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GEOTHERMAL CHEMISTRY IN-LINE INSTRUMENTATION

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ABSTRACT

During Fiscal Years 1986 and 1987, Pacific Northwest Laboratory (PNL) operated under declining budgets to achieve several major milestones:

- A Site Access Agreement with San Diego Gas and Electric Company was signed and since renewed for Fiscal Year 1987. The agreement allows PNL access to the Heber Binary Plant for conducting experiments.
- The PNL field laboratory was moved from East Mesa to the Heber Binary Plant.
- A subcontract was let to a commercial supplier of pH probes to build advanced transistor-based pH sensors.
- A field test determined response of the transistor-based pH probes to Heber brines.
- A filter test was performed to look at scaling tendencies of the Heber plant brine if it were cooled below 150°F.
- Two prototype particle counters based on ultrasonic sound and a laser beam scattering were tested in the laboratory and subjected to one field test.

CONTENTS

FIGURES

INTRODUCTION

Geothermal activities at Pacific Northwest Laboratory (PNL)[a] have always emphasized understanding of brine chemistry as it relates to potential scaling, corrosion, or reinjection problems. Development of instruments to aid in this understanding has been a major goal of all the work. Past work involved extensive corrosion monitoring and instrument testing at the Magma Electric Company East Mesa Plant. Corrosion probes, conductivity meters, redox probes, pH probes, CO_2 probes, particle meters, and leak detectors were all developed and evaluated there.

During 1986, PNL completed a Site Access Agreement with the San Diego Gas and Electric Company to install two trailers on site and test connections on the inlet and outlet brine line at the Heber Binary Demonstration Plant.

In Fiscal Year 1987, tests were started at the Heber Plant. Funding levels limited activities to testing transistor pH sensors, on-line and particle analyzers, and a small study of suspended solids in the geothermal brine at the Heber Plant.

FIELD TEST OF TRANSISTOR pH SENSOR

The pH sensor subcontractor developed five prototype pH sensors and two CO_2 partial pressure sensors. Both probes are based on Ion Sensitive Field Effect Transistor (ISFET) technology. The subcontractor designed and built the probes as well as tested them in autoclaves at their own laboratories.

The first field test was performed by PNL in January 1987. PNL built the test stand connected to the Heber Plant inlet and outlet brine. The test stand could evaluate four probes simultaneously. Capabilities existed for passing plant inlet brine, plant outlet brine, or a buffer solution past each sensor. Buffers of pH 4, 7, and 10 were prepared for the field test. Temperature of any of the fluids could be controlled using the heat exchangers.

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[a] Operated for the U.S. Department of Energy by Battelle Memorial Institute.

Fluid temperatures ranged between ambient (40°F) and the plant inlet brine temperature (350°F).

Of the five pH probes delivered by the subcontractor, three failed early upon exposure to low-temperature (150°F) plant outlet brine. The other two survived a calibration with buffer solutions of pH 4 and pH 7. Both pH solutions were circulated at temperatures of ambient, 145, 240, and 325°F. The two good probes lasted several hours in the plant outlet brine, but failed after less than an hour in the high-temperature brine. Figure 1 shows the laboratory and field calibrations for the pH sensor. The voltage offsets between the field and laboratory data are due to differences in reference electrodes used in the laboratory and the field. The important similarities are the slope of the curves and the gaps between pH 4 and pH 7 lines. The vertical gap between the two calibration lines at a given temperature indicates the mV/pH unit output of the probe. Both of the probes reproduced pH values quite closely in the field to what had been observed in the laboratory.

Subsequent analysis of the failed pH probes indicated the failures were due to a leak in a glass-to-glass sputtered metal seal and were not in the transistor sensor itself. Under the high pressure, water got into the probe and shorted the leads. The subcontractor has indicated a different design could eliminate this seal.

SCALING TENDENCIES OF THE HEBER BRINE

Any time a saturated brine is cooled, various minerals will reach their saturation limit and either crystallize on heat transfer surfaces or remain as particles suspended in the brine. These suspended particles represent a potential plugging problem in injection formations. Theoretically, the amount of solids formed will increase as the plant outlet temperature decreases. Actual amounts of solids which will form are difficult to predict because of the complex chemistry and limited kinetic data.

