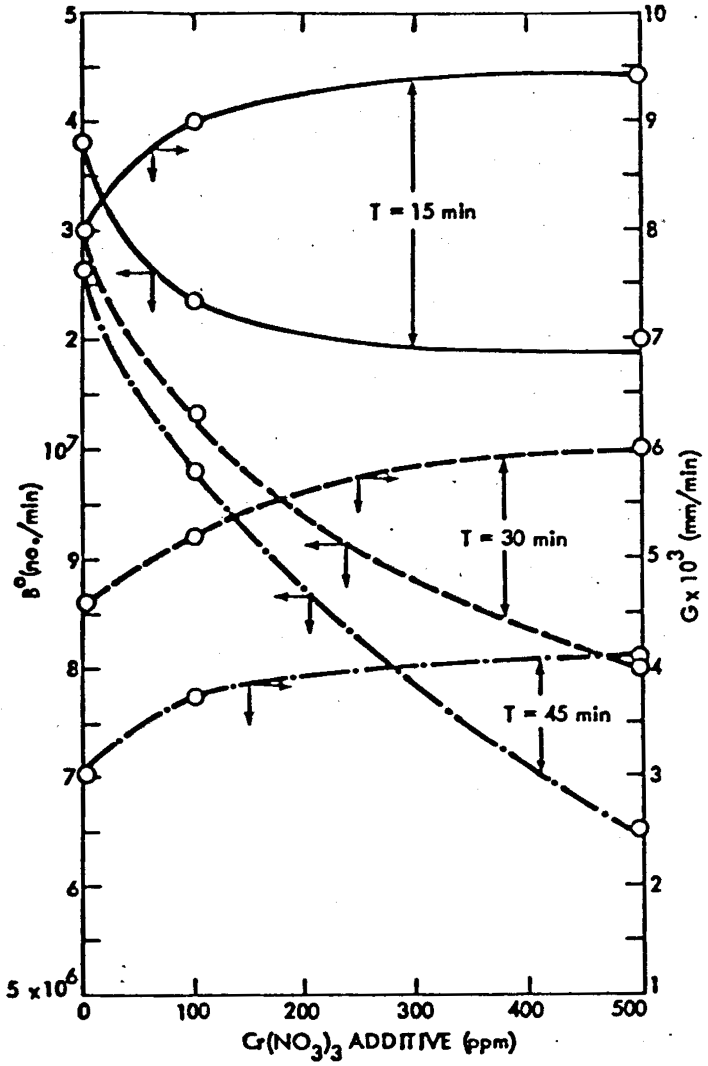

Fig. 39.
Effect of $Cr(NO_3)_3$ on nucleation and growth rates (Ref. 62).

C. Crystal Growth

The third area to consider in precipitation kinetics is growth rate. For the systems we are concerned with, two processes are usually considered to control growth rate: crystal surface reactions and supply of material to the reacting surface. For different system parameters, these effects may have widely differing behavior. But there is considerable evidence that each may play an important role.

In static systems where convective effects in the fluid are negligible, the supply of material to the surface is controlled by the mass transport equation $\partial_\rho/\partial t = \nabla \cdot J$, where the flux is written as $\vec{J}_i = \Sigma L_{ij} \cdot \vec{\nabla}\mu_j + \vec{v}\rho_i$. In the simplest case this reduces to the ordinary diffusion equation

$$\frac{\partial \rho}{\partial t} = D\nabla^2 \rho \quad .$$

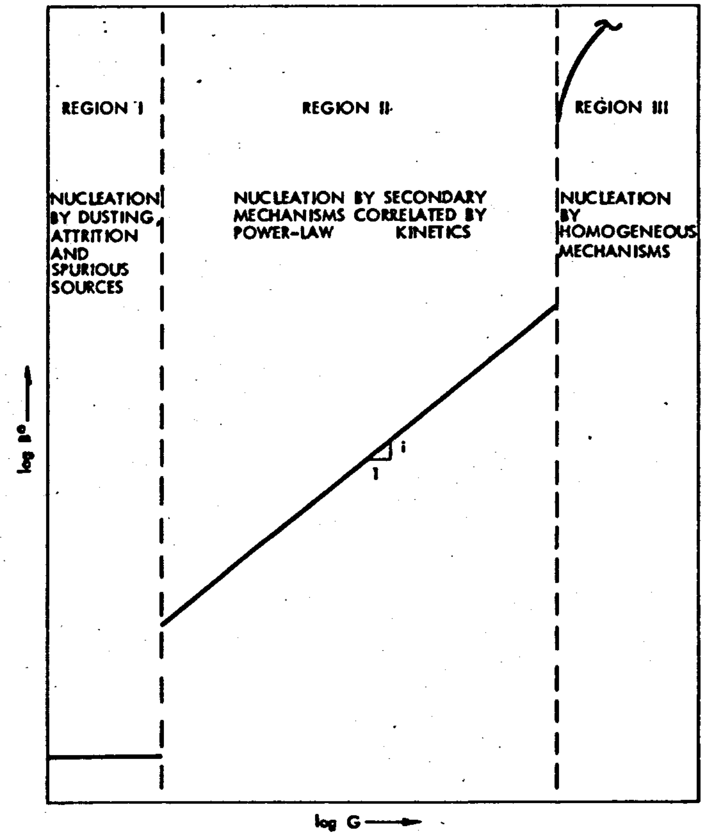

Fig. 40.
Hypothetical nucleation; growth rate plot (Ref. 63).

This system may be schematically represented (Fig. 41). The concentration gradients caused by diffusion present a problem for the experimentalist because it is difficult to measure the concentration at the surface. This is the concentration that should be used in a rate law. There is a further problem, however, in that in the data diffusion control may be difficult to separate from surface rate control. Consider the following simplified equations assuming a linear gradient in the boundary layer.

We represent each of the relevant mass balance equations as

$$\frac{dm}{dt} = \frac{AD(C^b - C^s)}{x} \quad \text{for diffusion ,}$$

and

$$\frac{dm}{dt} = KA\ (C^s - C^e) \quad \text{for surface reaction .}$$

These equations may be combined to give another linear rate law:

$$\frac{dm}{dt} = K(C - C^e) \quad ,$$

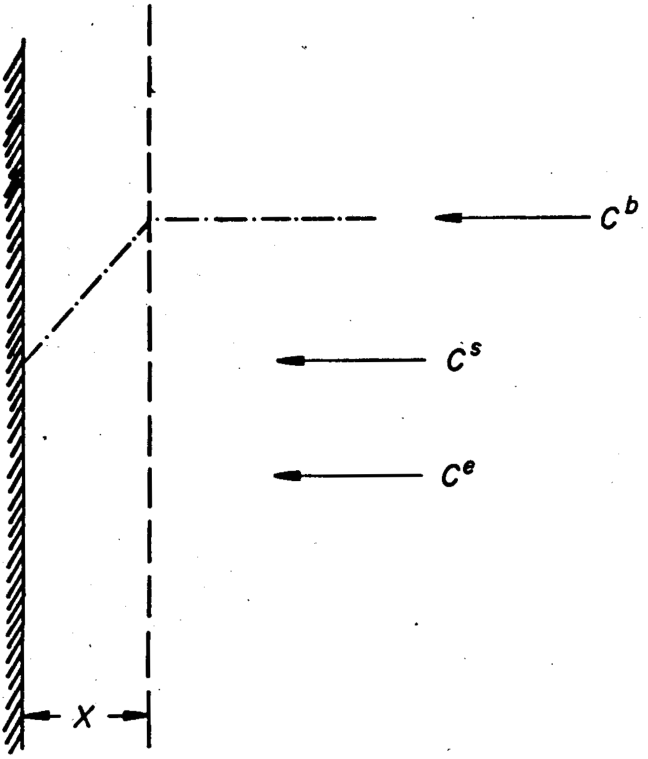

Fig. 41.
Schematic representation of concentration gradients at a boundary layer.

