CHEMICAL TRACER RETENTION IN POROUS MEDIA

A Report
Submitted to the Department of Petroleum Engineering
of Stanford University
in Fulfillment of the Requirement for the
Degree of Master of Science

Kenneth Allen Breitenbach
May, 1982

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to my research advisor, Roland N. Horne, for his advice, support and guidance throughout this work. Many thanks are due to Avrami Sageev and the rest of the department staff for helping me to finish this report. Lastly, a very special thanks to my parents, Laura, Whito, Bales, and the rest of my friends for giving me support when I thought I would never finish.

Financial support was provided through the Stanford Geothermal Program.

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

Section 1

INTRODUCTION

A tracer is an identifiable substance that can be followed through the course of a process providing information on the pattern of events in the process or on the redistribution of the parts or elements involved. A tracer is a simulator. It must be similar in behavior to the substance which it has to trace, yet it must be sufficiently different to be identifiable. These are two contradictory conditions. The selection of a tracer is thus a search for a compromise.

Tracers are often used in the oil industry to estimate residual oil saturation and volumetric sweep efficiency. In drilling, tracers are used to identify lost circulation zones. In hydraulic fracturing, tracers provide information on the location and orientation of fractures. During a multiple string well completion, tracers are used for orientation and depth correlation of perforators. Tracers are used in the identification of directional flow trends and delineation of flow barriers such as faults. The use of tracers throughout the industry is diverse and widespread.

In the management of geothermal reservoirs, tracers have become an important tool. They have provided valuable insight into the problem of short circuiting of waste water between reinjection and production wells. Tracer tests provide a method of evaluating the fractured nature of the system and thus the magnitude of the short circuiting problem. This report is an attempt to improve the understanding of tracer behavior in geothermal reservoirs. In particular, the degradation of commonly used tracer materials as they pass through typical rock types at high temperatures is examined in a quantitative way.

Tracers can be divided into two general groups: (1) chemical tracers; and (2) radioactive tracers. Chemical tracers are those which can be identified and measured quantitatively by general analytical methods such as conductivity, refractive index and elemental spectrometry. Radioactive tracers are detected by their emitted radiation, usually beta or gamma. This report is concerned exclusively with the use of chemical tracers.

Tracers can be further subdivided into those which can be made part of the natural system and those which cannot. The first group includes radioisotopes of constituent elements in the reservoir fluids. These tracers only have to achieve equilibrium with their own non-radioactive kind. The second group of tracers includes most chemical tracers. This group has to establish equilibrium with every other kind present in the system. As a result, non-equilibrium processes such as dissolution, ion exchange, diffusion inside solids, and adsorption can occur between tracer and reservoir rock. These non-equilibrium processes are of great importance not only in the field but in laboratory experiments which invariably start out with non-equilibrium conditions.

For the purpose of this paper, we have chosen to include the non-equilibrium processes of adsorption, dissolution, diffusion and ion exchange under the general category of retention. All of these various types of reactions occur at a microscopic level and lead to changes in tracer concentration as the tracer fluid flows through the porous media.

The selection of one or more tracers for any specific field application is a difficult problem. The operator must have a detailed knowledge of the following characteristics of each tracer:

1. Retention characteristics in reservoir rock.
2. Hydrothermal stability.
3. Analytical detectability.
4. cost.
5. Availability.
6. Safety.

This report is concerned with the characteristics of chemical tracer retention in reservoir rock. In most of the previous work done concerning tracer behavior in reservoirs, the retention parameter was not quantified and thus neglected in the material balance calculations. In order to gain a more precise understanding of reservoir tracer behavior, the process of tracer retention in reservoir rock has been investigated.

Section 2

LITERATURE REVIEW

In the past several decades, radioactive and chemical tracers have been used as an effective tool to verify or investigate critical characteristics of underground reservoirs. The results of these field tracer tests have been interpreted on a qualitative basis.

Strum and Johnson (1950) studied the results of several tracer tests using brine, fluorescein dye, and a surface active compound. Their results verified the existence of directional permeabilities which had already been measured on core samples. Their findings are generally considered the first to illustrate the important use of tracers in verifying reservoir characteristics.

A comprehensive list of information obtainable from tracer tests was presented by Wagner (1974) who studied the results of twenty tracer programs conducted in reservoirs undergoing waterfloods, gas drives and water solvent injection operations. His list includes the following items: (1) volumetric sweep; (2) identification of offending injectors; (3) directional flow trends; (4) delineation of flow barriers; (5) relative velocities of injected fluids; and (6) evaluation of sweep improvement treatments.

The use of tracer tests is evaluating the short circuiting problem found in geothermal reservoirs undergoing waste water reinjection was presented by Horne (1982). The fractured nature of the system (and thus the magnitude of the short-circuit problem) were evaluated using tracer tests.

To perform a quantitative analysis of tracer tests, one must have a thorough knowledge of the mechanism of tracer movement in the formation. Tracer movement can be divided into two general categories: (1) macroscopic processes; and (2) microscopic processes. Macroscopic processes include two phenomena, convection and hydrodynamic dispersion (Bear, 1972). Convection is due to bulk movement of fluids caused either by natural density differences or pressure gradients. Hydrodynamic dispersion is composed of two parts, molecular diffusion and mechanical dispersion. Molecular diffusion results from the concentration gradients established between two miscible fluids. Mechanical dispersion is the result of individual fluid particle movement through tortuous pore channels in a porous medium. These macroscopic processes are caused by heterogeneities of the reservoir or porous media and properties of the fluid composition.

Dispersion, diffusion and convection have received considerable attention in the literature; this report is primarily concerned with the second item above, microscopic processes seen in tracer flow. Microscopic processes include adsorption, ion exchange, dissolution and diffusion inside solids. These processes are due to chemical or physical changes in the tracer and lead to tracer retention in the reservoir. The processes causing retention are evaluated in the laboratory study described here. The mechanical dispersion effects are described in parallel papers by Horne and Rodriquez (1981) and Fossum (1982)

In most of the previous work concerning tracer behavior, the loss of tracer caused by retention processes was neglected in the material balance calculations. Vetter (1981) indicates that there is no published reference regarding acceptable laboratory methods to evaluate tracers for geothermal reservoir. This work is an attempt to fill that void. Vetter made an attempt to quantify radioactive tracer adsorption in porous media. This report focuses on chemical tracers and the parameters causing retention.

Section 3

STATEMENT OF THE PROBLEM

This laboratory study arose out of the need to know more about chemical tracer retention in geothermal reservoirs. The specific aims of this investigation were:

1. To design, build and test an instrument capable of measuring chemical tracer retention in reservoir rock at 300°F.
2. To use the instrument to investigate the retention process with different chemical tracers: potassium iodide and sodium bromide.
3. To study the effect on retention of varying the concentration of tracer.
4. To study the effect of temperature on retention.
5. To study the effect of residence time on tracer retention.

Section 4

EXPERIMENTAL APPARATUS

A rough 60° axonometric view of the apparatus is shown in Figure 1. It consists of an air bath, core holder, confining pressure system, water flow system, tracer flow system, temperature recording device, and cooling system. the confining pressure and water flow systems were designed by A. Sageev (Reference 7). Figure 2 is a schematic diagram of the entire system. A brief description of each component will be made in this section.

Porous Media

The core material is a volcanic andesite which was taken from a geothermal core sample in the Los Asufres field, Mexico. Due to the extremely low permeability, the rock was crushed and sieved to various size fractions. A mixture of 40 to 140 mesh size was selected to be used. The mesh range was rinsed and washed several times before packing into the core holder. Porosity measurements were done with a Russell Volumeter. The core geometry measurements are given in Section 6, Discussion of Results.