In a binary plant, one way to increase electrical output for a given brine flow is to cool the brine to a lower temperature. The danger in this is that cooling might add too much particulates to the outlet stream. PNL undertook a study to determine the effect of cooling on particle generation

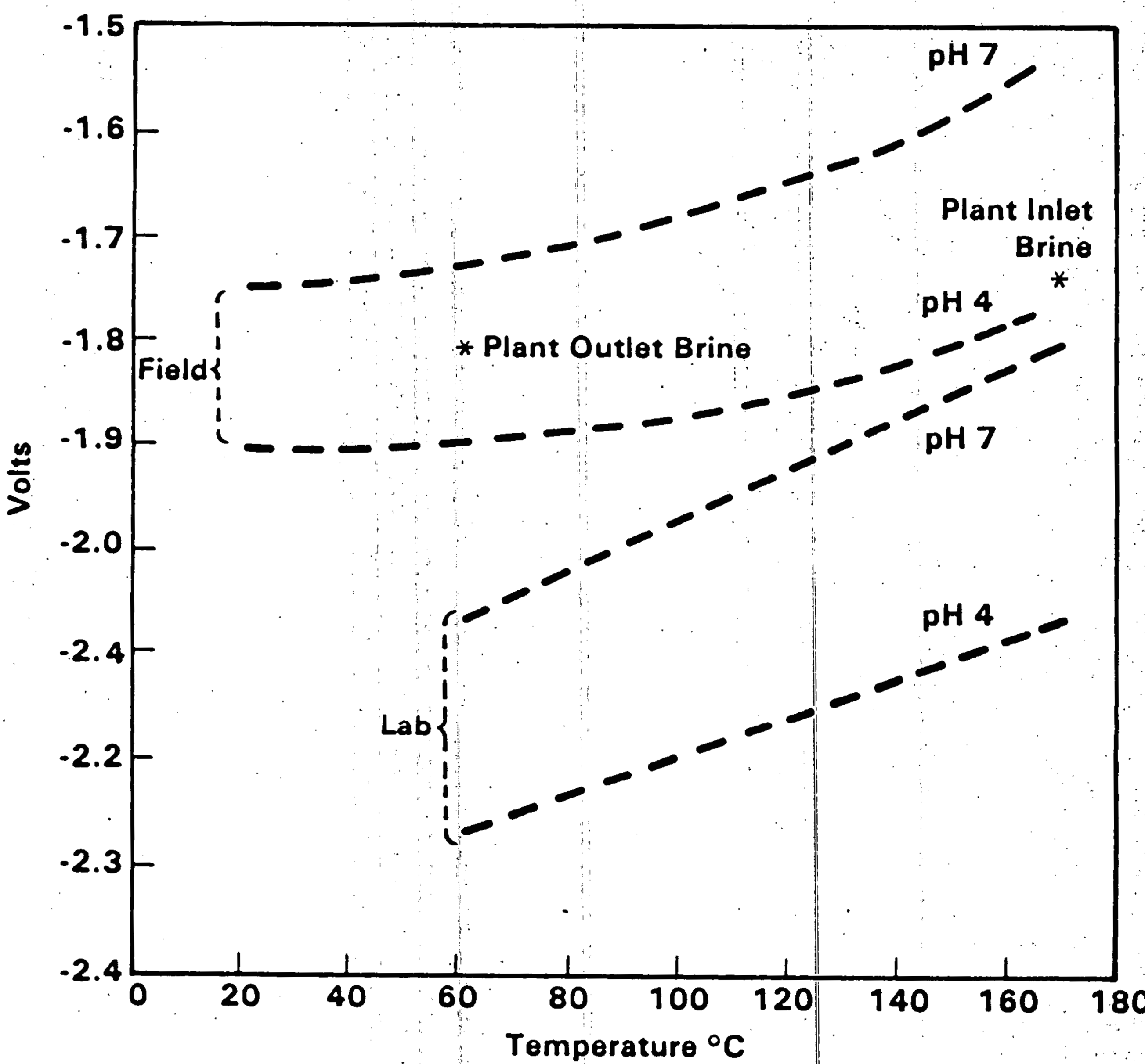

FIGURE 1. Response of pH Probe to Calibration Solutions and Geothermal Brines.

at the Heber Plant. Details are given in "Field Tests to Determine Scaling Tendency of Some Moderate-Temperature Geothermal Brines."[a]

Heber plant inlet brine was passed through the experimental test stand shown in Figure 2. The brine first passed through a 20 micron filter to remove large sand particles coming up the well. This hot prefiltered brine then passed through a 0.45 micron filter which captured particles smaller than 20 microns. The rest of the brine was cooled and then split in flow. Part was filtered immediately (designated "simulated plant outlet") and the remainder passed through a time lag vessel before being filtered again (designated "simulated well inlet"). The short lag time stream was held about 0.3-0.5 minutes before filtering; the long lag time stream was held 80 to 160 minutes.