C^b : *bulk concentration*

C^s : *surface concentration*

C^e : *equilibrium concentration*

X : *width of boundary layer*

where

$$K = \frac{AD}{x}(1 + D/xk)^{-1} \quad ,$$

so even if there is diffusion control, one may still obtain linear kinetics.

While there are no careful studies of diffusion control in geothermal precipitations, there has been a considerable amount of work on other systems. It is clear that because activation energies of diffusion are considerably smaller than those of reaction, the diffusion mechanism must take over at sufficiently high temperature. The systems should and do show the behavior shown schematically in Fig. 42.

Measured systems show both types of behavior. Lund et al.[58] found that for calcite dissolution the rate was purely diffusion controlled. On the other hand, feldspar was controlled by surface reaction for similar temperatures (Fogler and Lund[64]).

The effects of convective mass transport have also been studied. They may be thought of as reducing the boundary layer restricting diffusional mass flow. Rosen and Hulburt[65] found empirically the following growth rate law for K_2SO_4:

$$\frac{dL}{dt} = k_1 (1 - k_2 e^{-k_3 v})(\Delta C)^2 \quad ,$$

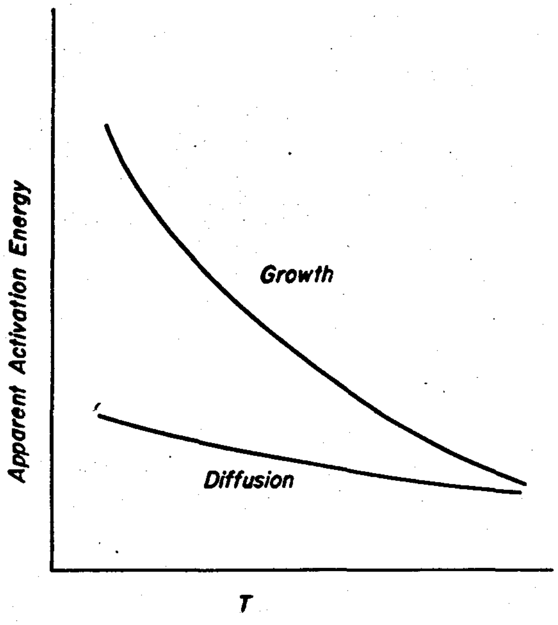

Fig. 42.
Activation energies for growth and diffusion.

where v is the velocity of the fluid streaming by the particle. Lund et al.[58] studied this phenomenon for calcite dissolution and found convective effects to be important. It must be emphasized that the assertion that $L_{ij} = 0$, $i \neq j$ is not very well satisfied for a concentrated brine and that the L_{ij}, $i \neq j$ in the solute-fixed frame are often of the order of magnitude of the L_{ij}'s. Data and extrapolations for brines have been given by Miller.[66]

VIII. PRECIPITATION AND TURBULENT FLOW

Essentially all the data we have collected refer to low-velocity systems. But in a flashing geothermal system, one would expect to see effects of high-velocity flow. These effects can have an influence on secondary nucleation because of high shear, as well as on reaction rates because of the enhanced mixing. There may also be effects on particle aggregation and transport of precipitant to boundaries. We would expect that the effect of high Reynolds numbers would be to enhance growth rates by reducing the boundary layer next to the growing face. In fact, general consideration indicates that boundary layer thickness in a turbulent system is approximately equal to the square root of the Reynolds number (Tennekes and Lumley[67]).

As usual, things are not so simple. As we see in Fig. 43 for NaCl precipitation (Koros et al.[68]), there are competing factors. The growth rate goes down at very high Reynolds numbers. There is,

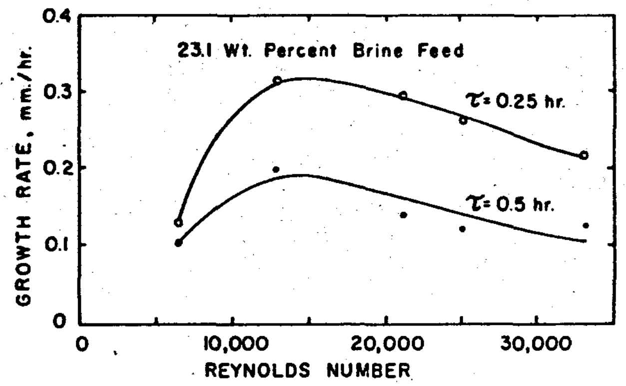

Fig. 43.
Crystal growth rate as a function of the agitator Reynolds number (Ref. 68).

however, a corresponding effect in the nucleation rate, which is believed to lower the supersaturation level and subsequently the growth rates (Fig. 44). There are very few studies of precipitation and chemistry in turbulent flows. Some work has been done on combustion problems. Turbulent mass transport enhancement comes from the highly random convective motion in the fluid. In general, the two types of models that have been suggested are injection and rejuvenation models and eddy diffusion models. In the first of these, transport enhancement is calculated directly by modeling convective transport of fluid elements to the surface followed by diffusion from the element. In the eddy diffusion approach, transport is considered by a phenomenological eddy diffusion equation such as

$$\frac{\partial \bar{\rho}}{\partial t} = D_e \frac{\partial^2 \rho}{\partial x^2} ,$$

where $\bar{\rho}$ is the time-averaged mass and D_e is determined experimentally and is a property of the flow. It may be orders of magnitude greater than the ordinary diffusion constant. Neither of these procedures is completely satisfactory because the existence of time and length scales other than those of viscous flow cannot be treated without careful investigation of the specific system configuration. In the work we have been able to find, neither complicated brine chemistry nor codiffusion has been considered, although Toor[69] investigated some of the effects of turbulence on reactions for very fast and very slow rates.