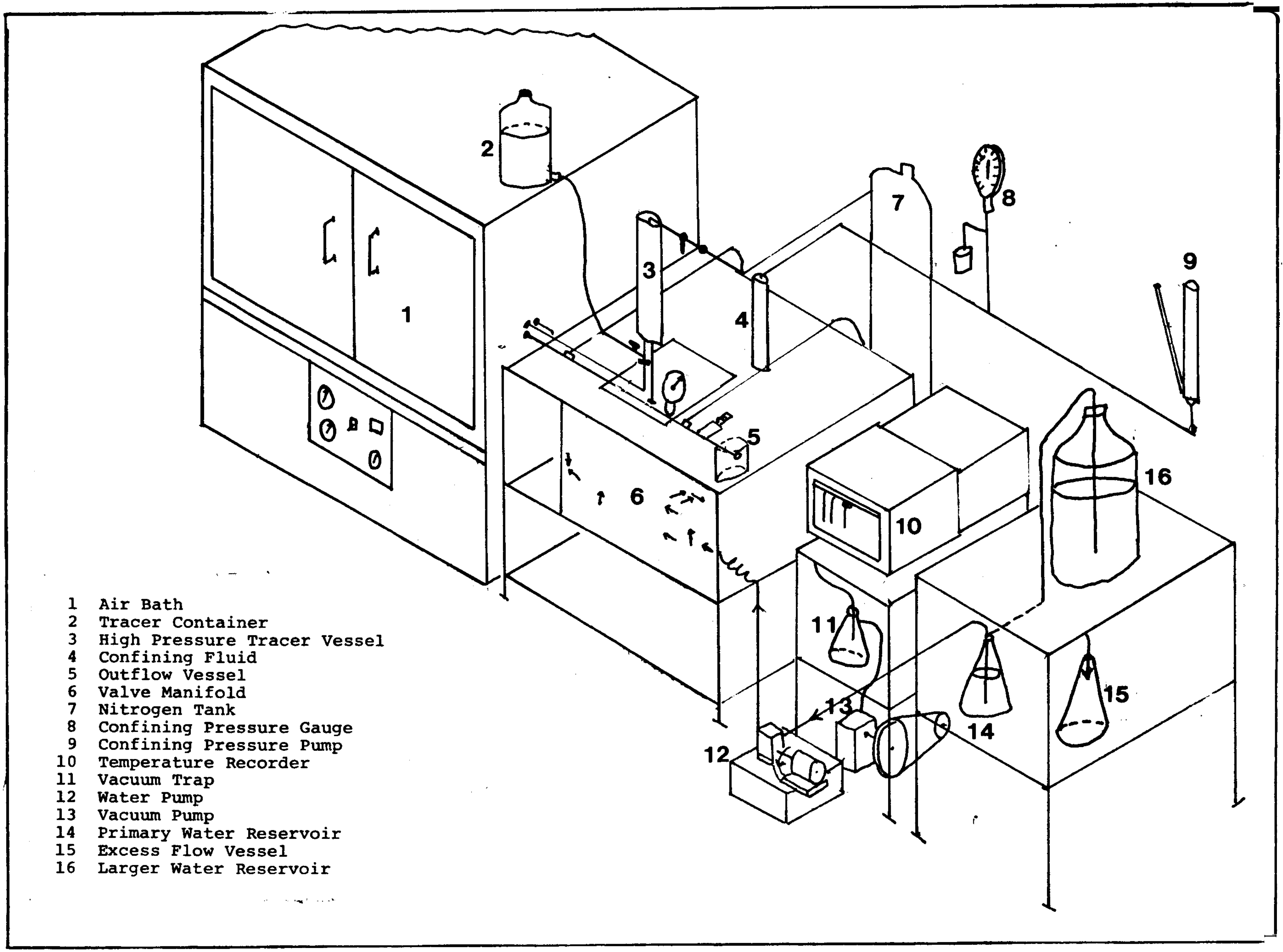


FIGURE 1 - General View of the Apparatus

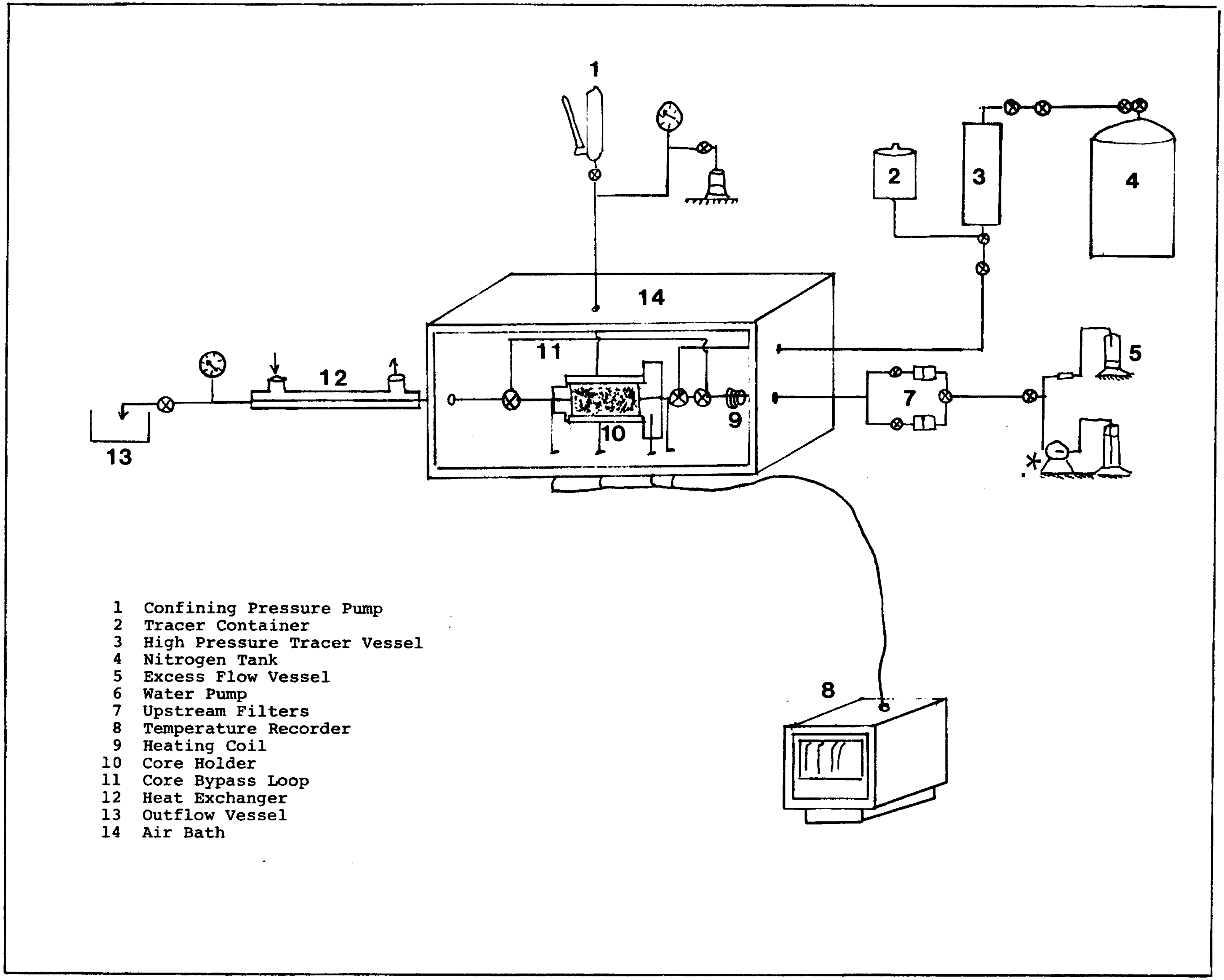
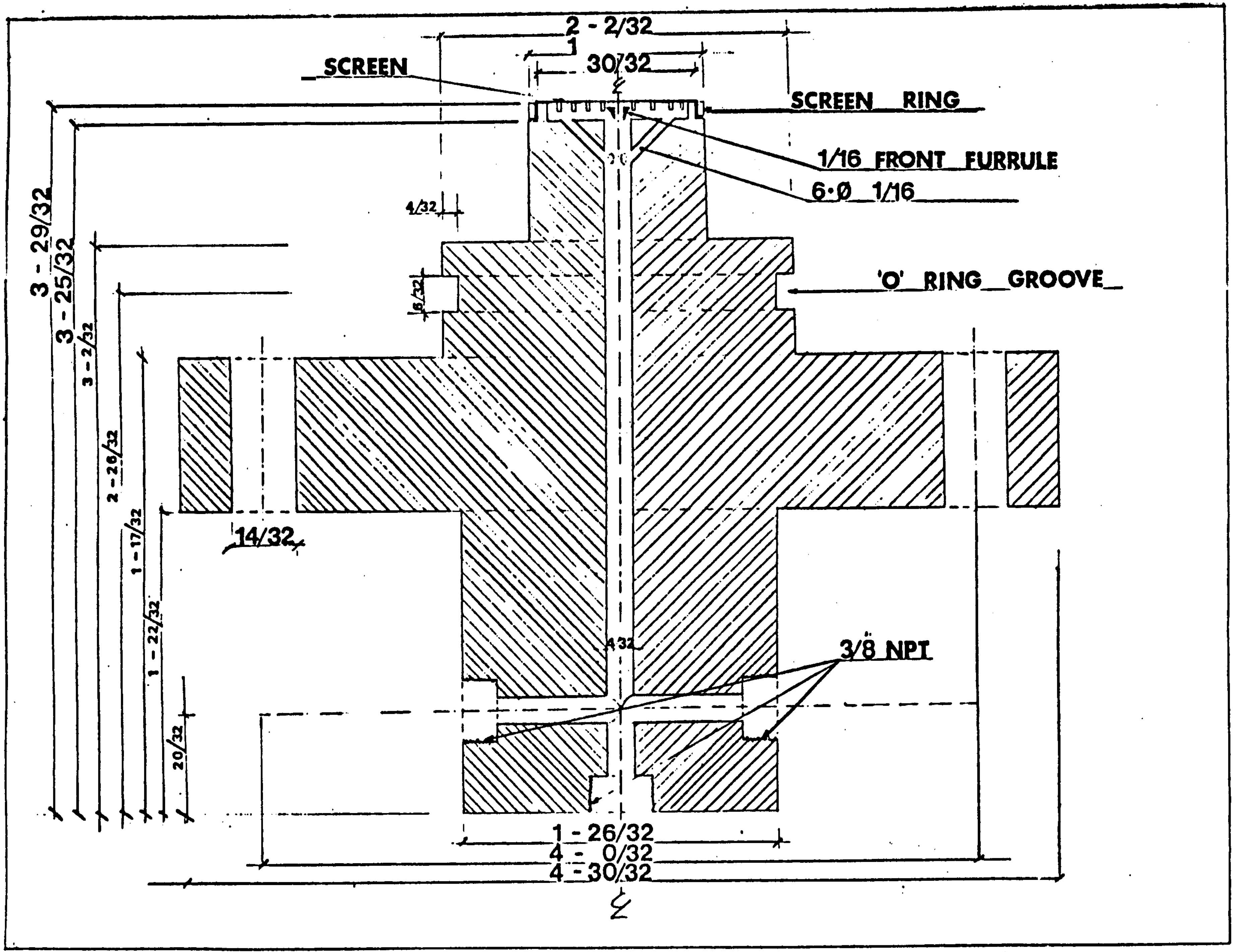


FIGURE 2 - Schematic Diagram of Entire Apparatus


2 - 2/32
1
30/32
SCREEN
SCREEN RING
1/16 FRONT FURRULE
6·Ø 1/16
4/32
'O' RING GROOVE
6/32
3 - 29/32
3 - 25/32
3 - 2/32
2 - 26/32
1 - 17/32
1 - 22/32
20/32
14/32
4/32
3/8" NPT
1 - 26/32
4 - 0/32
4 - 30/32

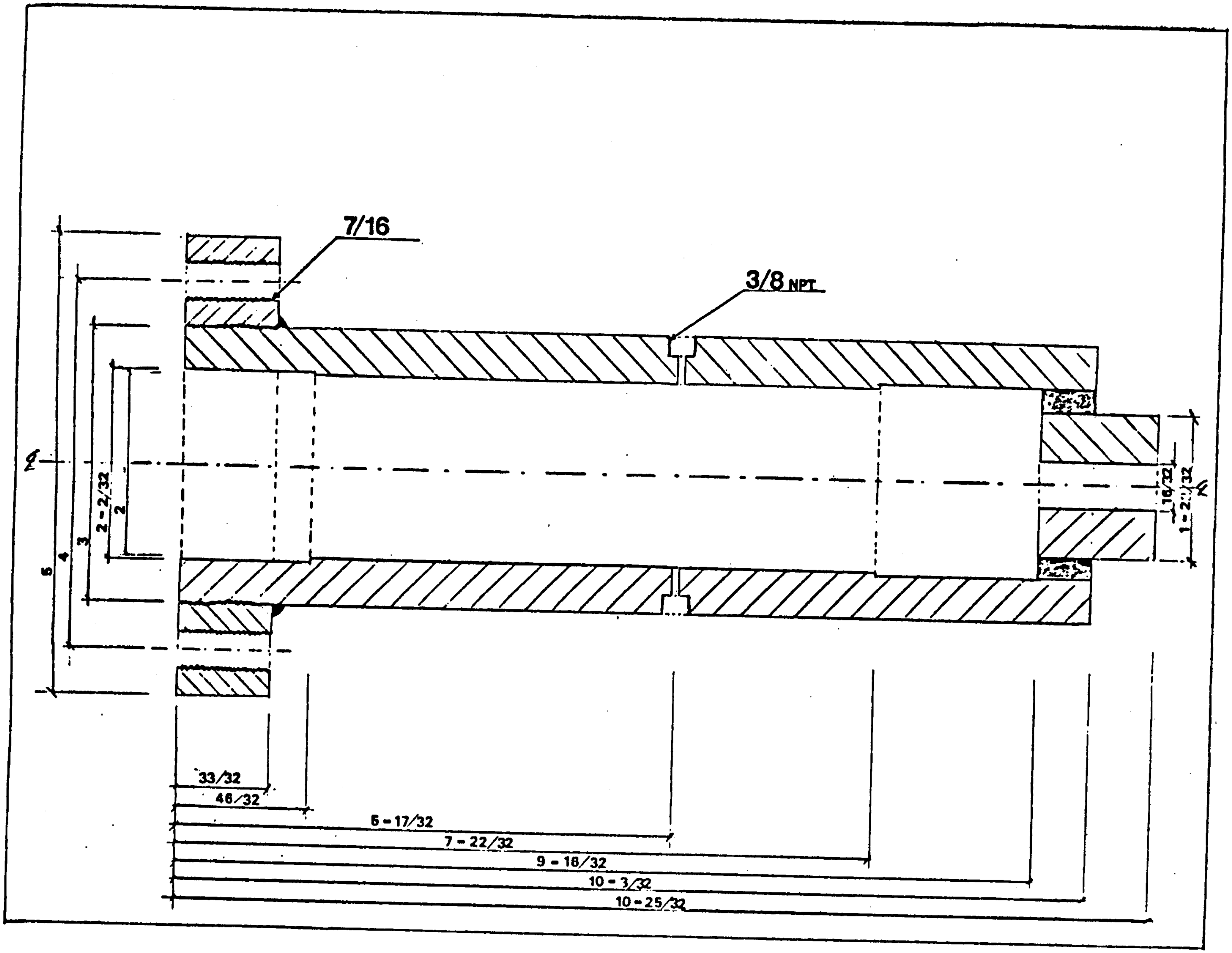


FIGURE 3 - Core Holder

Air Bath

Specifications:

Blue M
Blue M Electric Company
Model #: POM-1406C-1
Serial #: CD-10690
Line Voltage: 240 v, 1 PH, 60 HZ
Temperature Range: 0°F - 650°F
Line Currents: L_1 - 40A, L_2 - 40A

The air bath houses the core holder which hangs from the ceiling to minimize vibration while the air bath is operating. In addition, the air bath houses the heating coils ahead of the core, the core bypass loop, flow lines, high temperature 3-way valves, confining pressure line and thermocouples.

The air bath maintains a constant temperature. It has a variable heating capacity while maintaining small temperature oscillation. The bath is capable of increasing temperature in increments of 100°F over fifteen minutes. The core heating requires two to three hours. The bath is equipped with a vent which makes controlled cooling possible.

Core Holder

The core holder consists of three major parts: (1) the core holder body seen in Figure 3; (2) the up stream core plug, Figure 4; and (3) the down stream core plug, Figure 5.

The assembled core holder is presented in Figure 6. It is designed to withstand a maximum confining pressure of 4000 psig. The core plugs are sealed by "O" rings at both ends. The viton sleeve supporting the core material is rated not to

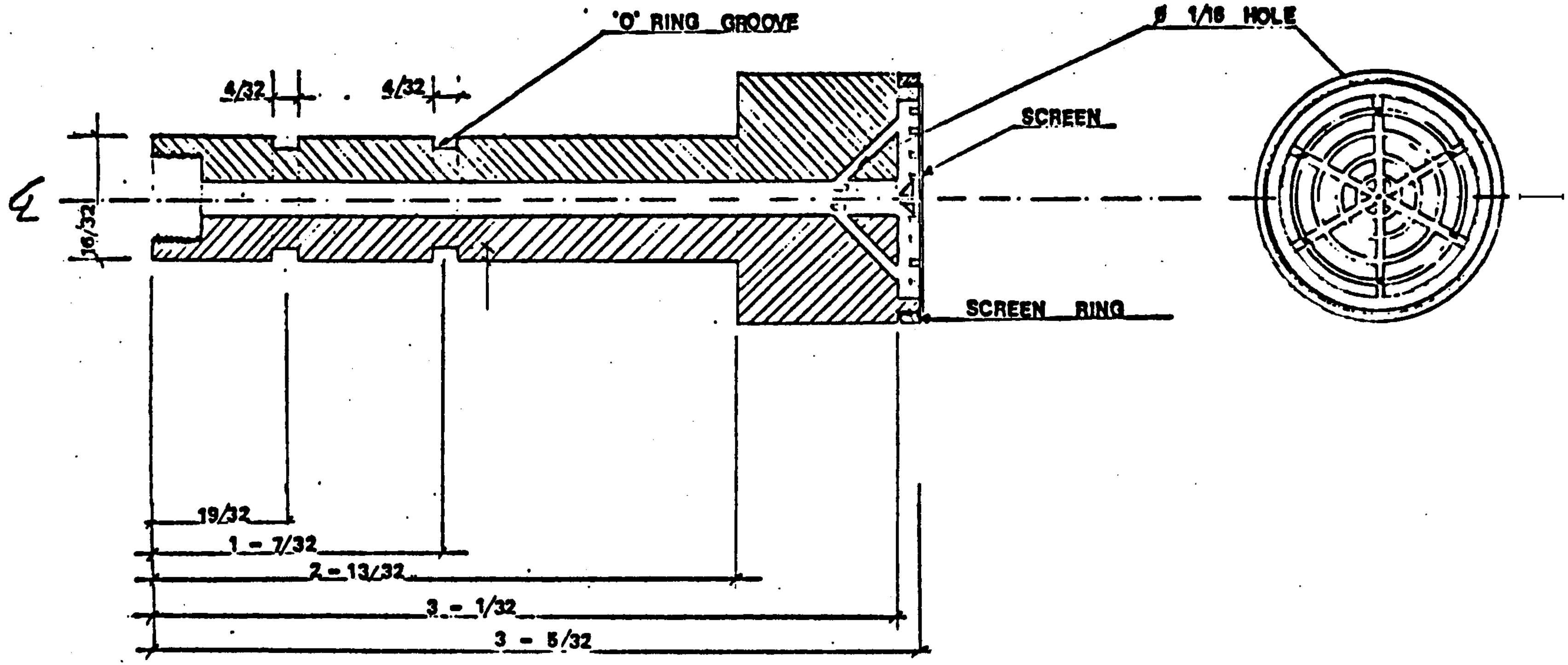


FIGURE 5 - Down Stream Core Plug, from Sageev (ref. 7)