The heat exchanger was sized to give residence times comparable to one-half of the Heber plant running at 6,000 GPM. Flow velocities were also matched in the two lines so there would be no anomalies due to particle settling. The lag vessel was sized to provide the same residence time from heat exchanger outlet to the bottom filter as the plant brine had in going from plant outlet to the injection well 2.5 miles away. This residence time is important because kinetics of silica deposition are known to be slow, especially at low supersaturations. The logic is that even if no silica formed in the heat exchangers, it might form in the reinjection line simply because more time was available for the precipitation reactions to occur.

While the filter stand was running, separate filters were collecting solids from the raw plant inlet and plant outlet streams.

The test plan called for first collecting samples with the simulated plant outlet brine cooled to 150°F. Then the brine was cooled in 10°F increments to 120°F in successive tests. Each test collected samples for about four hours.

Pertinent results are summarized in Figure 3. The shading in the circles shows graphically the relative particle loadings for each filter.

(a) Robertus, R. J., R. G. Sullivan, and D. W. Shannon. 1986. PNL-5991. Pacific Northwest Laboratory, Richland, Washington.

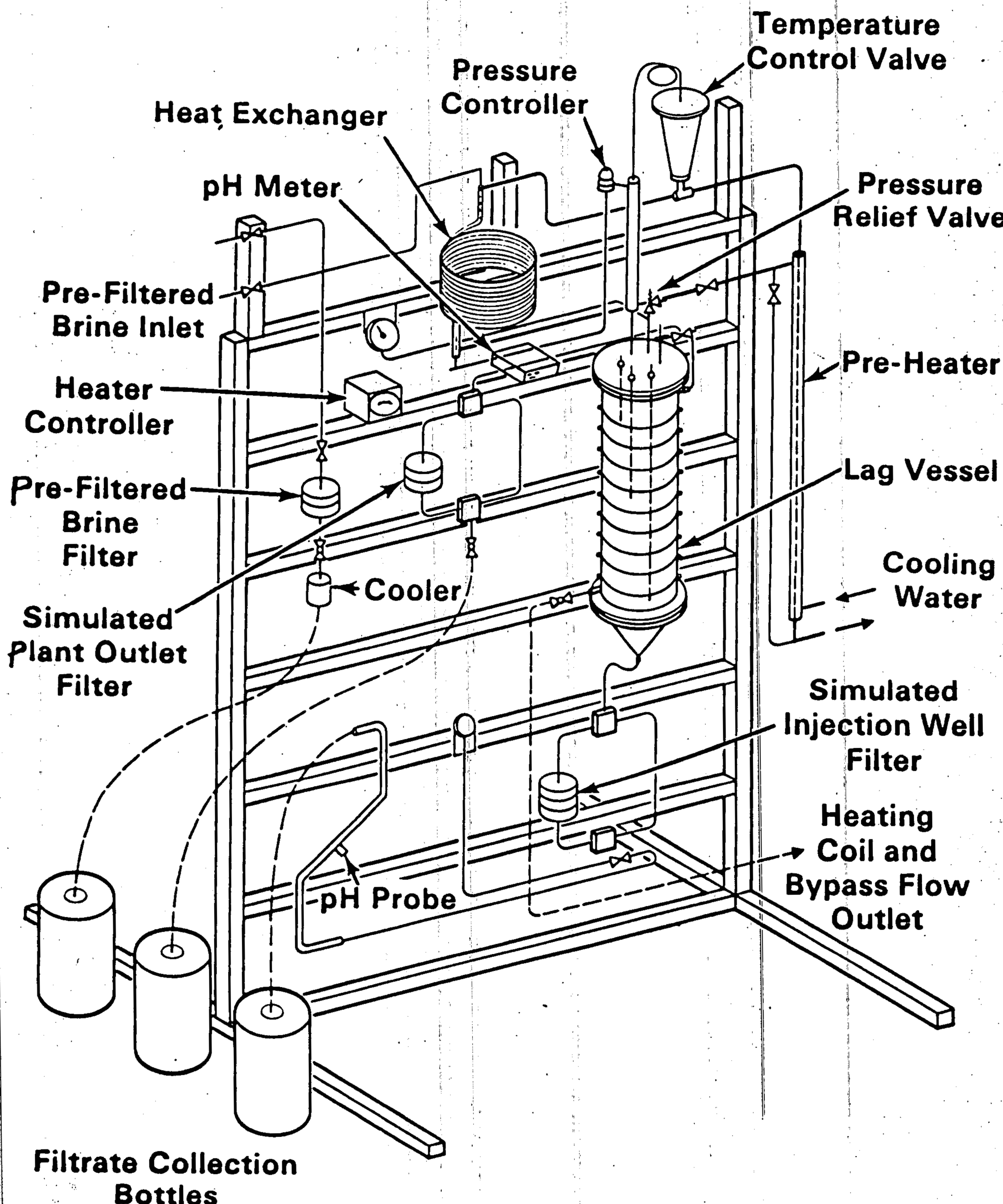

FIGURE 2. Solids Filtration Equipment

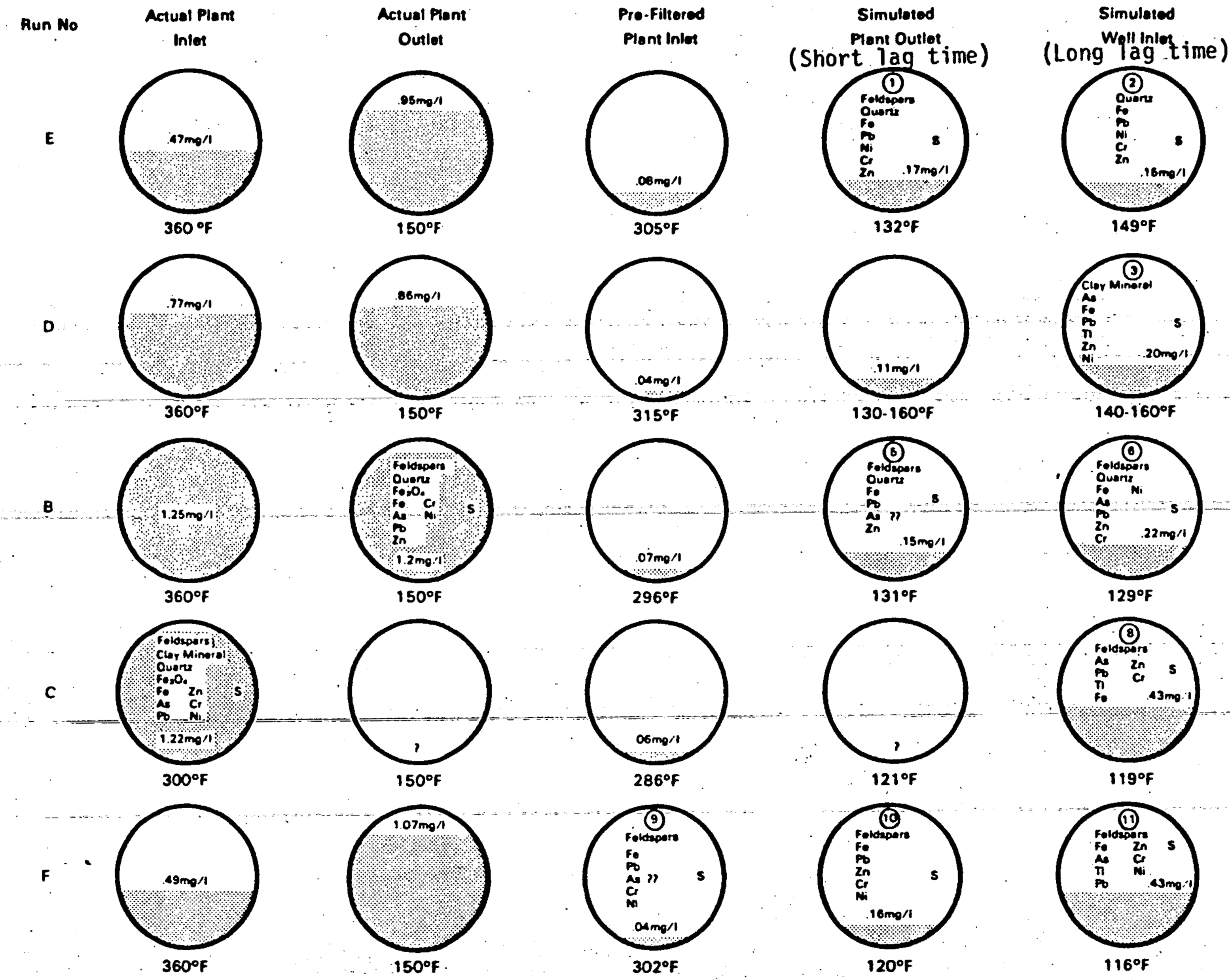

FIGURE 3. Solids Filtration Summary Information

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Chemical analyses were performed on selected samples and those results are also summarized in Figure 3.