IX. SUMMARY AND OUTLOOK

It seems to us that a great deal of work is necessary before we can understand the mechanism of scale growth. While the equilibrium data are in relatively good shape, the kinetics of scale growth are still poorly understood, at least for real systems. More experimental data are needed on the question of surface reaction rates independent of diffusion control and, of course, on a wider range of scale minerals, in addition to the silica studies. Transport coefficients should be measured for concentrated brines and empirical extrapolation techniques similar to those used for equilibrium

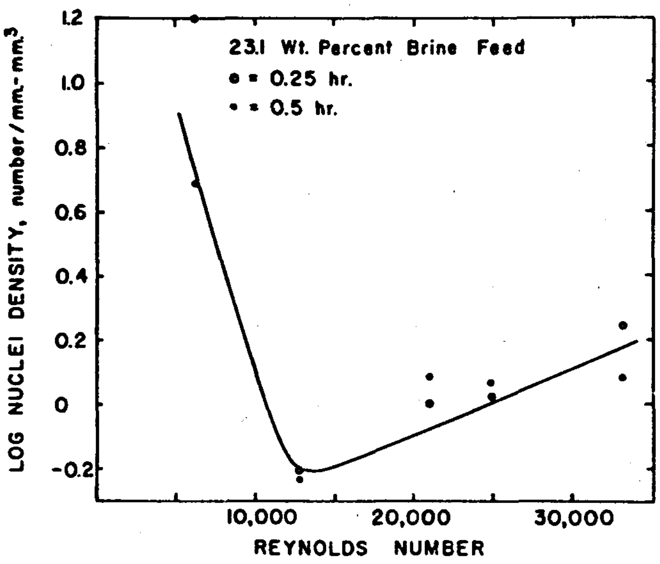

Fig. 44.

Nuclei population density as a function of the agitator Reynolds number (Ref. 68).

systems developed. These transport coefficients should be used to analyze growth data to extract surface reaction rates independent of diffusion control.

Finally, theories of turbulent flow in chemical fluids should be developed that include more complicated diffusion models appropriate to brine solutions as well as chemical reaction. Experiments should also be conducted on flashing geothermal systems to measure actual supersaturation levels in the pipe, as well as to develop parametric mass transport theories for turbulent flow.

A better understanding of scale formation depends on further research in a number of areas. In the following list we give some examples of important needs as we perceive them.

1. Better scale characterization.
2. Solubility data in solutions approximating geothermal brines, especially for amorphous silicates, calcite, and sulfides.
3. Thermodynamic data on scale minerals (amorphous silicates) and electrolyte solutions. Solubility constraints and activity coefficients.
4. Measurements of supersaturation along bore holes.
5. More complete studies of nucleation processes in realistic environments.
6. Kinetic data for a wider variety of systems and more careful determination of rate controlling steps.
7. Measurement of Onsager coefficient L_{ij} in concentrated brine solutions and development of extrapolations.
8. Begin to consider the effect of turbulent flow in both experiments and theory, and to develop phenomenological equation for turbulent flow.

REFERENCES

1. B. J. Skinner, D. E. White, H. J. Rose, and R. E. Mays, "Sulfides Associated with the Salton Sea Geothermal Brine," Econ. Geol. 62, 316-330 (1967).

2. S. Arnorsson, National Energy Authority, Reykjavik, Iceland, personal communication.

3. H. L. Barnes, W. F. Downs, J. D. Rimstidt, and D. O. Hayba, "Control of Silica Deposition in Geothermal Systems," Annual Report to U. S. Bureau of Mines, Pennsylvania State Univ., Grant No. G0-155140-1 (July 1977).

4. S. Mercado and J. Guiza, "Problems of Silica Scaling at Cerro Prieto Geothermal Power Station," Conf. Scale Management in Geothermal Energy Development, San Diego, California, August 2-4, 1976, NTIS report C00-2607-4 (1976), pp. 59-87.

5. R. Quong, "Scaling Characteristics in the Geothermal Loop Experimental Facility at Niland, California," Lawrence Livermore Laboratory report UCRL-52162 (1976).

6. A. L. Austin, A. W. Lundberg, L. B. Owen, and G. E. Tardiff, "LLL Geothermal Energy Program. Status Report, January 1976-January 1977," Lawrence Livermore Laboratory report UCRL-50046-76 (April 1977), pp. 58-73.

7. H. Harder and W. Fleming, "Quarzsynthese bei tiefen Temperaturen," Geochim. Cosmochim. Acta 34, 295-305 (1970).

8. O. W. Flörke, "Hydrothermal Transport and Deposition of Silica," Conf. Scale Management in Geothermal Energy Development, San Diego, California, August 2-4, 1976, NTIS report C00-2607-4 (1976), pp. 1-8.

9. S. Arnorsson, "Precipitation of Calcite from Flashed Geothermal Waters in Iceland," Int. Symp. Water-Rock Interaction, 2nd, Strasbourg, France, August 17-25, 1977, Vol. 3, pp. 152-169; Contrib. Mineral. Petrol. **66**, 21-28 (1978).

10. J. A. van Lier, P. L. de Bruyn, and J. Th. G. Overbeek, "The Solubility of Quartz," J. Phys. Chem. **64**, 1675-82 (1960).

11. M. Cordurier, B. Baudru, and J. Donnet, "Etude de la Polycondensation de l'Acide Dicilicique," Bull. Soc. Chim. France **9**, 3154-60 (1971).

12. L. B. Owen, "Precipitation of Amorphous Silica from High-Temperature Hypersaline Geothermal Brines," Lawrence Livermore Laboratory report UCRL-51866 (1975).

13. J. A. Apps, "The Kinetics of Quartz Dissolution and Precipitation," Conf. Scale Management in Geothermal Energy Development, San Diego, California, August 2-4, 1976, NTIS report C00-2607-4 (1976), pp. 145-152.

14. E. G. Bohlmann, A. J. Shor, and P. Berlinski, "Precipitation and Scaling in Dynamic Geothermal Systems," Oak Ridge National Laboratory report ORNL/TM-5649 (1976).

15. W. F. Downs, J. D. Rimstidt, and H. L. Barnes, "Kinetics of Silica Scaling," Conf. Scale Management in Geothermal Energy Development, San Diego, California, August 2-4, 1976, NTIS report C00-2607-4 (1976), pp. 9-18.

16. W. W. Harvey, A. C. Makrides, J. Slaughter, and M. J. Turner, "Kinetics of Silica Condensation in Brines," *ibid.*, pp. 25-36.

17. R. O. Fournier, "The Solubility of Amorphous Silica at High Temperatures and High Pressures," *ibid.*, pp. 19-23.

18. G. C. Kennedy, "A Portion of the System Silica-Water," Econ. Geol. **45**, 629-653 (1950).

19. C. S. Hitchen, "A Method for Experimental Investigation of Hydrothermal Solutions with Notes on Its Application," Bull. Inst. Mining Met., No. 364 (1935).

20. A. G. Volosov, I. L. Khodakovskii, and B. N. Ryzenko, "Equilibrium in Silicon Dioxide-Water System at High Temperatures (Along the Lower Three-Phase Curve)," Geochem. Intern. **5**, 362-377 (1972).

21. G. M. Anderson and C. W. Burnham, "Reactions of Quartz and Corundum with Aqueous Chloride and Hydroxide Solutions at High Temperatures and Pressures," Am. J. Sci. **265**, 12-27 (1967).