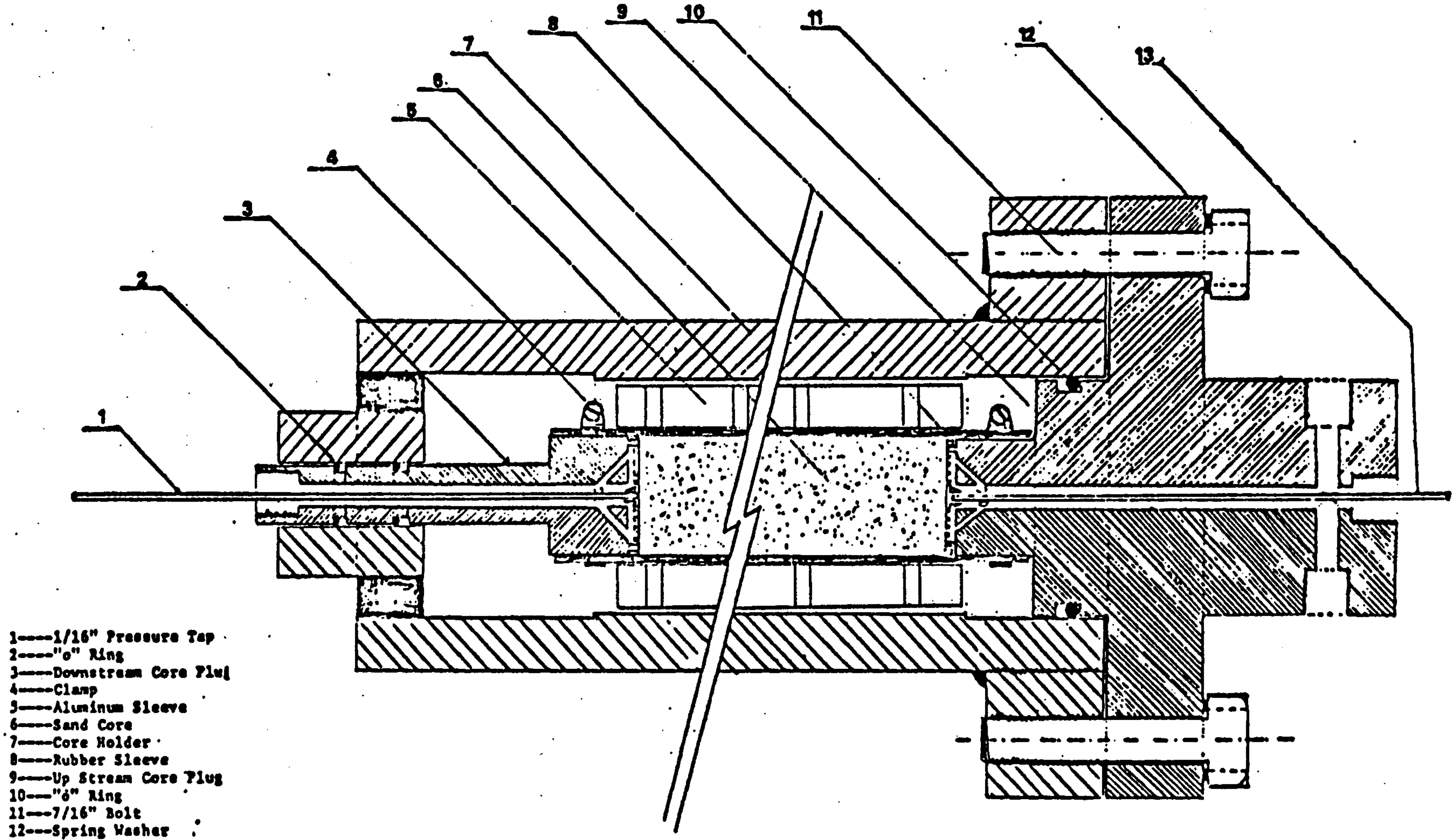


FIGURE 6 - Schematic of the Assembled Core Holder, from Sageev (ref. 7)

exceed 350°F, setting an upper temperature limit on all the experiments. The viton sleeve is held in an aluminum perforated sleeve between the core plugs.

Confining Pressure System

A schematic diagram of the confining pressure system is presented in Figure 7. The high pressure vessel is located outside the air bath and holds both oil and water. The water outlet is located on the lower end of the vessel while the oil outlet is on the upper end. Water was used in the confining chamber of the core holder to minimize the risk of contamination should a failure occur in the viton sleeve of the core holder. The pressure is applied by an Enerpac hand pump rated at 10,000 psig. The pump is oil operated. The confining pressure can be bled off through valve 33 by the discharge of oil into vessel A. The pressure gauge is a Helicoid USA, 8½W, 10,000.

Water Flow System

The water flow system is comprised of the intake reservoir, water pump, excess flow loop, filters, and core bypass loop. A schematic diagram of the flow system is seen in Figure 8.

The intake water reservoir is a two stage feeding system. Water is syphoned from the larger reservoir, #16 in Figure 1, into the primary reservoir (#14), a 4000 cc glass bottle that can be replaced. An adjusting valve is located on

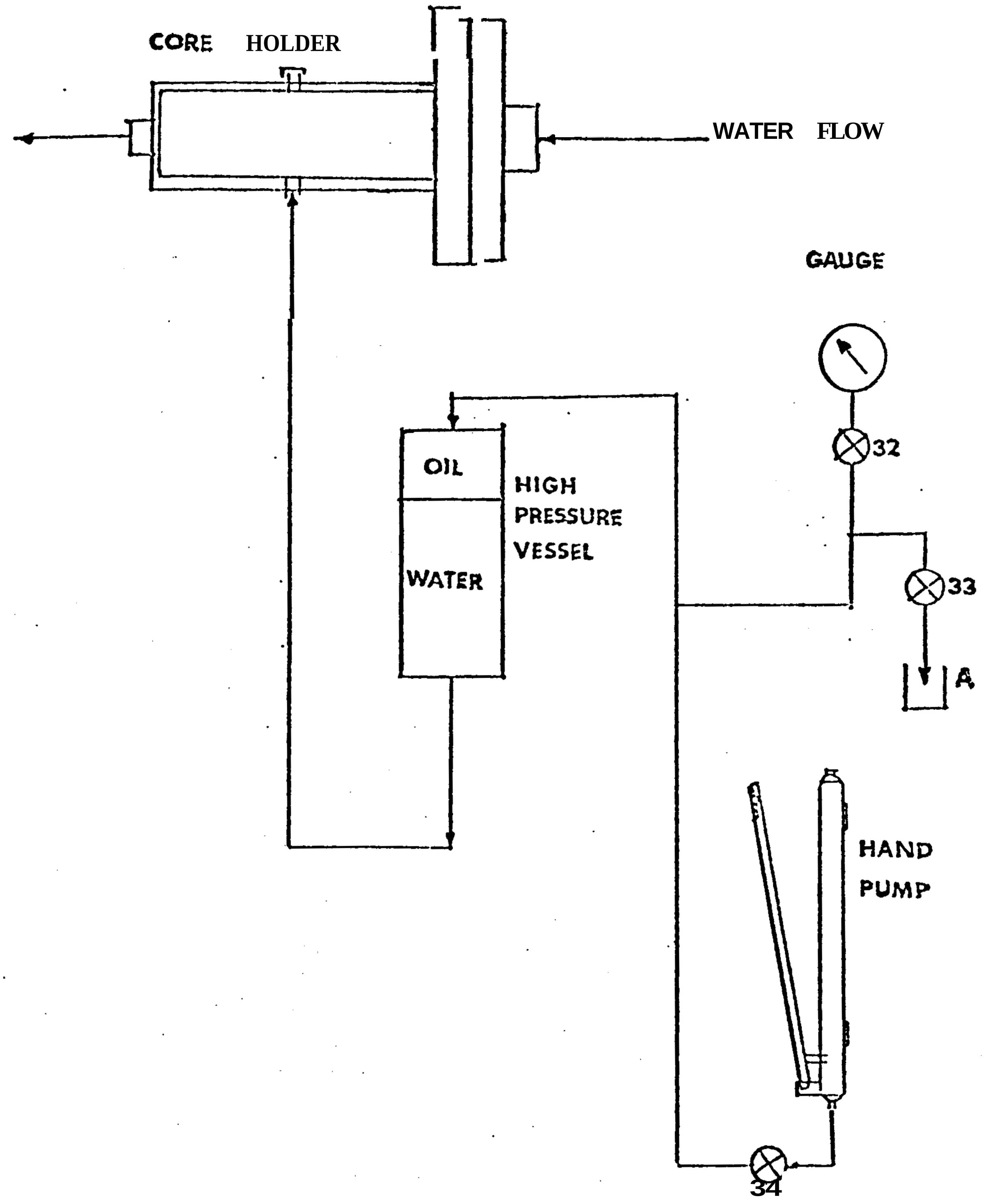


FIGURE 7 - A Schematic of the Confining Pressure System, from Sageev (ref.

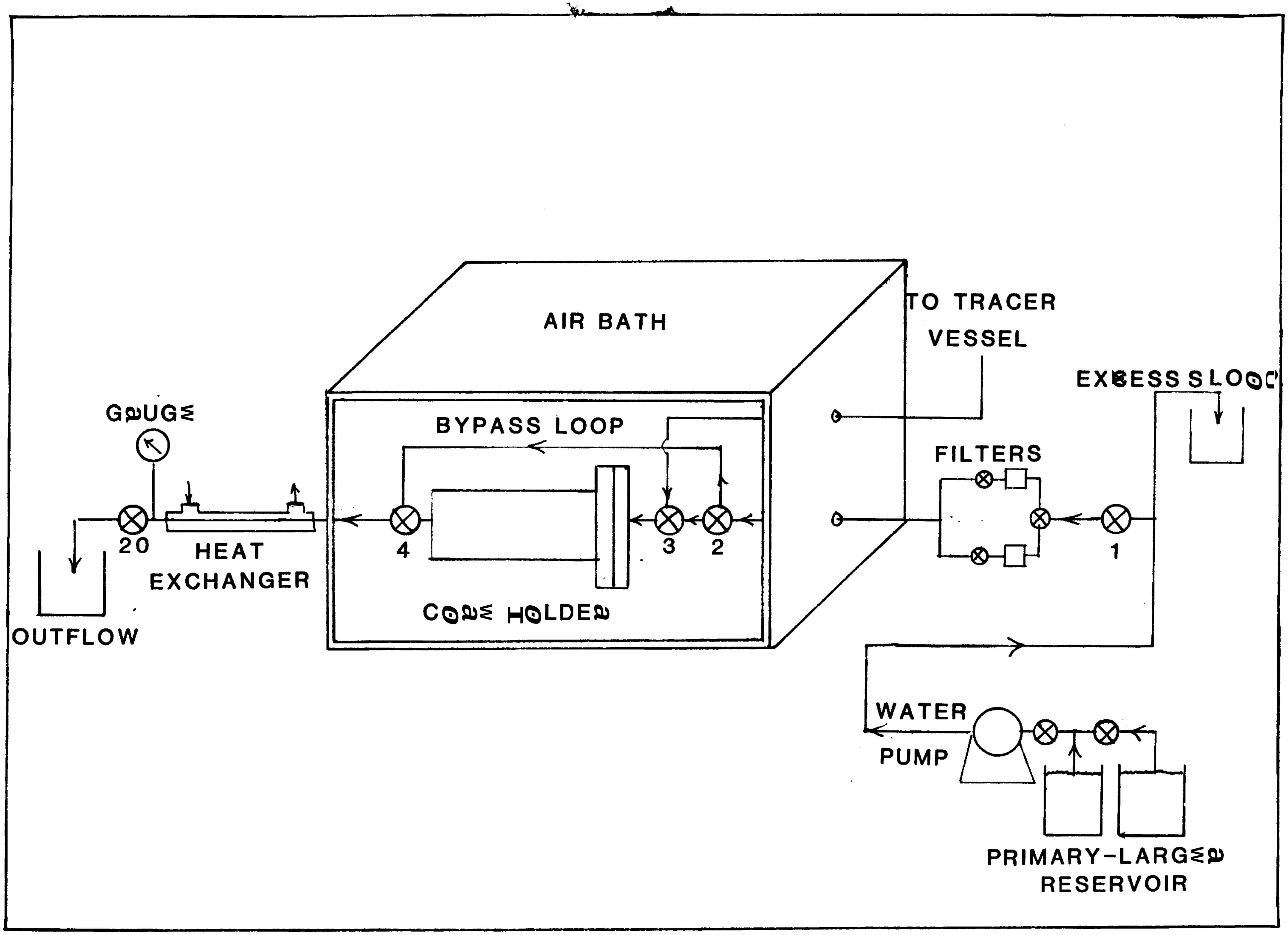


FIGURE 8 - A Schematic of the Water Flow System

the syphon between the two reservoirs and can be set in such a way to maintain a constant water level in the primary reservoir. The two stage feeding system allows for the primary water reservoir to be constantly recharged without shutting down the water pump.

The water pump specifications are as follows:

Lapp Pulsafeeder
Model #LS.20
Serial #X-7704
Process Equipment
Lapp Industries Co., Leroy, N.Y.

The pump is set directly on the floor so no vibrations are transferred to the recording tables. The pump is capable of producing a maximum flow of about 1150 cc/hr at room conditions. An accumulator is attached to the system and can be easily used if a constant flow rate is desired. It was not required in these experiments. Its description and use are described in Reference 7.

The excess flow loop seen in Figure 8 accepts the difference of flow between the pump's output and the flow into the core. The pressure regulator is a ¼" Nupro valve that can be set manually at a range of 150 psig to 450 psig.

From the water pump, the water flows through one of two parallel filters on its way to the core. Flow can be directed through either filter, doubling the time for plugging. These filters cannot be changed during a run due to the air that would be driven into the core. Seven micron filters were used although other types of filter elements can be used.