The data in Figure 3 show there is a very small increase of about 0.1 mg/ℓ in solids in the short-time lag stream which appears to be heavy metal sulfides. Further lag times of 100 times longer increased the solids loading 0.2 mg/ℓ at 140-150°F and about 0.4 mg/ℓ at 120°F. Both of these values are small and were difficult to measure accurately. Thus, very little additional solids formed during the lag time.

Chemically, the solids which did form on cooling were not silica even though the temperatures at 120°F reached the amorphous silica solubility. Typically, the amorphous silica solubility must be exceeded by 200% or more before precipitation begins. Most of the solids on the filters were heavy metal sulfides or iron carbonates.

ON-LINE PARTICULATE MONITORING

USES

There are three main areas at a geothermal power plant where the ability to monitor particulates on-line would improve the technical and economic operation of the plant. These are:

1. The Production Well: For example, the Milford Utah Plant uses downhole injection of a calcite scale inhibitor; an on-line particulate monitor may be able to accurately determine the minimum dosage.
2. Solids Removal Process: For example, the reactor clarifier/filtration and derivative processes in the plant would be able to use an on-line monitor to perform final adjustments for flow rate, residence time, and additive dose to find the optimum compromise between particle formation/removal and plant/injection well performance.
3. Injection Well: The lifetime of the injection well is directly related to the quantity and size of injected particulates; an on-line monitor would protect the well while providing indication of any problems upstream in the plant itself.

To achieve these goals, PNL is developing and testing two units (one laser and one ultrasonic) for operation at temperatures in the 150°F to 250°F range (injection side), the 350°F to 400°F (production side), and pressures in the 200 to 700 psi range.

Technical performance initiatives include:

- mechanical/electrical component durability
- stability during plant use
- on-site calibration.

TECHNOLOGY TRANSFER ANTICIPATION

In order to assure availability of final instruments to the geothermal industry, both units were manufactured to our specifications by instrument companies following a difficult and lengthy procurement and prototype manufacturing phase.

STATUS

The basis of the ultrasonic unit is a 15 megahertz transducer mounted in contact with the flowing stream (Figure 4). The unit responds to particulates well, and its control mechanism promises a large dynamic range which would make it suitable for applications even at the solids removal process in a geothermal plant with its relatively concentrated particulate loading. Laboratory tests to date have shown good concentration response (Figure 5) and the ability to size (and count) on either side of a user-adjustable diameter. The unit has had repeated mechanical/electrical reliability problems. Currently, PNL has two new prototype high-temperature transducers (designated ULTM) which should be more durable under geothermal plant conditions.