22. A. J. Ellis, "The Solubility of Calcite in Carbon Dioxide Solutions," Am. J. Sci. **257**, 354-365 (1959).

23. F. W. Dickson, C. W. Blount, and G. Tunell, "Use of Hydrothermal Solution Equipment to Determine the Solubility of Anhydrite in Water from 100°C to 275°C and from 1 Bar to 1000 Bars Pressure," Am. J. Sci. **261**, 61-78 (1963).

24. C. C. Templeton and J. Rodgers, "Solubility of Anhydrite in Several Aqueous Salt Solutions Between 250° and 325°C," J. Chem. Eng. Data **12**, 536-547 (1967).

25. W. L. Marshall, R. Slusher, and E. V. Jones, "Aqueous Systems at High Temperature. XIV. Solubility and Thermodynamic Relationships for $CaSO_4$ in $NaCl-H_2O$ Solutions from 40° to 200°C, 0-4 Molal NaCl," J. Chem. Eng. Data **9**, 187-191 (1964).

26. W. L. Marshall and R. Slusher, "Aqueous Systems at High Temperature. Solubility to 200°C of Calcium Sulfate and Its Hydrates in Sea Water and Saline Water Concentrates, and Temperature-Concentration Limits," J. Chem. Eng. Data **13**, 83-93 (1968).

27. G. Strübel, "Zur Kenntnis und genetischen Bedeutung des Systems $BaSO_4-NaCl-H_2O$," Neues Jahrb. Mineral., Monatsh. **1967**, 223-234.

28. C. C. Templeton, "Solubility of Barium Sulfate in Sodium Chloride Solutions," J. Chem. Eng. Data **5**, 514-516 (1960).

29. H. Gundlach, D. Stoppel, and G. Strübel, "Zur hydrothermalen Löslichkeit von Barit," Neues Jahrb. Mineral., Abh. **116**, 321-338 (1972).

30. S. D. Malinin, N. Y. Uchameyshvili, and N. I. Khitarov, "Application of the Theory of Strong Electrolytes to the Solubility of Barite in Aqueous Metal Chlorides under Hydrothermal Conditions," Geochem. Intern. **8**, 732-741 (1969).

31. C. W. Blount, "Barite Solubilities and Thermodynamic Quantities up to 300°C and 1400 Bars," Am. Mineral. **62**, 942-957 (1977).

32. W. D. Sinclair, "The Solubility of Copper and Copper Sulfides in Aqueous Chloride Solutions from 25 to 250°C with Geologic Applications," Ph. D. thesis, University of Wisconsin, 1973.

33. D. A. Crerar and H. L. Barnes, "Ore Solution Chemistry. V. Solubilities of Chalcopyrite and Chalcocite Assemblages in Hydrothermal Solution at 200°C to 350°C," Econ. Geol. **71**, 772-794 (1976).

34. D. A. Crerar, Princeton University, personal communication.

35. R. A. Robie and D. R. Waldbaum, "Thermodynamic Properties of Minerals and Related Substances at 298.15°K (25°C) and One Atmosphere (1.013 Bars) Pressure and at Higher Temperatures," U.S. Geol. Surv. Bull. 1259 (1968).

36. H. C. Helgeson, "Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures," Am. J. Sci **267**, 729-804 (1969).

37. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd Ed. (Butterworths, London, 1959).

38. L. F. Silvester and K. S. Pitzer, "Thermodynamics of Geothermal Brines. I. Thermodynamic Properties of Vapor-Saturated $NaCl_{(aq)}$ Solutions," Lawrence Berkeley Laboratory report LBL-4456 (1976).

39. W. T. Lindsay and C. -T. Liu, "Vapor Pressure Measurements for Determination of Thermodynamic Properties of Salt Solutions in Hot Water," Int. Corros. Conf. Ser., 1973, NACE-4 (1976), pp. 139-145.

40. C.-T. Liu, "Thermodynamics of Salt Solutions and Geothermal Brines at Elevated Temperatures," NTIS report PB-250733 (1975).

41. H. C. Helgeson and D. H. Kirkham, "Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures. II. Debye-Hückel Parameters for Activity Coefficients and Relative Partial Molal Properties," Am. J. Sci. **274**, 1199-1261 (1974).

42. J. R. Wood, "Thermodynamics of Brine-Salt Equilibria. I. The Systems $NaCl$-KCl-$MgCl_2$-$CaCl_2$-H_2O and $NaCl$-Mg_2SO_4-H_2O at 25°C," Geochim. Cosmochim. Acta **39**, 1147-1163 (1975).

43. J. R. Wood, "Thermodynamics of Brine-Salt Equilibria. II. The System $NaCl$-KCl-H_2O from 0 to 200°C," Geochim. Cosmochim. Acta **40**, 1211-1220 (1976).

44. H. C. Helgeson and D. H. Kirkham, "Theoretical Prediction of the Thermodynamic Properties of Aqueous Electrolytes at High Pressures and Temperatures. III. Equation of State for Aqueous Species at Infinite Dilution," Am. J. Sci. **276**, 97-240 (1976).

45. R. W. Potter and D. L. Brown, "The Volumetric Properties of Aqueous Sodium Chloride Solutions from 0° to 500°C at Pressures up to 2000 Bars Based on a Regression of the Available Literature Data," U.S. Geol. Surv. Open-File report 75-636 (1975).

46. R. W. Potter and D. L. Brown, "The Volumetric Properties of Vapor Saturated Aqueous Sodium Sulfate Solutions from 0°C to 325°C Based on a Regression of the Available Literature Data," U.S. Geol. Surv. Open-file report 76-255 (1976).

47. A. H. Truesdell and B. F. Jones, "WATEQ. Computer Program for Calculating Chemical Equilibria of Natural Waters," J. Res. U.S. Geol. Surv. **2**, 233-248 (1974).

48. H. C. Helgeson, "Evaluation of Irreversible Reactions in Geochemical Processes Involving Minerals and Aqueous Solutions. I. Thermodynamic Relations," Geochim. Cosmochim. Acta **32**, 853-877 (1968).

49. D. W. Shannon, R. A. Walter, and D. L. Lessor, "The GEOSCALE Computer Model for Geothermal Plant Scaling and Corrosion Analyses," Conf. Scale Management in Geothermal Energy Development, San Diego, California, August 2-4, 1976, NTIS report C00-2607-4 (1976), pp. 215-225.

50. D. Jackson, A. J. Piwinskii, and D. G. Miller, "Computational Methods for Estimating Precipitation from Geothermal Brines," *ibid.*, pp. 227-245.

51. R. O. Fournier and J. J. Rowe, "Estimation of Underground Temperatures from the Silica Content of Water from Hot Springs and Wet-Steam Wells," Am. J. Sci. 264, 685-697 (1966).

52. S. Arnorsson, "Application of the Silica Geothermometer in Low Temperature Hydrothermal Areas in Iceland," Am. J. Sci. 275, 763-784 (1975).

53. R. O. Fournier and A. H. Truesdell, "An Empirical Na-K-Ca Geothermometer for Natural Waters," Geochim. Cosmochim. Acta 37, 1255-1275 (1973).