A core bypass loop was built into the water flow system so that the core could be isolated during specific parts of an experimental run. The bypass loop is presented in Figure 8. After tracer has been injected into the system, water flow is diverted through the core bypass loop, cleaning the system of chemical tracer from the down stream core plug to the outflow vessel. The result is that during the displacement of tracer, only tracer that has been in the core, and not the flow tubing, is collected and analyzed. This procedure is discussed more specifically in the Appendix.

Tracer Flow System

The tracer flow system is presented in Figure 9. It consists of a gas system, tracer container, and a high pressure tracer vessel.

A 2200 psig nitrogen bottle supplies gas to charge the high pressure tracer vessel. The pressure is regulated by a "T" valve on the bottle, and read on the gauge adjacent to the valve. Nitrogen served as the displacement fluid driving chemical tracer through the core. All experimental runs were made with a gas pressure of 250 psig.

The tracer container is a 1000 cc glass bottle. It is connected to the high pressure vessel by ¼" I.D. clear plastic tubing. The high pressure vessel is stainless steel and capable of holding 260 cc of chemical tracer under pressures up to 1000 psig. Before each run, the high pressure vessel is

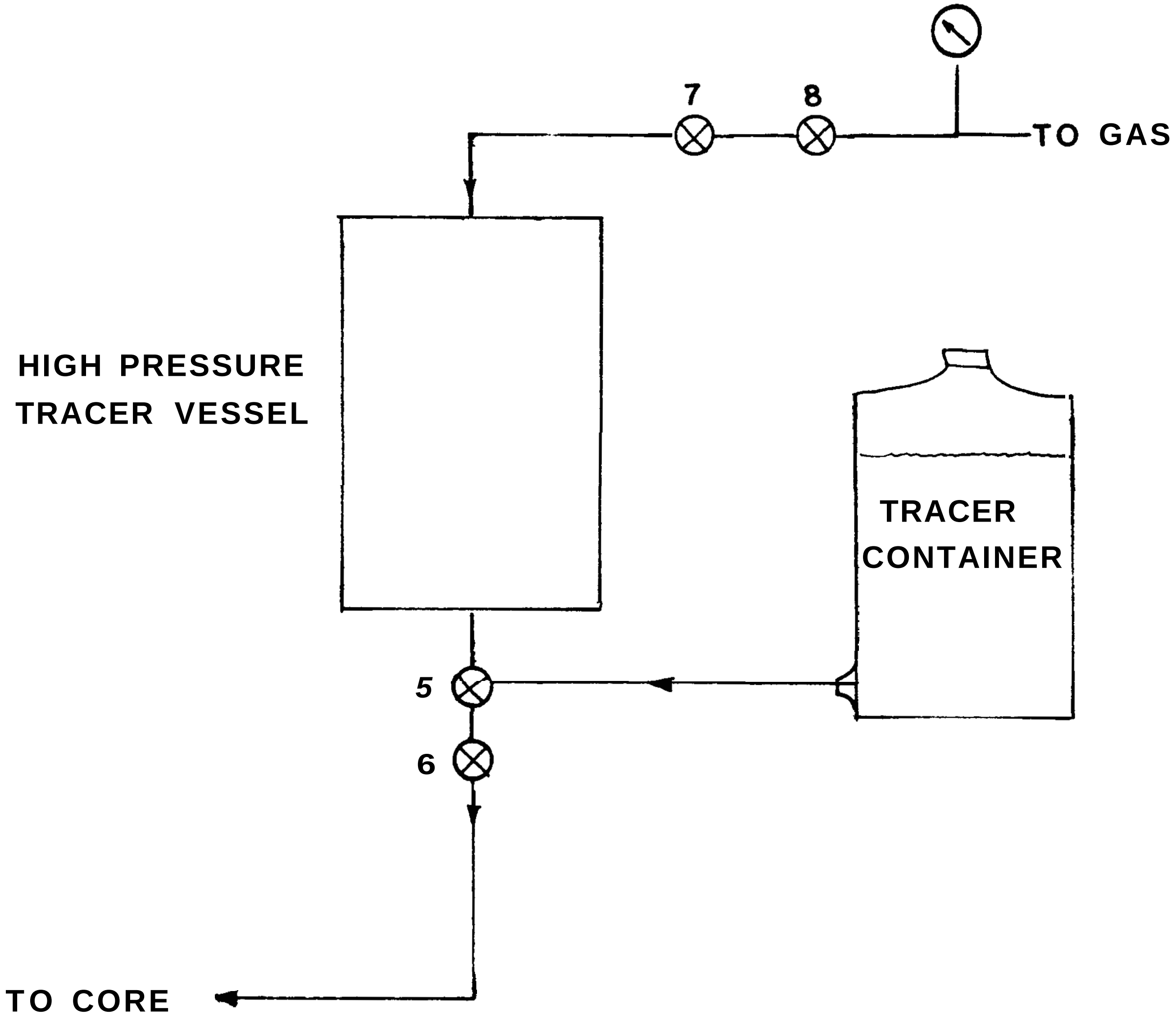


FIGURE 9 - A Schematic of the Tracer Flow System

filled with tracer from the tracer container by gravity drainage.

Temperature Recording

Five thermocouples are scanned once every ten seconds by a Leeds and Northrup Speedomax Recorder. The recorder has twenty-four channels and a range of 0°F to 600°F. The thermocouples are attached: (1) instream, up stream of the core; (2) instream, down stream of the core; (3) to the up stream core plug metal; (4) to the core holder body surface; and (5) outside the air bath to record room temperature. These thermocouples give an accurate indication of when a constant temperature is reached throughout the entire core holder and porous medium. Figure 10 illustrates a profile of the heating cycle.

Cooling System

Figure 11 presents the cooling system. It consists of a heat exchanger, pressure gauge rated to 800 psig, and a needle valve. The heat exchanger is made up of 4” I.D. tubing inside of ¼" I.D. tubing. Tap water flows in the annular space, countercurrent to the tracer and water flow. The needle valve is used to regulate the downstream pressure. It is important to keep the pressure above 100 psig to prevent flash vaporization during the displacement of tracer from the core. The needle valve also helps to maintain a constant flow rate.

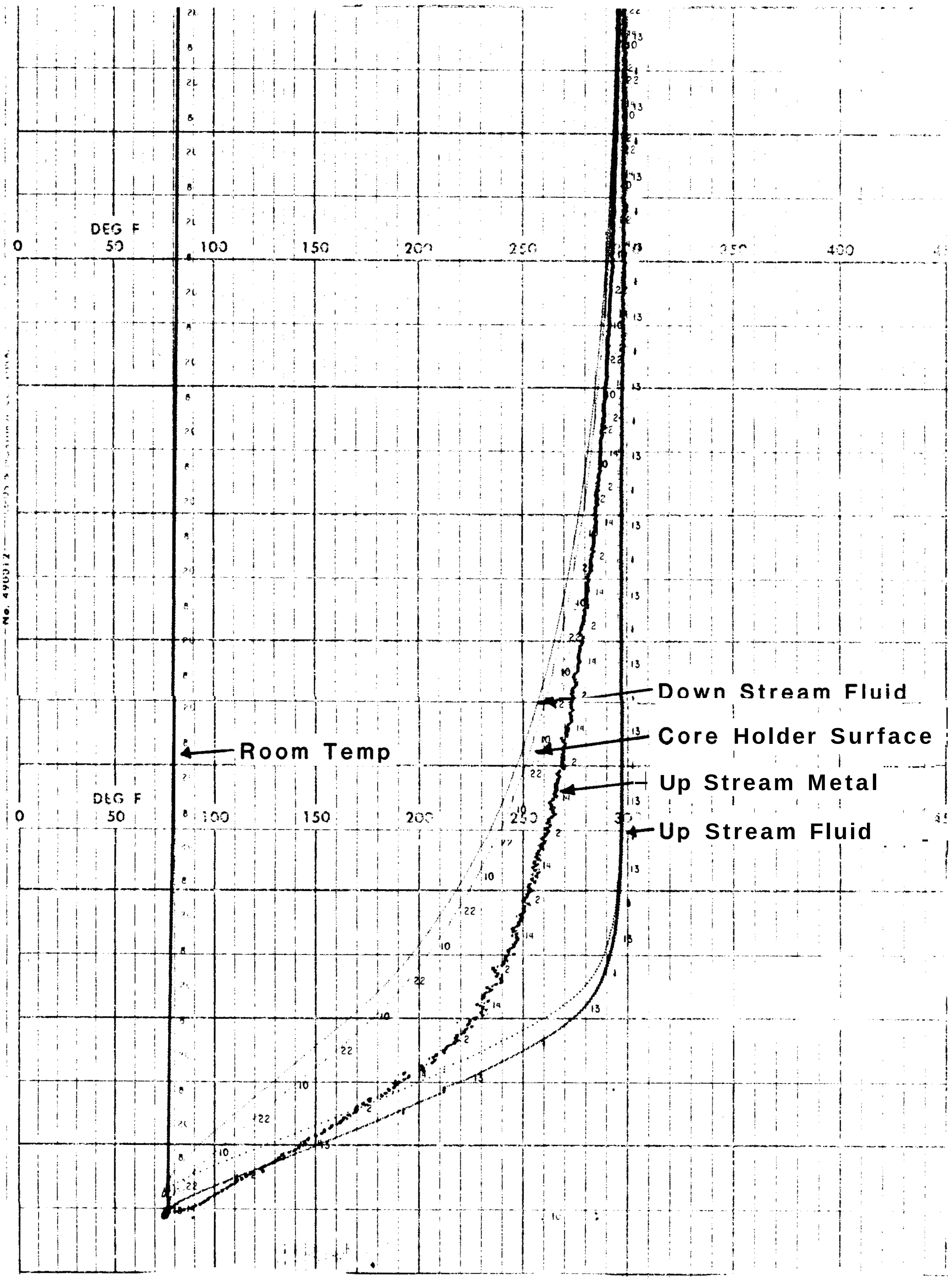


FIGURE 10 - **Heating Cycle** Profile: **Room** Temp to 300°F

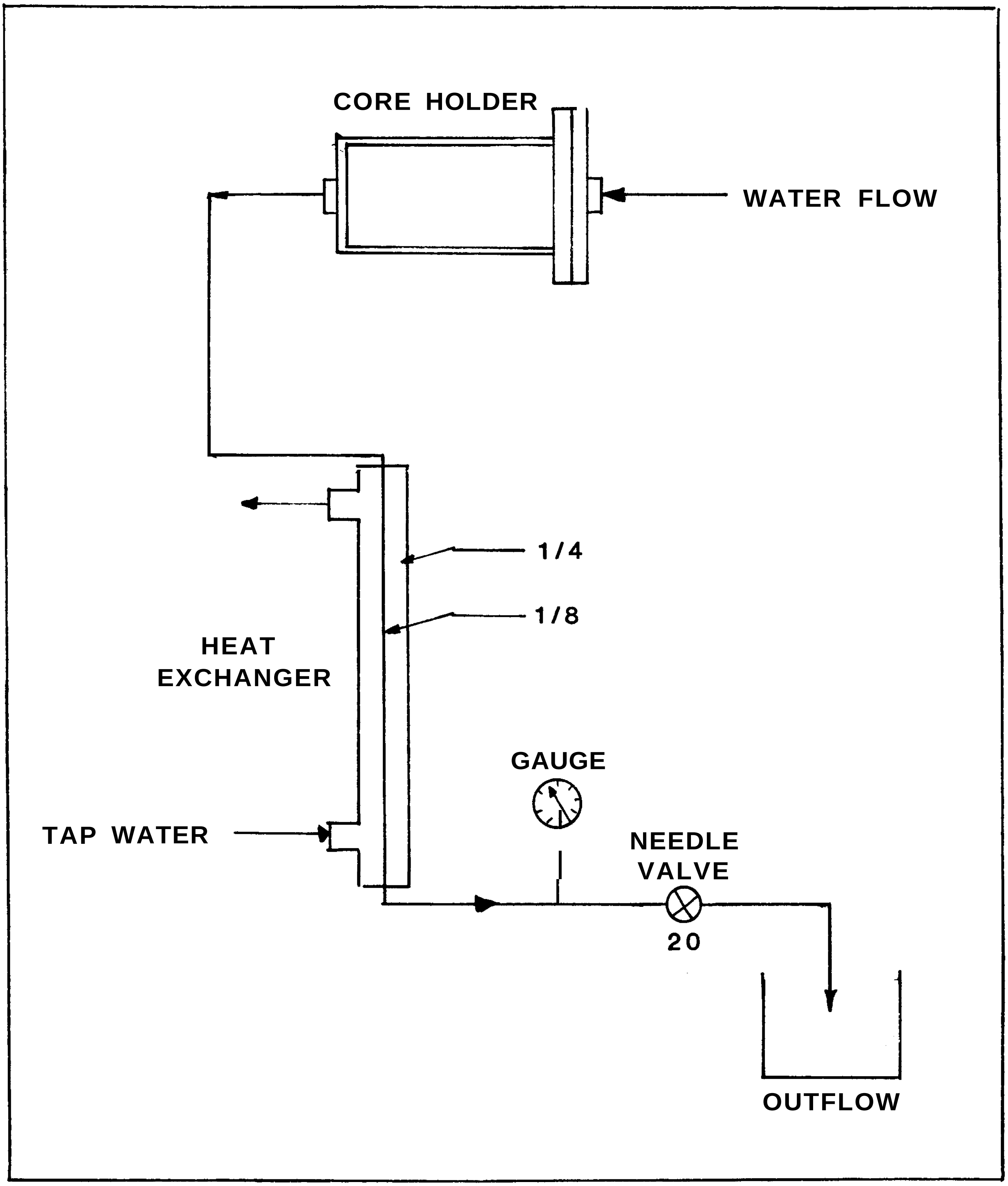


FIGURE 11 - A Schematic of the Cooling System

Chemical Tracer Analysis

Tracer analysis was performed with an Orion Model 94 single junction reference electrodes. Model 94-53 is iodide specific, and Model 94-35 is bromide specific. Ion specific electrodes allow for ion concentrations to be measured quickly and accurately. Estimated accuracy is ± 0.2 ppm. Measurements are read off the Orion Model 901 ionalyzer meter.