The basis of the laser is the forward scattering from individual particulates at a specified angle from the beam. In a timed sequence, the reflected light pulse amplitude is measured and related to size and the detector is electronically relaxed to await the next pulse. The flowing pressurized stream is contained in a special high-pressure cell with sapphire

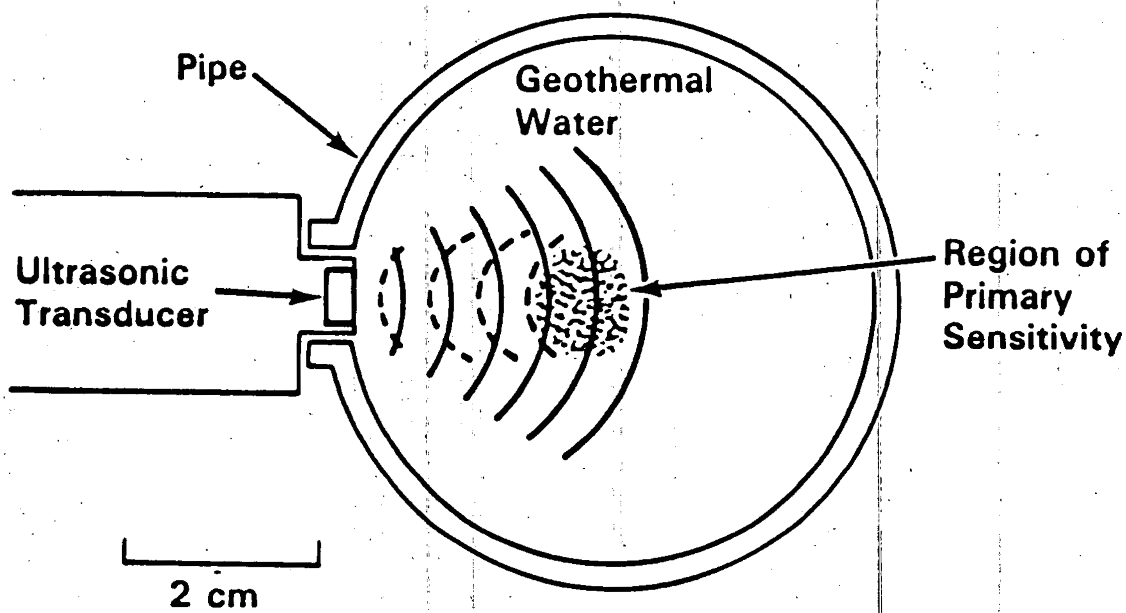

FIGURE 4. In-Line Ultrasonic Particle Monitor

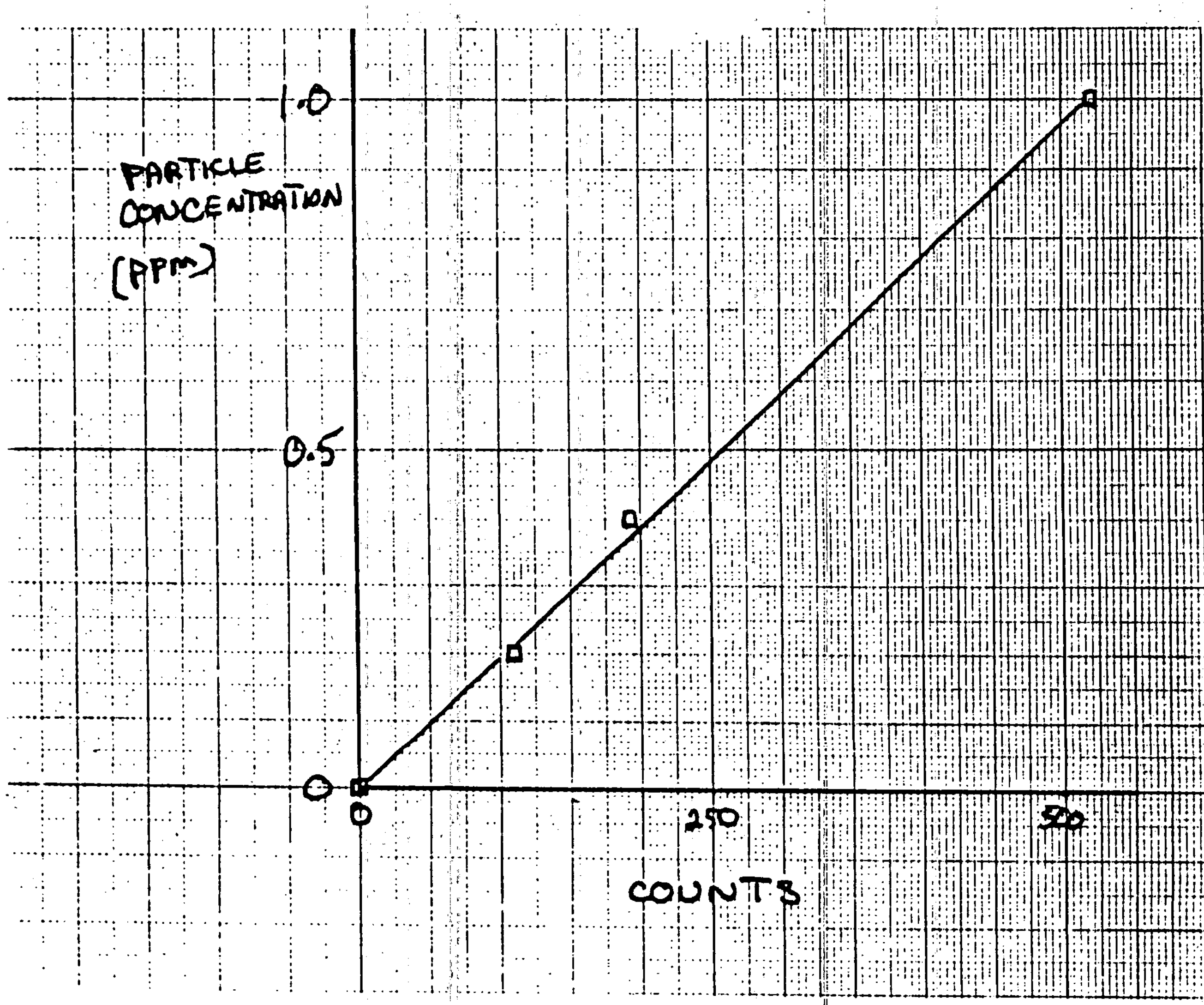

FIGURE 5. Prototype High-Temperature Response of ULTM Transducer (Unit C) to Low Concentration Particulates.

windows (Figure 6). In laboratory tests the unit has shown the ability to size particulates (Figure 7). This sizing ability may be concentration dependent and degrade as the suspension becomes more concentrated because of the difficulty in relating a light pulse to a single laser/particulate interaction.

A field test at the Heber Plant site in April 1987 is designed to:

1. Monitor the plant outlet for particulates, and
2. Establish the durability of two separate on-line particle counters under plant operating conditions.