54. R. O. Fournier, "Chemical Geothermometers and Mixing Models for Geothermal Systems," Geothermics 5, 41-50 (1977).

55. R. O. Fournier, "Prediction of Aquifer Temperatures, Salinities, and Underground Boiling and Mixing Processes in Geothermal Systems," Int. Symp. Water-Rock Interaction, 2nd, Strasbourg, France, August 17-25, 1977, Vol. 3, pp. 117-126.

56. A. E. Nielsen, *Kinetics of Precipitation* (Macmillan Co., New York, 1964).

57. J. W. Mullin, *Crystallization* (Butterworths, London, 1961).

58. K. Lund, H. S. Fogler, C. McCune, and J. W. Ault, "Acidization. II. Dissolution of Calcite in Hydrochloric Acid," Chem. Eng. Sci. 30, 825-835 (1975).

59. R. A. Berner and J. W. Morse, "Dissolution Kinetics of Calcium Carbonate in Sea Water. IV. Theory of Calcite Dissolution," Am. J. Sci. 274, 108-134 (1974).

60. A. E. Nielsen, "Homogeneous Nucleation in Barium Sulphate Precipitation," Acta Chem. Scand. 15, 441-442 (1961).

61. N. A. Clontz and W. L. McCabe, "Contact Nucleation of Magnesium Sulfate Heptahydrate," Chem. Eng. Progr., Symp. Ser. 67(110), 6-17 (1971).

62. S. M. Shor and M. A. Larson, "Effect of Additives on Crystallization Kinetics," Chem. Eng. Progr., Symp. Ser. 67(110), 32-42 (1971).

63. A. D. Randolph, "Comments on Recent Advances in the Analysis of Crystallization Processes," Chem. Eng. Progr., Symp. Ser. 67(110), 1-5 (1971).

64. H. S. Fogler and K. Lund, "Acidization. III. The Kinetics of the Dissolution of Sodium and Potassium Feldspar in HF/HCl Acid Mixtures," Chem. Eng. Sci. 30, 1325-1332 (1975).

65. H. N. Rosen and H. M. Hulburt, "Continuous Vacuum Crystallization of Potassium Sulfate," Chem. Eng. Progr., Symp. Ser. 67(110), 18-31 (1971).

66. D. G. Miller, "Application of Irreversible Thermodynamics to Electrolyte Solutions. II. Ionic Coefficients L_{ij} for Isothermal Vector Transport Processes in Ternary Systems," J. Phys. Chem. 71, 616-632 (1967).

67. H. Tennekes and J. L. Lumley, *A First Course in Turbulence* (MIT Press, Cambridge, Massachusetts, 1972).

68. W. J. Koros, D. A. Dalrymple, R. P. Kuhlman, and N. F. Brockmeir, "Crystallization of Sodium Chloride in a Continuous Mixed Suspension Crystallizer," Chem. Eng. Progr., Symp. Ser. 68(121), 67-73 (1972).

69. H. L. Toor, "Mass Transfer in Dilute Turbulent and Non-Turbulent Systems with Rapid Irreversible Reactions and Equal Diffusivities." AIChE J. 8, 70-78 (1962).

70. H. L. Barnes, "Chemistry of Silica Scale Formation," Proc. 2nd Workshop Materials Problems Associated with Development of Geothermal Energy Systems," El Centro, California, May 16-18, 1975.

WORKSHOP RECOMMENDATIONS

A. Engineering Panel

Before dividing into two subpanels, the engineering panel spent some time discussing the proposed 1-MW Mobile Test Unit described earlier in the Workshop by Robert R. Reeber/DGE. The following is a summary of the engineering panel recommendation.

There is general agreement that geothermal system design and analysis are seriously limited by lack of scaling test data for various resources, and that engineering design must accommodate a highly variable resource. There are various ways to obtain the test data. Most of the options have had the benefit of serious discussion by previous DGE committees that meet periodically.

Because of the cost impact of and possible duplication by the proposed Mobile Test Unit, it is recommended that the Mobile Test Unit proposal be submitted to such a DGE committee for consideration along with

- well head generators,
- EPRI Mobile Test Unit,
- future of the East Mesa Test Facility,
- Raft River Mobile Components Test Trailer,
- Secondary Loop Facility at the UC Richmond Field Station,
- various other test facilities proposed to DGE and EPRI,
- DOE/EPRI 5-MW HXR test at Heber (1977/78), and
- LLL test facility at Niland.

Other comments or suggestions concerning the proposed 1-MW Mobile Test Unit included the following.

1. The production well feeding the Unit should be run at full capacity to insure representative brine. A small side stream can be taken for the scaling or other loops. Most of the brine therefore would be reinjected at a relatively high temperature. However, effluents from the loops could be flashed down to a relatively low temperature and passed through filters to determine potential reinjection problems. Although this procedure will not evaluate all problems at full-scale reinjection rates, for which operation of wells for periods of many months would be required, and may be subject to unknown hydrodynamic/kinetic interactions, a very rapid answer may be possible to the question of good correlations between results of small-scale tests and the half-lives of injection wells.
2. Thought must be given to provisions for cleaning the system between tests. Because any scale remaining will promote scaling in future tests, thorough demonstrable cleanup is essential. Also, disposal or regeneration of cleanup solutions is a substantial matter.

The engineering panel was divided into two subpanels to consider field engineering problems and plant problems, respectively. Both subpanels made their recommendations from a review of the questions and comments submitted by Workshop participants and from discussions conducted within each group.

1. Field Engineering Subpanel (E. Bohlmann, E. Khalifa, R. Miller, G. Tardiff).

The major issues that need resolution may be classified into the following categories:

- fluid handling,
- materials and components, and
- production and injection strategy.

The recommendations of the subpanel are summarized in Table I. Most of the questions are related to injection, and it is the consensus that this problem must have highest priority. This is

TABLE I

FIELD ENGINEERING PROBLEMS

Unresolved Issues	Availability of Technology Available	Near Term	Requires Major R & D
Injection			
a. effluent mixing		x	
b. fracturing	x		
c. formation characteristics		x	
d. water treatment		x	
e. criteria for injection			x
f. effluent processing		x	
g. injection pumps	x (low salinity)	x (high salinity)	
h. subsidence		?	
i. solid waste disposal		x	
j. injection temperature		x	
k. casing materials	x (low salinity)	x (high salinity)	
Production			
a. flow problems (slugging, etc.)		x	
b. brine mixing		x	
c. downhole pumps		x (low salinity)	x (high salinity)
d. scale removal	x		
e. downhole brine treatment	x		x (acid resistant materials)
f. casing materials	x (low salinity)		x (high salinity)
g. downhole instrumentation			x
h. site specificity		x	
Gathering			
a. well head separation		x	
b. components		x	
c. materials		x	

true for all resources. As noted in Table I, the need for R & D for other issues depends on the salinity of the resource. The details of solutions to the field engineering problems are closely related to the type of conversion system employed.

2. **Plant Engineering Subpanel** (J. Addoms, H. Bishop, J. Hankin, J. King, R. McKay, T. Merson, J. Parkinson, W. Pope, H. White, A. Whitehead, J. Wilson).