Section 5

PROCEDURE

This section will briefly describe the procedure followed in these experiments. The procedure can be divided into three groups: initialization, operation, and tracer analysis. The initialization includes those tasks performed before the experimental runs can proceed. The operating procedure includes all the tasks that need to be performed to complete every experimental run. The tracer analysis procedure includes those steps taken to measure the tracer content in the produced outflow. A detailed description of the procedure can be found in Section 9, Appendix, so that this work can be reproduced.

Initialization

1. Sand Preparation
2. Insertion of Core into Sleeve
3. Core Geometry Measurements
4. Core Holder Assembly
5. Install Core Holder in Air Bath
6. Preload Confining Pressure
7. Inspect and Install Filters
0. Set Excess Loop Pressure for Water Flow System
9. Pull Vacuum on System including Core

Section 6

DISCUSSION OF RESULTS

In this section, a summary **of** the results and discussion **of** the experimental runs will be presented. In addition the results of the core geometry, porosity, permeability, and surface area measurements will be discussed.

Core Geometry

The core dimensions were taken with a micrometer. The up stream measurements are taken 90° apart, while the down stream measurements are taken 120° apart to ensure accuracy around the core plugs. The results are presented below:

Length_{sand} = 15.348 cm

Diameter_{sand} = 2.596 cm

Area_{sand} = 5.293 cm^2

Volume_{sand} = 81.237 cc

Weight_{sand} = 126.5 g

Sand Density (Packed) = 1.557 g/cc

Porosity

As discussed earlier, porosity measurements were taken with a Russel Volumeter. The results are presented here.

Volume_{sand} = 81.2 cc

Initial Reading = 3.6 cc

Final Reading = 41.5 cc

Porosity = **46.7%**

Pore Volume = **37.9 cc**

10. Prepare Proper Tracer Concentrations
11. Calibrate Temperature in Air Bath

Operating Procedure

1. Charge Confining Pressure
2. Install Tracer Fluid and Pressurize
3. Flow Water Through Core and Record
4. Flow Tracer Through Core and Record
5. Flow Water Through Core Bypass Loop
6. Heat Core at Specified Temperature for Specified Residence Time
7. Flow Water Through Core to Displace Trace and Record
8. Depressurize Tracer Flow System
9. Turn Off Water Flow System
10. Cool the System
11. Clean the System

Tracer Analysis Procedure

1. Analyze series of samples collected over a period of time for at least one run.
2. Analyze bulk sample for remainder of runs.

Surface Area

The surface area was calculated using the Carman–Kozeny equation shown below:

$$k = \frac{\phi}{K_z S_p} \qquad (3)$$

k = permeability, cm²

ϕ = fractional porosity

k_z = Kozeny constant, dimensionless

s_p = internal surface area per unit pore volume, cm²/cm³

The Kozeny constant is assumed to equal 5 for unconsolidated porous media. Rearranging Equation 3 for S_p, and substituting in values yields:

$$s_p = \left[\frac{(.467)}{(2.299\times10^{-11})\ (5)}\right]^{1/2}$$

$$s_p = 6.37 \times 10^{4}\ \mathrm{cm^2/cc}$$

$$s_p = \underline{\underline{2.42 \times 10^{6}\ \mathrm{cm^2}}}$$

Water Background

In order to quantify tracer retention under different conditions, it was necessary to analyze the water before and after it had been in the core for background concentrations of the traced ions (I, Br). The analysis of water before it had been through the core revealed trace amounts (< 0.5 ppm) of iodide and bromide.

The water background was analyzed after a three day residence in the core at 300°F. The results are as follows:

Permeability

The core used was cylindrical in shape. Fluid flows through a circular cross section in the axial direction. Flow was considered to be linear and laminar. Laminar flow was proven under very similar experimental conditions in reference 7. For linear laminar flow, Darcy's Law applies:

$$q = \frac{Ak\Delta p}{\mu L} \qquad (1)$$

where:
q = cc/sec at standard conditions
A = cm^2
Δp = atmosphere
L = cm
μ = cp
k = darcies

Δp is measured in psi and converted to atmospheres. Rearranging Equation 1 above for k:

$$k = \frac{(14.969)(q_{sc})(\mu)(L)}{(A)(\Delta p)} \qquad (2)$$

The flow rate was calculated to be q_{sc} = .022 cc/sec under a pressure drop of Δp = 410 psi. The water viscosity at room conditions is μ = 1 cp. Plugging these numbers into Equation 2 yields a permeability value for the core. The results are presented below:

$$k\text{, darcies} = \frac{(14.969)(.022)(1)(15.348)}{(5.293)(410)}$$

$$k\text{, darcies} = .00233$$

$$k\text{, millidarcies} = \underline{\underline{2.3}}$$

	Concentration (ppm)
Iodide	0.26
Bromide	1.0
Bicarbonate	70.0
Calcium	19.0
Chloride	9.0
Magnesium	0.0
Potassium	4.5
Sodium	16.0
Sulfate (SO_4)	<4.0
Total Dissolved Solids	210.0

The total of the common salts equals one half of the total dissolved solids. Some other salt must be present, perhaps silica. The low concentrations of iodide and bromide made it possible to select them as tracers. In addition, the water background analysis made it possible to account for tracer amounts in the material balance calculations.

Experimental Runs

In all of the experimental runs, complete saturation of the core with tracer was achieved by flowing three pore volumes (114 cc). It was assumed in all the calculations that as long as complete saturation of tracer in the core was achieved, the amount of tracer retained was not dependent upon the amount of tracer injected.

In order to ascertain that all the "non-retainable" tracer had been produced during the displacement phase, a series of samples were analyzed for tracer concentration to produce a transient relationship. The results from the 100 ppm potassium iodide run are presented in Figure 12. The area under the curve represents the total mass of %on-retainable" tracer to be produced from the core. As can be seen from the figure, after three pore volumes have been produced, the amount of tracer produced is negligible and considered to be zero.

A summary of the experimental runs and results are presented in Table 1. Column 6 represents the mass of tracer to occupy one pore volume of the core. Column 7 represents the total mass of tracer to be produced from the core. The tracer retained in the core (column 8) is simply the difference between column 6 and column 7. Column 9 represents the percentage of tracer retained (column 8) to the amount that occupies one pore volume (column 6). Column 10 is derived by dividing the internal surface area (2.42 x 10^6 cm^2) into column 8.

The first three runs (#1, #2, #3) were made at room temperature with a two hour residence time. The results from Table 1 show that there was an increase in the amount of retention with an increase in tracer concentration. However, the percentage of tracer retained was so small (0.6% to 4.5%) that for all practical purposes, it can be assumed that

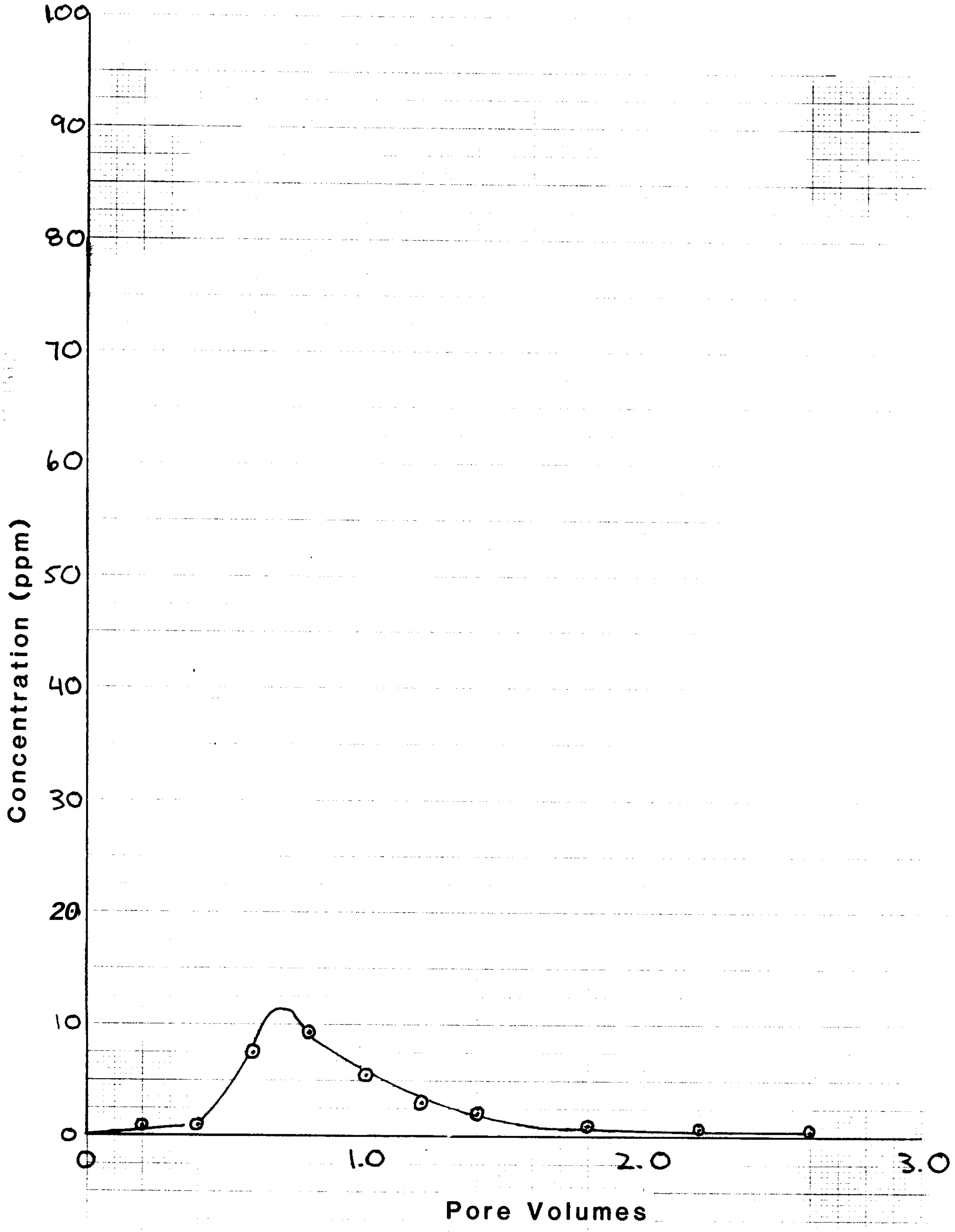


FIGURE 12 - Outflow Tracer Concentration vs. Pore Volumes Displaced

TABLE 1

Summary of Experimental Runs

(1) Run #	(2) Tracer	(3) Concentration (ppm)	(4) Residence Time	(5) Temperature (°F)	(6) Mass of Tracer Into Core (mg)	(7) Mass of Tracer Out of Core (mg)	(8) Tracer Retained (mg)	(9) Tracer Retained (%)	(10) Amount Retained Per Unit Surface Area (mg/cm^2)
1	K1	10	2 Hour	Room	.379	.368	.011	2.9	$4.55\text{x}10^{-9}$
2	K1	50	2 Hour	Room	1.895	1.81	.085	4.5	$3.52\text{x}10^{-8}$
3	K1	500	2 Hour	Room	18.95	18.84	.11	0.6	$4.55\text{x}10^{-8}$
4	K1	10	3 Day	300	.379	.263	.116	30.6	$4.8\text{ x}10^{-8}$
5	K1	20	3 Day	300	.758	.238	.52	68.6	$2.15\text{x}10^{-7}$
6	K1	50	3 Day	300	1.895	.616	1.28	67.5	$5.3\text{ x}10^{-7}$
7	K1	100	3 Day	300	3.79	1.16	2.63	69.4	$1.09\text{x}10^{-6}$
8	K1	500	3 Day	300	18.95	7.28	11.67	61.6	$4.83\text{x}10^{-6}$
9	K1	10	3 Day	300	.379	.59	—	—	—
10	K1	10	1 Day	300	.379	.281	.098	25.9	$4.1\text{ x}10^{-8}$
11	K1	10	3 Day	Room	.379	.065	.314	82.8	$1.3\text{ x}10^{-7}$
12	K1	10	2 Hour	300	.379	.315	.064	16.9	$2.6\text{ x}10^{-8}$
13	NaBr	10	3 Day	300	.379	.243	.136	35.9	$5.6\text{ x}10^{-8}$

retention is negligible under these conditions (2 hour residence, room temperature).

The next series of experimental runs (#4, #5, #6, #7, #8) were made under identical conditions (3 day residence, 300°F) but with the tracer concentration increasing from 10 ppm to 500 ppm. The objective of these runs was to test the effect Of increasing tracer concentration on retention. The results are seen graphically in Figure 13. As can be seen, there is an increase in the mass of tracer retained with an increase in tracer concentration. If the last data point is ignored, a linear relationship between retention and concentration is exhibited. The percentage retention illustrates a behavior that is quite different. For the 20 ppm to 500 ppm runs, the percentage retention was quite constant, oscillating between 61.6% and 69.4%. The 10 ppm run showed a percentage retention of 30.6%, significantly smaller than the other runs. The reason for this is unknown; however, it is enlightening due to the fact that it appears 10 ppm to be the economic limit for the proposed field test at Los Asufres.

Figure 14 presents retention per unit internal surface area (column 10) vs. tracer concentration. The results are similar to those presented in Figure 13. Retention per unit surface area increases with concentration. If the 500 ppm data point is ignored, a linear relationship is exhibited.

Due to the apparent10 ppm economic limit for the field test, the remaining experimental runs were made using this

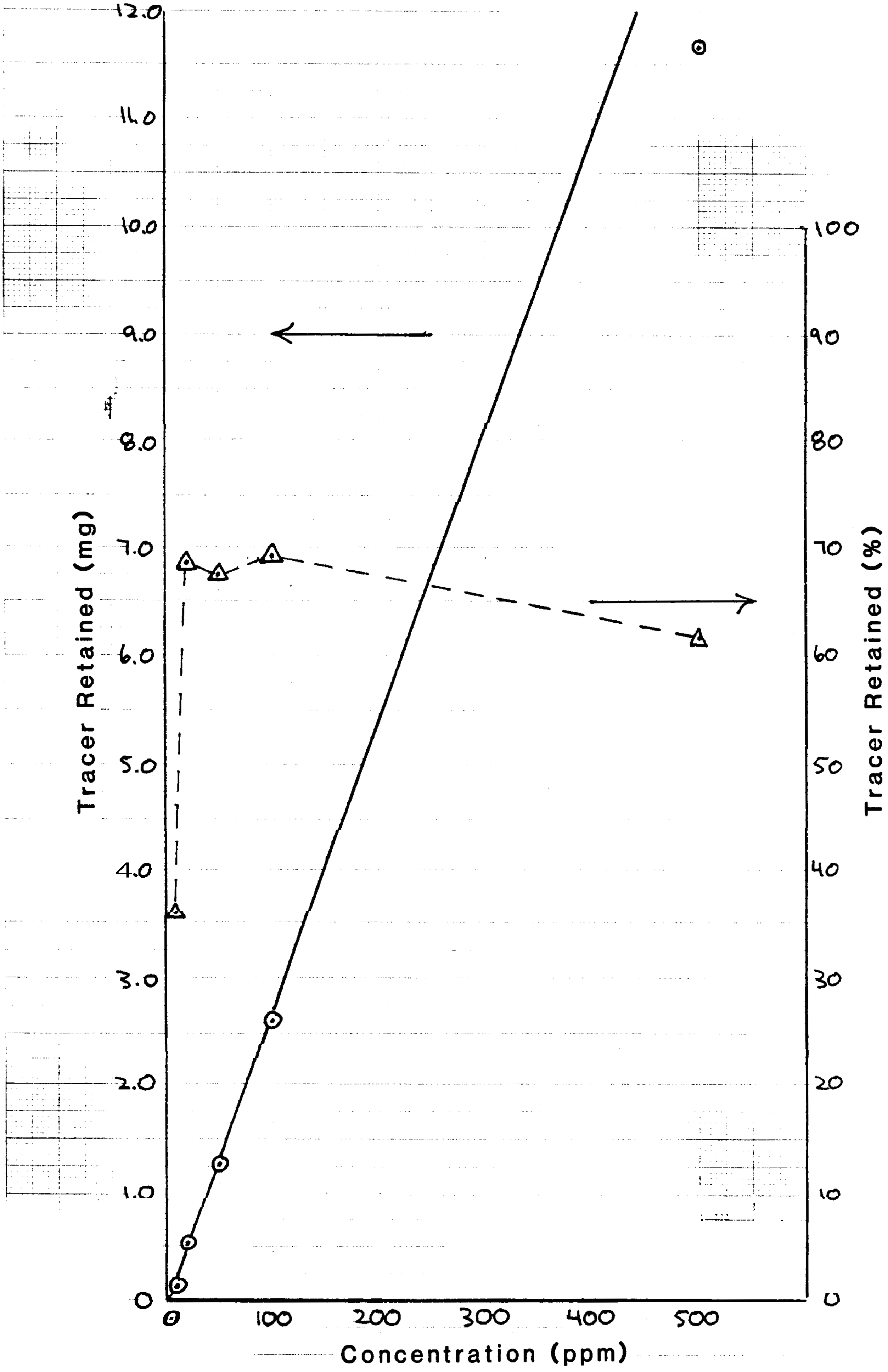


FIGURE 13 - Potassium Iodide, 3 Day Residence, 300°F

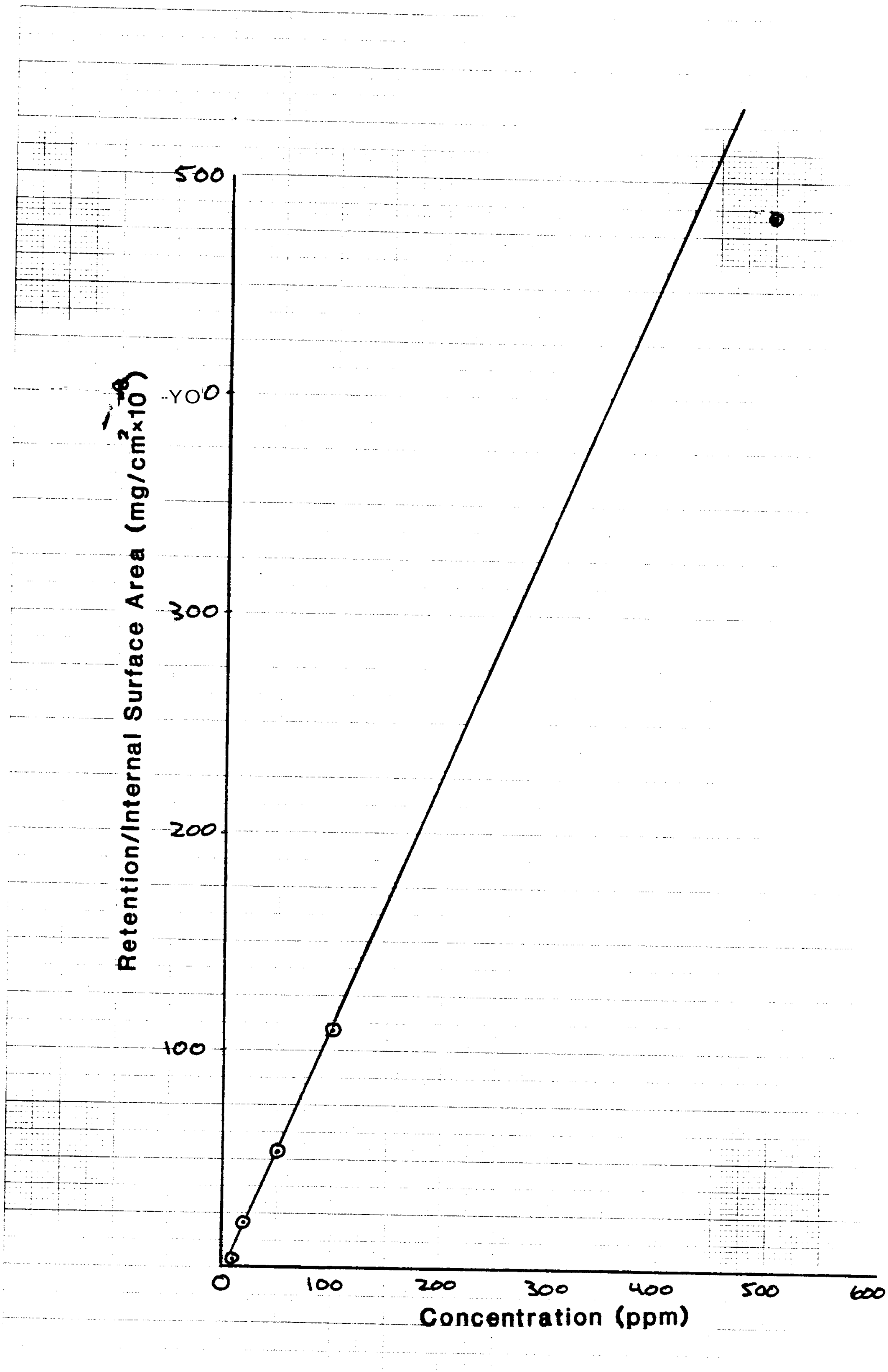


FIGURE 14 - Potassium Iodide, 3 Day Residence, 300°F.

concentration of tracer. Run 19 was with potassium iodide for 3 day residence at 300°F. This run followed runs #4-#8 which used increasing tracer concentration. The objective of run #9 was to reverse back with a low concentration of tracer to see if the microscopic processes causing retention are reversible. The pore volume was injected with 0.379 mg of tracer. At the end of the residence time, more tracer was produced (0.59 mg) than had been injected. Assuming that all the tracer had been produced from the previous run (#8), this clearly shows that retention is reversible.

To study the effect of residence time on tracer retention, runs #10 and #12 were made using 10 ppm potassium iodide at 300°F, but with residence times of 1 day and 2 hours, respectively. The results of these two runs, together with run #4 (3 day residence) are seen in Figure 15. Tracer retention appears to be time dependent, with increasing residence time producing an increase in tracer retention. From Figure 15, it appears that an equilibrium value of retention will be reached given a long enough residence time.

The effect of temperature on retention is seen by comparing run #11 with run #4 and run #1 with run #12. Run #11 was made with 10 ppm potassium iodide for 3 day residence at room temperature (70°F). Run #4 was identical except it was made at 300°F. In run #11, 82.8% of the tracer was retained on the rock, while 30.6% of the tracer was retained in run #4. Run #1 and #12 were made with 10 ppm KI and 2 hour residence.

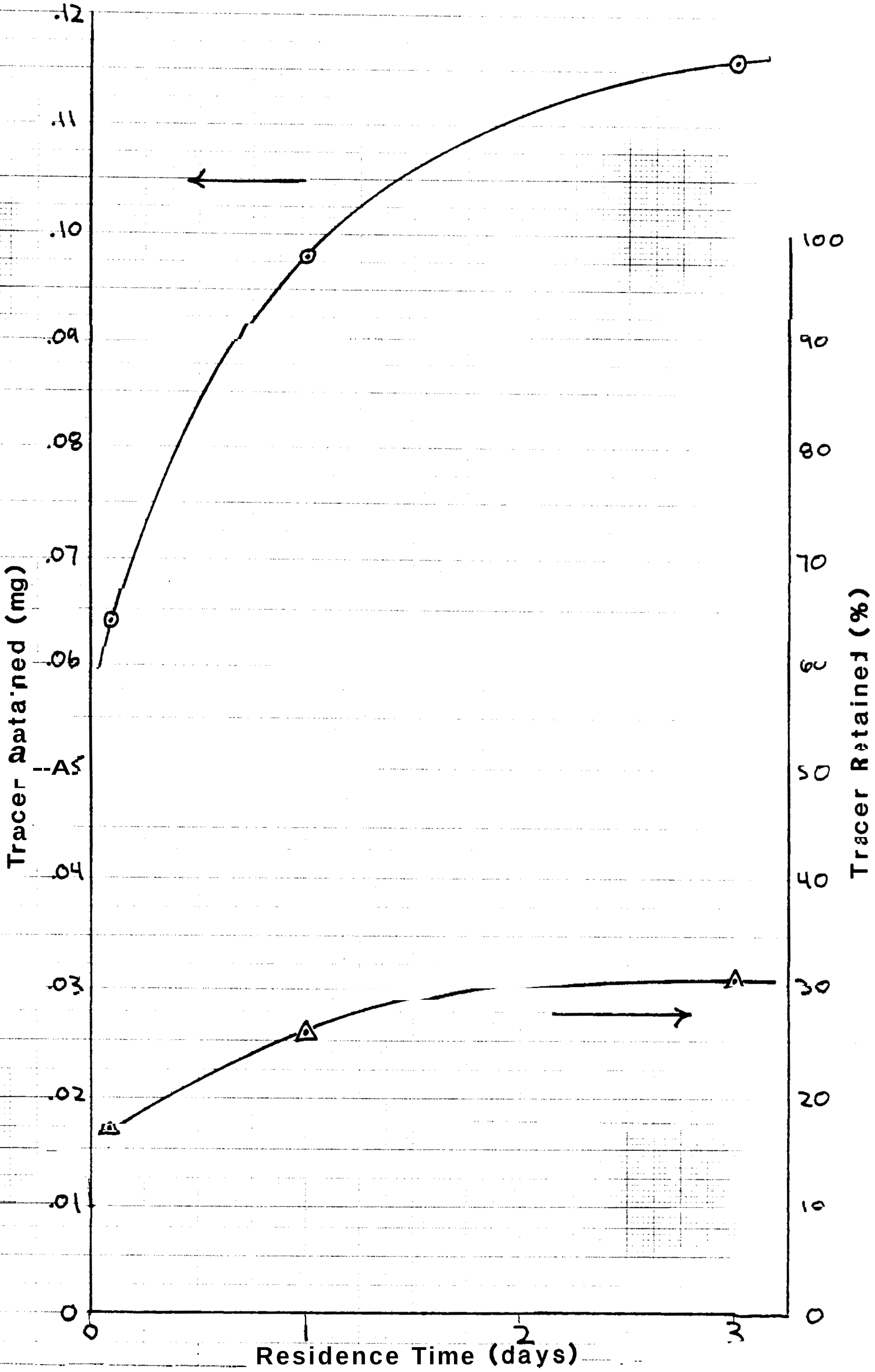


FIGURE 15 - Potassium **Iodide**, 10 ppm, 300°F

Run #1 was at room temperature and showed 2.9% retention. Run #12 was at 300°F and showed 16.9% retention. Comparing these two sets of runs, the results are contradictory. A decrease in retention with increasing temperature in the first set, and an increase in retention with increasing temperature in the second set of runs. The effect of temperature on tracer retention appears to be a minor factor, with tracer concentration and residence time being the dominating factors controlling the processes.

The last run (#13) was made using a different chemical tracer, sodium bromide, at 10 ppm for 3 day residence at 300°F. The result was that 0.136 mg were retained, representing 35.9% of the amount injected. Comparing this result to potassium iodide (run #4) under identical conditions, the potassium iodide showed 30.6% tracer retention. The results are close, but it appears potassium iodide will illustrate smaller values of retention under identical conditions.

Section 7

CONCLUSIONS

The factors causing chemical tracer retention in unconsolidated andesite were evaluated in this laboratory study. The microscopic processes producing tracer retention include adsorption, diffusion, dissolution and ion exchange. It is their composite effect, retention, that we are most concerned with. An apparatus was designed and built capable of measuring tracer retention in porous media under high temperature (300°F). The apparatus produced accurate and reliable results.