Unresolved issues and needs identified by the subpanel included the following items.

a. Formation of Steering Committee. A small committee of experts should be set up. The committee should meet, agree, and propose a plan of study (analytical, laboratory testing, field testing, etc.) toward the solution of important scaling problems in geothermal systems with near-term economic viability. Membership on the committee should be broad-based, and should include utilities, A & E's, energy companies, and universities. Such a committee might be organized by the ASME, AIChE, or SPE. The proposed study plan (along with a suggested management plan) should then be submitted to DOE (and EPRI, NSF, etc., if necessary) to obtain the required funding.

***b. Geothermal Engineering and Materials Handbook*.** An engineering and materials handbook is needed to aid in the selection of materials for process hardware. A starting point can be the information already available in desalination handbooks (for temperatures to 250°F and deaerated sea water). This information should be extended to higher temperatures and supplemented with data for new materials and brine compositions unique to geothermal systems. OSW and CPI data will be useful for this purpose. The information is needed to study the effect of pH and assess the effect of coating materials (e.g., Teflon) on plant design. Much information already exists, which needs to be made readily available to designers. Other areas to be covered are scale control and hardware design considerations and experience.

***c. Waste Water Disposal*.** The various methods for geothermal waste water disposal (reinjection, evaporation ponds, surface disposal to pre-existing bodies of water, etc.) and the environmental and legal requirements that are operative for reinjection should be reviewed. Regulations vary widely from place to place, which places an extra burden on the plant designer. The regulations are frequently unnecessarily restrictive when compared with those applied to other industries. Data available from the OSW work and from experience with oil field water reinjection and secondary flooding should be considered. There is a need to lobby for a more logical and uniform set of specifications.

***d. Scale Removal Technology*.** The removal of silica scale is difficult, and more work needs to be done on both mechanical and chemical methods. More can be done by using existing technology and extending it to the specific needs of geothermal systems.

There was disagreement as to whether methods currently available for scale removal from various process equipment should be compiled as part of a technology handbook. Con: There are "thousands" of companies who provide cleaning services, mostly to the petroleum industry. Pro: The utility companies are not necessarily familiar with these services, and the services may not be sufficient for all types of scale. Geothermal scales are formed at higher temperatures than those from the petroleum industry.

At the very least, information is needed on which of the various cleaning methods is successful and on its economic feasibility.

***e. Process Selection to Mitigate Scaling*.** A study should be made of which geothermal energy conversion process is appropriate to which geothermal fluid. Which cycles are really better for various types of solutions? What are the trade-offs between thermodynamic efficiencies and operating costs, the advantages and disadvantages with regard to scaling of the various cycles? To what extent can or should attempts to tailor plant design to specific fluids be replaced by engineering designs matched to the variability of fluids? What is the interaction between the way processes are designed and operated and the formation of scale? The effect of pH control on plant design is also of great interest.

***f. Scale Avoidance*.** This general subject needs more attention. In particular, scale avoidance by brine pretreatment using chemical or other methods should be studied further. Although pretreatment might result in a lower thermodynamic efficiency, the potential economic payoff is significant. As a variation on direct upstream precipitation of brine components (e.g., by pH modification), seeding might be a feasible way to nucleate precipitation and produce a nonadherent suspension. Modifications of cycle configurations might also confine precipitation to more tolerable parts of a process. Postplant but preinjection treatment also needs more work. It has different problems, but the same potential economic payoff.

g. Hardware Needs. Some of the items mentioned here may already be funded, but are included for a complete listing. The need is for equipment especially designed for a scaling environment.

- Pumps — with seals and bearings that will withstand geothermal temperatures and corrosion,
- Valves — with seals and controls that will withstand corrosion and scaling,
- Process instruments — a two-phase flow meter and pH meter for input control.

Turbines are not thought to be a major problem.

h. Steam Cleaning. Possible alternatives to the Holt-Hutchinson scrubber for steam cleaning should be examined. For example, the Bechtel Corporation has been proposing wash demisters in some of their designs. This much simpler system has been used in desalination plants, but more work should be done for application to geothermal systems. In this system a little wash water is used to keep the demister from scaling.

i. Data on Fouling Rates for Heat Exchanger Design. Information is needed by the designer of plant/process heat exchangers from chemistry studies to aid in the specification of process state points, the determination of subsystem cost, and therefore the selection of optimum system design.

The brine-side fouling factor R_f (thermal resistance) will be influenced in part by

- local brine composition C,
- local bulk temperature T,
- local Reynolds number R_e, or mass flux,
- local heat flux Q/A,
- local cumulative time from clean conditions θ, i.e., $R_f = f\ (C, T, R_e, Q/A, \theta)$.

Other possible factors include materials, coatings, and boundary layer effects. Chemistry study or test data that could be put into the above form for use in existing exchanger design routines of general process codes would be very helpful to the designer. Ideally, what is wanted are chemistry data for the above general functional model, and the coefficients in that model could be adjusted depending on the resource. In practice there are not enough of these kinds of data, and they are very expensive to obtain. From EPRI experience, a representative fouling factor for one well from one resource can take up to 6 months and cost $800 000. Thought should be given to better ways of obtaining the required data, perhaps by constructing a simple mobile test rig that could be easily carried from site to site, instrumented and operated in such a way as to satisfy needs of both chemists and engineers.

j. Plant Economic Data Base. The rationale for this item is the possibility that there exists a usable but uncollected data base based on real experience for the effect of scaling on plant operating and maintenance costs as a function of type of geothermal cycle. Just how important is scale prevention to the successful operation of a geothermal plant? Input is needed from industry for systems that have succeeded and systems that have failed. Non-US geothermal installations may be a source for this information. Is there a trade-off between plant capacity and operating and maintenance costs? Will field experience permit the prediction of down-time due to scaling, and how long it will take to clean a heat exchanger?

k. Use of Chemical and System Codes. Code development should continue, with regard for the various possible applications. Some of these possible applications are

- avoidance of plant operating regimes that will cause scaling,

- prediction of optimum plant state conditions corresponding to a decreasing resource temperature,
- use as a real-time plant control or monitor, e.g., optimization of plant output for a binary cycle as a function of wet bulb temperature.

l. ***Condenser Design*.** This item refers particularly to condenser needs for a total flow system. Although a flashed steam system is forced to include a steam cleaning step, this is not necessarily so for a total flow system, and the steam available to the condenser is much dirtier. If no design is available, R & D will be needed. It may be appropriate to integrate a separator, cleaner, and condenser into one combined package, rather than to try to put the pieces together. The whole subject of heat rejection is extremely important to all conversion approaches and will benefit from the techniques of cycle analysis.

***m. Alternative Concepts for Heat Exchangers*.** Work on the direct contact and fluidized bed systems is important and should be encouraged.