The effects of different chemical tracers, tracer concentration, residence time and temperature on retention were evaluated. The following conclusions were reached:

1. An increase in tracer concentration produces an increase in retention.
2. An increase in residence time produces an increase in tracer retention.
3. The microscopic processes comprising retention are reversible.
4. Potassium iodide showed smaller retention values than sodium bromide under identical conditions.
5. The effect of temperature on retention was not conclusive, but appears to be a minor factor.

In order to expand these conclusions, it is recommended that future work be conducted. This work could study a range of consolidated and unconsolidated porous mediums with different chemical and radioactive tracers. The apparatus is designed to accomplish this need. In addition, future experiments should be made at higher temperatures to more closely simulate geothermal reservoir conditions.

Section 8

REFERENCES

1. Amyx, J. W. Bass, D. M., and Whiting, R. L. Petroleum Reservoir Engineering, McGraw-Hill Book Company, New York, 1960.

2. Bear, J. Dynamics of Fluids in Porous Media, Elsevier, New York, 1972.

3. Fossum, M. P. Tracer Analysis in a Fractured Geothermal Reservoir, fulfillment of Masters of Science Degree, Stanford University, Stanford, CA, June 1982.

4. Horne, R. N., "Geothermal Reinjection Experience in Japan," paper SPE 9925 presented at the 1981 California Regional Meeting of SPE, Bakersfield, California, March 1981.

5. Horne, R. N., "Tracer Analysis of Fractured Geothermal Systems," Stanford Geothermal Program, Draft Paper, 1982.

6. Horne, R. N., Rodriquez, R., "Dispersion in Tracer Flow in Fractured Geothermal Systems," Draft Paper, 1982.

7. Sageev, A., Design and Construction of an Absolute Permeameter to Measure the Effect of Elevated Temperature on the Absolute Permeability to Distilled Water of Unconsolidated Sand Cover, fulfillment of Masters of Science Degree, Stanford University, Stanford, CA, December 1980.

8. Strum, P. W., Johnson, W. E., "Field Experiments with Chemical Tracers in Flood Waters," Producers Monthly, Vol. 15, No. 2, 1951, 11-18.

9. Tester, J. N., Bivins, R. L., and Potter, R. M., "Interwell Tracer Analysis of a Hydraulically Fractured Granitic Geothermal Reservoir," paper SPE 8270 presented at the SPE-AIME 54th Annual Fall Meeting, Las Vegas, Nevada, September 1979.

10. Wagner, O. R., "The Use of Tracers in Diagnosing Interwell Reservoir Heterogeneities-Field Results," Journal of Petroleum Technology, November 1977.

11. Vetter, O. J., Evaluation of Well-to-Well Tracers for Geothermal Reservoirs, LBL-11500, Earth Sciences Division, Lawrence Berkeley Laboratory, University of California, August, 1981.

12. Vetter, O. J., "Use of Tracers in Geothermal Injection Systems," 2nd DOE Invitational Well-Testing Symposium, Berkeley, California, September, 1978.

13. Vetter, O. J., "Tritium Tracer As A Means For Reservoir Verification In Geothermal Reservoirs," Report No. EPRl ER-660, January, 1978.

Section 9

APPENDIX

This section is intended to advance an operating description of the procedure so that the work can be reproduced. A detailed description of the initialization procedure is given in reference 7. Many schematics and diagrams from other sections will be referred to in the following section.

1. OPERATING PROCEDURE

I. Charge Confining Pressure (refer to Figure 7)

1. Close valve 33.
2. Open valve 34.
3. Hand pump to pressurize.
4. Pressurize to 2500 psig.
5. Close valve 34.
6. Pressure decreased by bleeding oil through valve 33 into vessel A.

II. Install Tracer Fluid and Pressurize (refer to Figure 9)

1. Close valve 6 and valve 8.
2. Open valve 5 and valve 7.
3. Fill tracer container with proper concentration until high pressure vessel is full and returns are visible from valve 7.
4. Close valve 7 'and valve 5.

5. Record amount of tracer added to tracer container to complete step 3.

6. Open nitrogen gas valve.

7. Open "T" valve on gas to pressurize.

8. Pressurize to 250 psig.

9. Open valve 8 to pressurize tracer vessel.

111. Flow Water Through Core
(refer to Figure 8)

1. Check water level in primary reservoir.

2. Maintain water level at 4000 cc in primary reservoir.

3. Close valve 1.

4. Turn on water pump.

5. Pressure up until discharge of water from excess flow loop.

6. Open valve 1.

7. Open valve 2 to position 1.

8. Open valve 3 to position 2.

9. Open valve 4 to position 1.

10. Open valve 20 to regulate flow.

11. Allow 1000 cc to flow through core.

IV. Flow Tracer Through Core
(refer to Figure 8)

1. Close valve 2.

2. Close valve 20.

3. Open valve 3 to position 1.

4. Open valve 6 to flow trace through core.

5. Allow downstream pressure to reach 250 psig.

6. Open valve 20.
7. Catch outflow and record.
8. Flow tracer until 140 cc* (3 pore volumes plus tubing) flow into bucket.
9. Close valve 4.

V. Flow Water Through Core Bypass Loop (refer to Figure 8)

1. Open valve 2 to position 2.
2. Open valve 4 to position 2.
3. Open valve 20.
4. Flow water until 100 cc flow into bucket to assure cleansing of all tracer in downstream end.
5. Close valve 2.
6. Close valve 4.
7. Close valve 1.
8. Turn off water pump.

VI. Heat Core at Specified Temperature and Residence Time

1. Turn on temperature recorder.
2. Set dial setting on air bath to desired temperature (300°F).
3. Turn on air bath.
4. Maintain constant confining pressure during heating.

---

* It is possible to vary the amount of tracer injected by varying this number accordingly.

5. Bleed oil through valve 33 to maintain constant confining pressure. Bleeding should be done gently to prevent surges.
6. Constant temperature (300°F) achieved throughout core in about 2 hours.
7. Turn off temperature recorder.
8. Record temperature and residence time of run.
9. Allow heating for specified residence time.

VII. Flow Water Through Core to Displace Tracer (refer to Figure 8 and Figure 11)

1. Turn on tap water for heat exchanger.
2. Turn on water pump.
3. Open air bath.
4. Open valve 2 to position 1.
5. Open valve 3 to position 2.
6. Open valve 4 to position 1.
7. Close valve 20.
8. Open valve 1.
9. Maintain downstream pressure above 100 psig to prevent flash vaporization.
10. Open valve 20 to regulate pressure and flow.
11. Catch outflow and record.
12. Record rate of flow of outflow.
13. Maintain constant flow rate.
14. Flow until 140 cc have been caught.
15. Turn off tap water for heat exchanger.

VIII. Depressurize Tracer Flow System
(refer to Figure 9)

1. Close valve 6.
2. Turn off nitrogen gas.
3. Close "T" valve on gas.
4. Open valve 5 to back flush tracer remaining in high pressure vessel into tracer container.
6. Close valve 5.
7. Open valve 7.
8. Record amount of tracer in tracer container.

IX. Turn Off Water Flow System

1. Close valve 1.
2. Turn off water pump.

X. Cool the System

1. Open air bath doors.
2. Open valve 20.
3. Maintain constant confining pressure during cooling, see Part I.
4. Allow entire system to cool to room temperature (70°F).

XI. Clean the System

1. Repeat Part III.
2. Repeat Part V.

2. <u>TRACER-ANALYSIS-PROCEDURE</u>

Due to the lack of necessary equipment and time required, tracer analysis was performed by Sequoia Analytical

Laboratory, Redwood City, California. The attached pages were taken from the equipment manufacturer's (Orion) manual. They provide general information on the equipment, set **up,** construction of calibration curve and analytical procedure.

general information

introduction

The halide electrodes, Model 94-17 (chloride), Model 96-17 (combination chloride), Model 94-35 (bromide), and Model 94-53 (iodide), allow free halide ions in aqueous solutions to be measured quickly, simply, accurately, and economically. Apparatus and solutions required for measurement, general analytical procedures, electrode characteristics, and electrode theory are discussed in this manual. Specific instructions for maintenance of the Model 96-17 combination chloride electrode are found on pages 27-29.

Orion's combination chloride electrode, Model 96-17, was developed specifically for measuring chloride in very small samples with minimal flow and should not be used in conventional stirred solutions.

required equipment

meter – Orion Model 701A digital pH/mv meter or Orion Model 901 ionalyzer for precise laboratory measurements or Orion Model 407A specific ion meter for laboratory, field, or plant measurements.

reference electrode (none required for 96-17) – Orion Model 90-01 single-junction reference electrode for bromide and iodide. For chloride, use Orion Model 90-02 double-junction reference electrode.

magnetic stirrer – recommended for laboratory measurements with Models 94-17, 94-35, and 94-53. **Do** not use with Model 96-17 combination chloride electrode.

graph paper – (for use with digital pH/mv laboratory meters) 4-cycle, semilogarithmic paper for preparing calibration curves.

polishing strips – Orion Cat. No, 94-82-01 for restoring etched or coated membrane (sample supplied with electrode).

required solutions

distilled or deionized water – to prepare all solutions and standards.

ionic strength adjustor (ISA) – to keep a constant background ionic strength. For samples with a total ionic strength less than 0.1 M (see page 26 for how to calculate ionic strength), prepare 5 M $NaNO_3$ by dissolving 42.5 g reagent-grade sodium nitrate in 100 ml distilled water. 2 ml ISA is added to 100 ml standard or sample solutions to bring the background to 0.1 M. For samples above 0.1 M in ionic strength, prepare standard solutions similar to the sample composition.

standard solutions – ***chloride*** – 0.1 M NaCl, Orion Cat. No. 94-17-06 or 100 ppm Cl^- (for low-level measurements), Orion Cat. No. 94-17-07.

bromide – 0.1 M NaBr, Orion Cat. No. 94-35-06.

iodide – **0.1** M NaI, Orion Cat. No. 94-53-06.

For measurements in parts per million, prepare 1000 ppm stock solutions:

chloride – place 1.65 g reagent-grade NaCl in a 1-liter volumetric flask. ***bromide*** – place 1.29 g reagent-grade NaBr in a 1-liter volumetric flask. ***iodide*** – place 1.18 g reagent-grade NaI in a 1-liter volumetric flask. Add about 500 ml distilled water, swirl to dissolve, and dilute to the mark with distilled water.

reference electrode filling solutions – ***Models 94-17, 94-35, 94-53*** – use filling solutions provided with the reference electrodes.

Model 96-17 – Orion Cat. No. 90-00-17 for most chloride measurements. For samples more concentrated than 10^{-2} M (355 ppm Cl^-), Orion Cat. No. 90-0001 filling solution may be used.

connecting electrodes to meter

Remove the protective rubber cap covering the membrane of the solid-state (94 Series) electrodes. Fill the combination chloride electrode according to instructions on page 28.

Insert the reference electrode phone-tip connector and the sensing electrode connector into appropriate jacks on the digital pH/mv meter or specific ion meter. Non-Orion meters may require special adaptors. Consult your meter instruction manual.

checking electrode operation with 701A digital pH/mv meter or 901 digital ionalyzer

Note: Check electrodes daily.

1. Put 100 ml distilled water and **2** ml **ISA** into a 250 ml beaker. Turn 701A Function Switch to MV position. Turn 901 Mode Switch to REL MV. Place electrodes in the solution. Press CLEAR/ READ MV on the 901.

2. Place electrodes in solution. Pipet 1 ml 0.1 M or 1000 ppm standard into the solution. Stir thoroughly. Read electrode potential in millivolts on the 701A and record. Press SET CONCN on the 901.
3. Add 10 ml 0.1 M or 1000 ppm standard. Stir thoroughly. Read electrode potential in millivolts and record. Determine the difference between the first and second potential readings on the 701A. Read the difference directly on the 901. Correct electrode operation is indicated by a difference of 53-59 mv assuming the solution temperature is between 20° and 25°C. If the change in potential is not within this range, see the troubleshooting check list section in the centerfold,

   NOTE: The above procedure measures electrode slope. Slope is defined as the change in potential observed when the concentration changes by a factor of ten.

checking electrode operation with 407A specific ion meter

Note: Check electrodes daily.

1. Put 100 ml distilled water and 2 ml ISA into a 250 ml beaker, Turn Function Switch to the X^- position.
2. Place electrodes in solution. Pipet 1 ml 0.1 M or 1000 ppm standard into the solution. Stir thoroughly. Adjust the Calibration Control until the meter needle points to "1" at the center of the red logarithmic scale.
3. Add 10 ml 0.1 M or 1000 ppm standard. Stir thoroughly. Adjust the Temperature Compensator until the meter needle points to "10" at the extreme right of the red logarithmic scale. Turn the clear Slope Indicator dial until the white arrow on the Temperature Compensator points to the temperature of the solution. Read the percent electrode slope on the lower scale of the dial. Correct electrode operation is indicated by a percent slope between 90 and 100%. If the slope is not within this range, see the troubleshooting check list in the centerfold.

using the electrode

units of measurement

Halide ions can be measured in units of moles per liter, parts per million, or any other convenient concentration unit. See table 1 for conversion factors.

sample requirements

The epoxy electrode body is resistant to all aqueous solutions. The halide electrodes may be used intermittently in methanol, benzene, or acetonitrile. Consult Orion's Technical Service Group for recommendations on use of the electrode in other organic solvents.

Samples and standards should be at the same temperature.

analytical procedures

Direct measurement is a simple, direct procedure for measuring the free halide concentration of a large number of samples. Only one meter reading is required for each sample.

In the absence of complexing agents, results can be verified by a known addition procedure (see pages 15 to 21). Known addition is also a useful method for measuring occasional samples as the preparation of a calibration curve is not required. As it measures total halide ion concentration rather than free halide ion concentration, known addition is useful when a large excess (50-100 times) of complexing agent is present. As in direct measurement, any convenient concentration unit can be used.

table 1

concentration unit conversion factors

moles per liter	ppm Cl^-	ppm Br^-	ppm I^-
10^{-2}	355	799	1270
10^{-3}	35.5	79.9	127
10^{-4}	3.5	8.0	12.7

figure 1

typical iodide electrode calibration curve

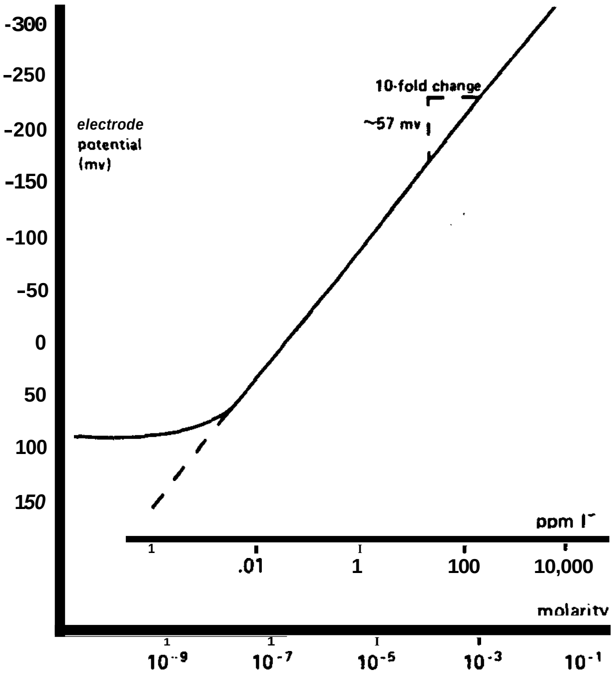


figure 2

typical chloride electrode calibration curve

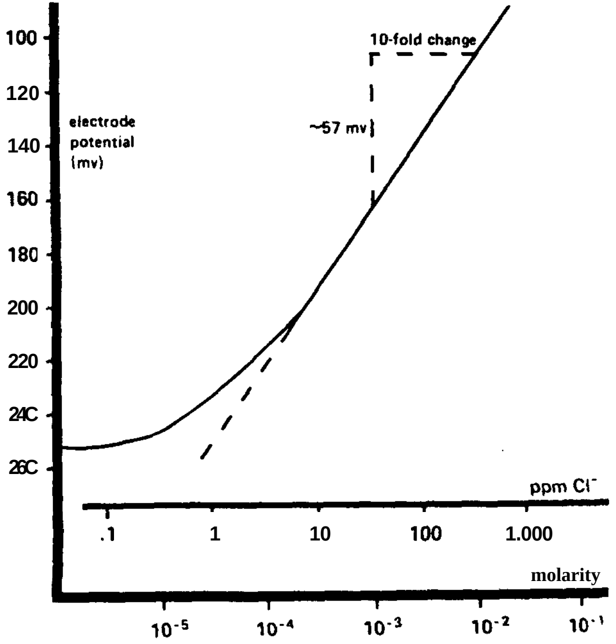
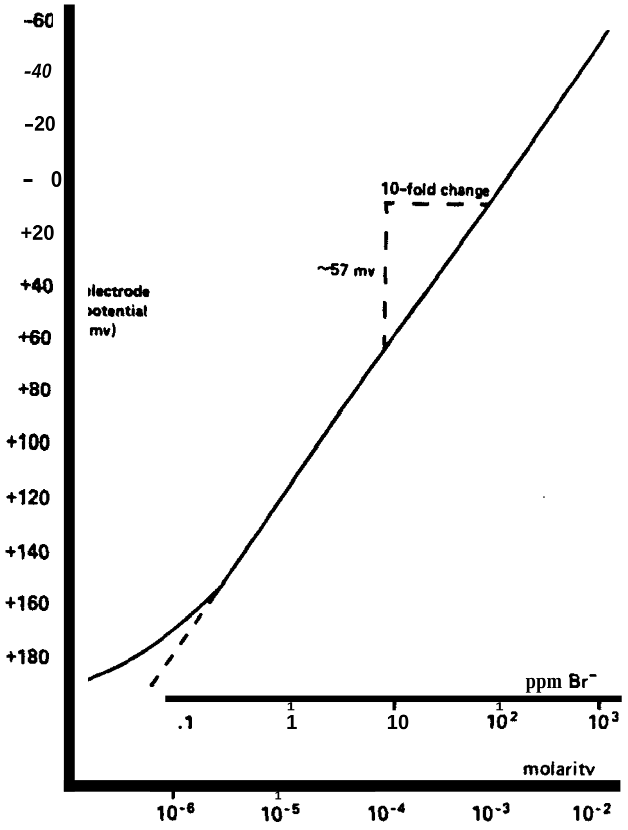


figure 3

typical bromide electrode calibration curve



In the direct measurement procedure, a calibration curve is constructed ***on*** *semilogarithmic paper. Electrode potentials of standard solutions are measured and plotted* ***on*** *the linear axis against their concentrations on the log axis. In the linear regions of the curves,* ***only*** *three standards are needed to determine a calibration curve. In nonlinear regions, more points must be taken. The direct measurement procedures in this manual are given for concentrations in the region* ***of*** *linear electrode response. Low-level measurement procedures are given for measurements in the* ***non-*** *linear region.*

electrode characteristics

electrode response

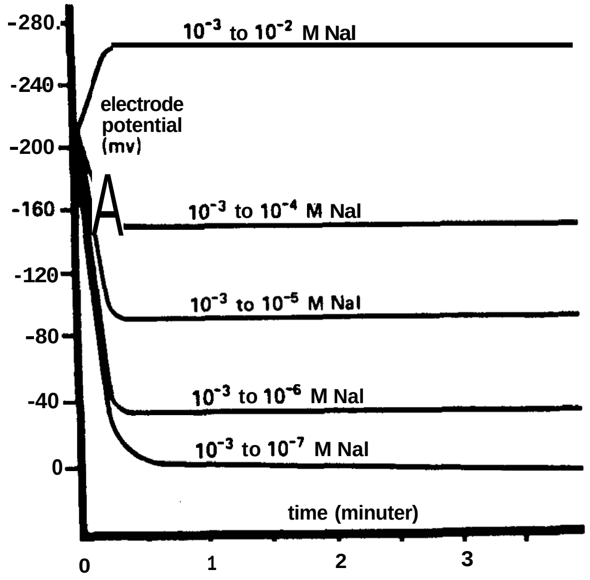
Electrode potential plotted against halide concentration on semilogarithmic paper results in a straight line with a slope of about 59 mv per decade. See figures **1-3.**

The electrode exhibits good time response **(99%** response in one minute or less) for halide concentrations above 10^{-5} **M.** Below this value, response times are considerably longer. See figure **4.**

If the electrode response drops off or the potential reading becomes drifty, the membrane may need repolishing. Use the special Orion polishing strips, Cat. No. 94-82-01. To polish, cut off a one-inch length of the paper and wet the frosted side. Using a circular motion, polish the electrode sensing element for about thirty seconds. Rinse and soak in a standard solution for about five minutes before use.

figure 4

typical electrode response to step changes in iodide concentration



interferences

High levels **of** ions which form very insoluble salts **of** silver may deposit a layer of the salt on the membrane, causing electrode malfunction. In addition, strongly reducing solutions may form a surface layer of silver. In either case, restore performance by polishing.

Mercury should be absent from samples.

Measurements can be made in solutions containing oxidizing agents such as Cu^{++}, Fe^{+++}, and MnO_4^-.

Table **5** gives the maximum allowable concentration of the more common interfering ions, expressed as the ratio of the interfering ion molarity to the sample halide molarity. If the ratio is exceeded, readings will be in error. If the ratio is less than that listed in the table, neither the accuracy of the measurement nor the surface of the electrode membrane will be affected. To convert molarity to ppm, see table **1** on page 5.

table 5

maximum allowable ratio of interfering ion to halide (moles per liter)

	interference	maximum ratio for each electrode		
		chloride	bromide	iodide
(a)	**OH-**	80	3×10^4	–
(b)	Cl^-	–	**400**	10^6
(b)	Br^-	3×10^{-3}	–	5×10^3
(b)	**I-**	5×10^{-7}	2×10^{-4}	–
(c)	$S^=$	$<10^{-6}$	$<10^{-6}$	$<10^{-6}$
(c)	CN^-	2×10^{-7}	8×10^{-5}	**0.4**
(d)	NH3	**0.1**2	2	–
(d)	$S_2O_3^=$	0.01	$20\, C_{Br^-}$ $+0.01$	10^5

(a) Hydroxide interference can be removed by acidifying to pH **4** with 1 M HNO_3.

(b) Mixed halides in solution can be measured by a Gran's plot titration. Write or call Orion's Technical Service Group for information.

(c) Sulfide and cyanide may be removed by adding a nickel (+2) solution.

(d) Represents a complexing species. Maximum level can be exceeded without electrode damage. Value shown is for 1% error.

For example: For the bromide electrode, what is the maximum level of chloride tolerable in a sample whose bromide concentration is 10^{-3} M? From table 5 the maximum ratio is:

$$\frac{[Cl^-]}{[Br^-]} = 400$$

or

$$[Cl^-] = 400\,[Br^-] = 400 \times 10^{-3} = 0.4$$

= **0.4** M maximum chloride concentration for no interference

limits of detection

The lower limits of detection are determined by the very slight water solubility of the membranes. At low levels electrodes respond to halide ions in the sample as well as to ions dissolved from the membrane. The dashed line in figures 1-3 shows the theoretical linear response compared to actual response (full line); the discrepancy between the curves is due to response to the dissolved membrane. For measurements in the nonlinear region below 2×10^{-4} M or 7 ppm (chloride) or 2×10^{-6} M or 0.2 ppm (bromide), a low-level procedure is recommended. Low-level procedures are not necessary for iodide, which is linear to 2×10^{-8} M or 2×10^{-3} ppm.

complexation

Halide ions form complexes with some metal ions. Since the electrode responds only to free halide ions, the presence of any complexing agents lowers the measured Concentration. Table 6 lists the levels of complexing metals causing a 10% error.

Total concentration in the presence of a large excess (by a factor of at least 50-100) of complexing agent can be measured by the known addition method (pages 15-21).

table 6

maximum levels of complexing agents

complexing agent		electrodes:	
	chloride	bromide	iodide
Bi^{+++}	4×10^{-4} M (80 ppm)	4×10^{-4} M (80 ppm)	2×10^{-5} M (4 ppm)
Cd^{++}	2×10^{-3} (200 ppm)	2×10^{-3}	5×10^{-4}
Mn^{++}	2×10^{-2} (1100 ppm)	–	–
Pb^{++}	2×10^{-3} (400 ppm)	8×10^{-3} (1600 ppm)	5×10^{-3} (1000 ppm)
Sn^{++}	6×10^{-3} (700 ppm)	2×10^{-2} (2400 ppm)	–
Tl^{+++}	4×10^{-5} (8 ppm)	2×10^{-5} (4 ppm)	–

reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift, and noise. Within the electrode's operating range, reproducibility is independent of concentration. With calibration every hour, direct electrode measurements reproducible to ±2% can be obtained.

electrode storage

Rinse electrode, blot dry, and replace the protective rubber cap for storage. Do not store electrode in distilled water.

temperature effects

Changes in temperature cause electrode response to change in slope and shift somewhat in millivolts. Temperature changes require recalibration of meter and electrode. Standards and samples should be within ±1°C (±2°F) of one another. The slope of a monovalent anion electrode increases in magnitude by 1 millivolt per 5°C change in temperature.

theory of operation

The halide electrodes consist of silver halide/silver sulfide membranes bonded into the tip of an epoxy electrode body. When the membrane is in contact with a halide solution, silver ions dissolve from the membrane surface and the electrode develops a potential due to the silver ion concentration. This concentration is, in turn, determined by the sample halide ion concentration. This potential is measured against a Constant reference potential with a digital pH/mv meter or specific ion meter. The measured potential Corresponding to the level of the halide ion in solution is described by the Nernst equation:

$$E = E_0 - S \log (A)$$

where:

E = measured electrode potential
E_0 = reference potential (a constant)
A = halide ion level in solution
S = electrode slope (about 59 mv at 20°C)

The level of halide ion in solution, **A,** is the activity or "effective concentration". The halide activity, **A,** is related to the halide ion concentration of free halide ions, C_f, by the ionic activity coefficient, γ:

$$A = \gamma C_f$$

Ionic activity coefficients are variable and largely depend on total ionic strength.

Ionic strength is defined as:

$$\text{ionic strength} = \tfrac{1}{2}\Sigma C_i Z_i^2$$

where:

C_i = concentration of ion **i**

Z_i = charge of ion **i**

If the background ionic strength is high and constant relative to the sensed ion concentration, the activity coefficient is constant and activity is directly proportional to concentration.

Ionic strength adjustor (ISA) is added to all standards and samples so that the background ionic strength is high and constant relative to variable concentrations of halide. For all halide electrodes, $NaNO_3$ is the recommended **ISA.** Other solutions can be used as long as they do not contain ions that would interfere with the electrode's response to halide.

specifications

concentration range	***chloride:*** 1M to 5 x 10^{-5} M 35,500 to 1.8 ppm ***bromide:*** 1M to 5 x 10^{-6} M 79,900 to **0.4** ppm ***iodide:*** 1M to **5** x 10^{-8} M ,127,000 to **5** x 10^{-3} ppm
pH range	pH **0** - 14
temperature range	**0** to 50°C continuous use 51 to 100°C intermittent **use** **10** to 100°C **for** Model 96-17
electrode resistance	less than **0.1** megohm
reproducibility	***2%**
minimum sample size	3 ml in a ***50*** ml beaker, 0.3 ml **in** Orion Microsample **Dish** (Cat. No. 92-00-14), 10µl for Model 96-17
storage	dry, with protective rubber cap in place (94 Series); keep Model 96-17 upright, immersed in standard solution
size	length: 13.9 cm diameter: 12 mm cap diameter: 16 mm cable length: 75 cm

specifications subject to change without notice.