B. Chemistry Panel

Rather than base its recommendations on the questions and comments submitted by Workshop participants on the first day, the chemistry panel preferred to draw up its own list of problem areas or categories. Those areas were

- Basic kinetic processes (experimental and theoretical)
- Modeling procedures
- Collection and summary of field experiments and observations
- Scale prevention methods (chemical)
- Basic thermodynamic data (experimental and theoretical)
- Parameters important to precipitation mechanisms
    - chemical
    - thermodynamic
    - fluid mechanical (including turbulent flow)
    - kinetic
    - transport
    - surface chemical (adhesion and colloidal behavior)
- New *in situ* experimental data
- Collection, summary, and categorization of existing laboratory data
- Experimental methodology (sampling and analysis)
- Environmental impact
- Scale characterization
- Optimum injection chemistry
- Condensate chemistry
- Corrosion
- Crystal growth

These categories were then divided among four chemistry subpanels, and their recommendations of research needs are summarized as follows.

1. Chemistry Subpanel 1 (J. Apps, C. Herrick, H. Levine, L. Owen, R. Reeber, D. Shannon, L. Silvester, O. Vetter).

This subpanel concentrated on optimum injection chemistry, and considered such details as suspended solids, crystal and scale growth, interaction rates of various types, and the effect of process additives.

In order to dispose of vast volumes of waste brines, the designer of a plant must understand what will lead to a loss of injectability or to injection pressure increases. He must design his plant power cycle, control equipment, and process conditions to assure reasonable life of the injection wells. This may be site specific, and data are needed soon for eight near-term KGRAs.

The failure to provide the data, technology, and methods could lead to total plant shutdown, loss of very expensive injection wells, and could make a geothermal plant an economic failure.

The cost of thoroughly defining the technology for ten sites is estimated to be $10 000 000 and to require 6 yr. The cost is an average of estimates by the eight subpanel members, which ranged from $1 750 000 to $30 000 000. The large spread of the estimates is due to the difficulty of defining the overall scope of the program without further investigation to define the extent of the problem. Certainly it is expected that the cost of rejuvenation of an injection well will be less than that of a production well. However, the cost of the program is high because it is assumed to include equipment development (excluding cost of wells). The following will define the information, data, methods, technology, equipment, and options needed by the plant designer and operator to assure trouble-free brine disposal for reasonable plant life.

***a. Suspended Solids*.** Establish the maximum size and concentration of suspended solids produced and arrive at a specification for the maximum permissible sizes for given operating conditions.

Characterize and define the chemical properties of the solids.

Define the origin of the solids (sand, scale from the plant, precipitate in the brine, corrosion products).

Determine the tendency of the solids to plug pores. An engineering description is needed of the pores in the rock and of the connectivity between them.

Determine the rate of formation of precipitates as a function of selected chemical/process/hydraulic variables.

Develop removal methods to meet size specifications (filtration, flocculation, settling, etc.).

Perform simulated well injection tests at the surface on cores of the injection strata.

***b. Crystal and Scale Growth*.** Measure the kinetics of precipitation, i.e., the crystal growth as a function of chemistry/process parameters such as CO_2 pressure, pH, salinity, etc. We need to determine if the size of the precipitated solids can be controlled and the conditions necessary to keep them in suspension. Field experiments are needed in which precipitation is induced under flow conditions, those conditions noted, and the data analyzed for any trends.

Obtain thermodynamic data (K_{sp}) for all candidate precipitates as a function of temperature (to 370°C) and pressure (silica, carbonates, sulfates, sulfides, silicates, and solid solutions).

Evaluate the possibility for crystal growth from reaction of injected brine with reservoir rock.

Evaluate the possibility of precipitation when using surface water for injection make-up.

***c. Brine-Rock Interaction*.** Determine the volume change and the effect on core connections which result from brine reaction with rock.

Assess cooling of reservoir by injected brine.

Determine the kinetics and themodynamics of both of the above processes.

Evaluate any chromatographic effects due to ion exchange of injected brine with reservoir rocks.

***d. Effect of Process Additives*.** Candidate additives are scale inhibitors, O_2 scavengers, pH controls, injected acids, flocculents, corrosion inhibitors, and drilling fluids.

Do additives plug reservoir formations and, if so, why, and at what rate?

What are the effects of additives on injected brine-rock interactions, e.g., reaction of sulfate ion with barium or calcium ions, oxidation of sulfide ion to sulfate ion, etc.

2. Chemistry Subpanel 2 (D. DeBerry, R. Mesmer, W. Midkiff, J. Murphy, F. Schoepflin). From the original list of problem areas this subpanel primarily considered methods of scale prevention and divided the topic into research needs for process treatment and those for preinjection treatment. The cost of this research is estimated to be $500 000.

Process Treatment

a. Prevention of Scales Other Than Silica. Systematic research should be done on the effect of pH, the efficacy of chelating agents and other additives as a function of brine type, and concentration of additive.

b. Prevention of Deposition of Amorphous Silica and Silicates. More research should be done on the effect of pH, added chelating agents, and oils. Also research on substrate control by material selection, process modifications (chemical additions at particular points, reduced flashdown, turbulence, etc.), slurries, and fluidized beds is needed. For particular resources supersaturation of amorphous silica may be avoided by defining a lower temperature limit for process streams.

c. Scale Modification. Polyacrylates and coprecipitating additives may be useful for this purpose.

d. Prevention of Nucleation. This may be feasible for certain low-TDS brines.

Preinjection Treatment for Solids Removal

e. Flocculation. Polyacrylates, etc., should be studied.

f. Precipitation. Precipitation of iron, calcium, or magnesium hydroxides may be useful as scavenging procedures.

g. Deposition on Beds. This may be feasible for amorphous silica without hold-up.

h. Filtration. Possible physical filtration media are amorphous silica, sand, calcite, etc.

The following techniques are likely to be slow, but may have special applications.

i. Membranes. Ultrafiltration might show promise for colloidal material if such material proves to be a problem and if costs are realistic. Reverse osmosis and electrodialysis are other possibilities, if economical.

j. Ion Exchange. Ion exchange has potential application for very low TDS brines.

As a general comment, the lack of knowledge about the composition of proprietary chemicals for scale control continues to be a problem because of the difficulty of assessing the deleterious effects of these chemicals or their decomposition products on plant or reinjection systems. This subpanel also agreed that an operating manual for scale control methods should be developed.

3. Chemistry Subpanel 3 (W. Downs, H. Eugster, C. Holley, D. Miller, R. Robie, J. Weare, O. Weres).

The third chemistry subpanel considered the data and models essential for applied programs. Total cost of the recommended program is estimated to be ≥ $3 500 000 over 5 yr. In the summary tables below, a task assigned a priority of 1 has the highest priority. Times required are designated as S (2 yr), I (5 yr), or L (10 yr). The research needs are classified as thermodynamics, transport and kinetics, scale characterization, and modeling. The technology is believed to be available for most of the needs.

THERMODYNAMICS

a. Solubility of Solids

Need	Priority	Time Required
Carbonates	1	S
Amorphous silica	3	S
Silicates	1	S
Sulfides	2	S
Sulfates	3	S
b. Solubility of Gases in Brines		
CO_2	1	S
H_2S	1	S
NH_3	1	S
HCl	1	S
H_3BO_3	3	S
H_4SiO_4	3	S
Mixtures		
NH_3-HCl	1	I
Other	3	I
c. Thermodynamic Properties of Solids		
$\Delta G°(T)$		
Amorphous silicates	1	L
Chalcopyrite	1	S
d. Thermodynamic Properties of Electrolytes		
H, C_p, ϕ (for power plant) Na^+, Ca^{++}, K^+, Cl^- (pure components and mixtures)	2	I
H, C_p, ϕ (for scaling) Mg^{++}, Cu^{++}, Zn^{++}, Fe^{++}, Fe^{+++}, Cl^-, $NaHCO_3$	1	I
K_{eq} (for scaling and reservoir) Other complex ions	2	L

(H = enthalpy, C_p = heat capacity,
ϕ = osmotic coefficient,
K_{eq} = equilibrium constant)

TRANSPORT AND KINETICS

Need	Priority	Time Required
e. Kinetics		
Dissolution, precipitation, and polymerization		
Silica (saturated solutions)	1	S
Calcite and aragonite, CO_2 hydration/dehydration	1	I
Barite, anhydrite, and gypsum	3	S
Amorphous scale (Ca, Fe, and Al silicates)	1	L
Sulfides	2	I
Growth rates, nucleation, and adhesion of crystals	2	L
f. Transport		
Transport properties of major constituents and principal mixtures of brines—application to plant and reservoir		
Viscosity	1	S
Heat conductivity	2	I
Electrical conductivity	2	I
Diffusion coefficient	2	I
Onsager coefficient	3	L
Transport properties of minerals		
Diffusion	3	L
g. Handbook of Field Scales	1	S
Mineralogy		
Petrography		
Textural data		
h. Continuing Handbook Update	1	L

MODELING

i. Improved Equilibrium Models	1	S
Applied to reservoir and plant		
j. Kinetic Models of Scaling	1	I
Applied to plant		
k. Turbulent Hydrodynamics-Chemistry	2	L
Applied to plant		
l. Percolation Reactions and Kinetics	2	I
Applied to reservoir		

4. Chemistry Subpanel 4 (D. Jackson, C. Keizer, D. Michels, P. Needham, L. Ross).

The research areas considered by this chemistry subpanel were scale characterization, scaling phenomenology, and *in situ* analysis. All the identified needs are believed to be attainable in relatively short periods of time. Estimated costs are given separately for each item.

a. Scale Characterization. This item is actually a description of and an appeal for a complete characterization of scale in all laboratory and field work in which scale forms. Scale formation is a phenomenon which is currently under-described in comparison with fluids depositing the scale. Because scale formation is really the subject of interest in doing a lot of fluid sampling and analysis, scales that form are at least as good a characterization of the wells as the fluids themselves.

Scale characterization should include a description of mineralogy, density, structure, texture, adherence, gross composition, trace material content, and the substrate. It should be related to brine composition, the flow conditions, variables of state, the context of the flow path, and thermodynamic expectations.

Direct financial support may not be necessary or appropriate for this item.

b. Standardized Field Experiments to Determine Scaling Phenomenology. There have been virtually no field scaling *experiments* done. This is in contrast to *observations* that are made for operating systems.

Reference techniques and apparatus are needed for experiments to measure such scaling parameters as the scaling rate vs various specific expected plant operating conditions of pressure, temperature, average brine chemistry, construction materials, etc. Such an experimental apparatus could then be used on other wells in the same geothermal field so that direct comparisons could be made.

This will probably be the single most important kind of data necessary to design new test facilities or pilot plants. Estimated cost is $75 000-$150 000.

c. Sampling and Analysis of Noncondensable Gases. Although there is some difference of opinion about the significance of noncondensable gases (e.g., CO_2, NH_3, H_2S) to power plant design and operation, it is possible that they could determine whether economic power can be produced. Also it is highly desirable to monitor changes in the identities and amounts of noncondensable gases with changing reservoir composition. Unfortunately sampling and analytical techniques for these gases are particularly weak. It is therefore recommended that

- Standardized methods of gas sampling and analysis should be used for all wells in a given geothermal field (perhaps by means of a mobile unit incorporating a gas chromatograph).
- New techniques and methods should be developed for on-site analyses.
- Data available from all operating areas should be collected and correlated.

d. Real-Time Detection of Two-Phase Flow. Both operating techniques and sampling are more difficult in a two-phase flow regime. A real-time detection of the onset of this regime would enable the operator to change flow rates until the single-phase condition was restored. Sampling would thereby be simplified and the results would be more representative.

The availability of a detection device would increase the quality of input data (chemical, thermal, mass flow) for plant design. Complications during plant operation would be less frequent, which would increase overall plant efficiency.

A suitable device might be a small probe that uses electrical signals based on resistance, magnetic susceptibility, or impedance. It would require suitable mounts and seals to operate at geothermal temperatures and pressures. The output signals would have to be correlated with various flow regimes.

It is estimated that about 2 man-yr would be required to develop such a device at a cost of $100 000 to $150 000.

e. Downhole Sampling. No reliable sampler for use in flowing wells is available. One is needed for the characterization of brine chemistry before separation of noncondensable gases at the surface. Also, knowledge of which horizons in the well are producing what kind and quality of geothermal fluid would permit the producer to select fluid of optimum characteristics. All wells need to be sampled at some time during their lives, and the analyses are needed to assess reservoir and downhole conditions for purpose of material selection, etc.

It is believed that a relatively small research program is required for the development of a suitable sampler. Estimated cost is $100 000-$175 000.

f. Electrical Conductivity for Plant Control. The electrical conductivity of flowing fluid provides a real-time measurement that could be correlated with steady-state plant operation. It could be used for long-term tests on a pilot plant or plant scale. Operational upsets could be immediately detected and corrected. Conductivity measurements may be a unique technique for this purpose. A suitable device would have an impact throughout the hydrothermal power industry. Estimated cost is $15 000-$20 000.

g. Measurement of Flow Rates. A technique is needed for the direct, *in situ*, measurements of brine flow rates. Orifice plate or end-point measurements (e.g., the levels in a Baker tank storage system) are completely unsatisfactory for pilot plant operation. An operator needs real-time indications of flow rates at many points and a nonscaling, noncorroding device.

The device will have a high impact for operators, e.g., the quick detection of scaling in a specific part of the system. Estimated cost is $50 000-$75 000.

h. Collection, Summarization, and Indexing of Available Field and Laboratory Experimental Data. There is a recurring problem of disagreement about results obtained from similar experiments. Therefore, a need exists to carefully specify the conditions under which each experiment is run.

Further, a data collection center should be organized. The center should set up an indexing system to summarize and document experimental conditions so that a proper comparison of experiments can be made. The center could also summarize the phenomena observed and their interpretation. Such a center would serve the longer range function of preparing mechanisms for information transfer in anticipation of the time when one-to-one communication becomes more difficult.

Someone or some organization should be selected promptly to collect the small amount of available data. A possible organization is the Geothermal Resources Council. Estimated cost is $25 000-$50 000/yr.

☆U.S. Government Printing Office: 1979 — 677-013/78

Printed in the United States of America. Available from
National Technical Information Service
US Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

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