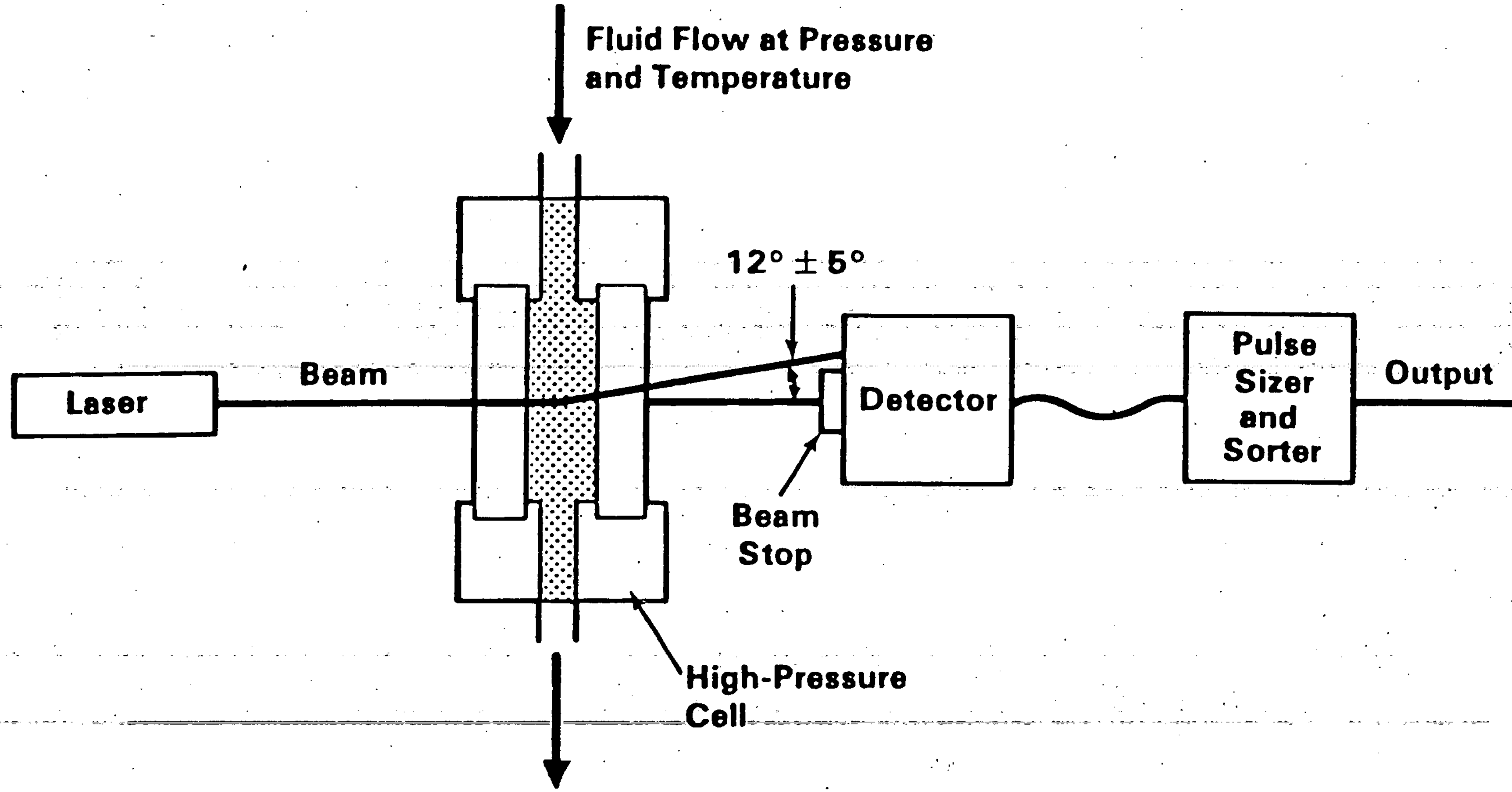

FIGURE 6. On-Line Laser Particle Counter

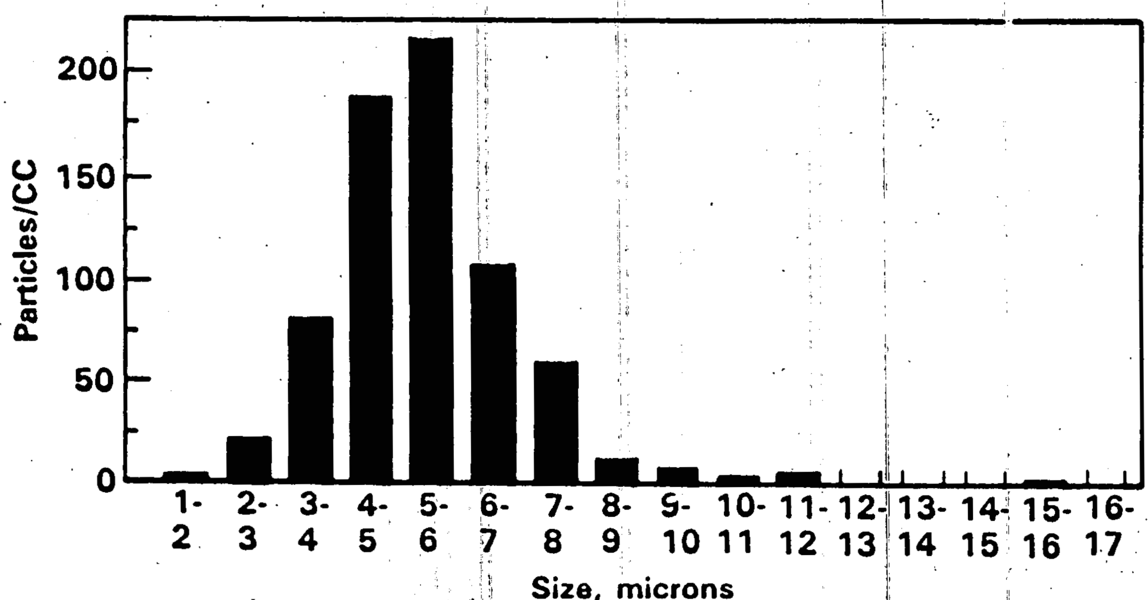

FIGURE 7. Lab Test of On-Line Laser Sizing for 4.8 Micron Particles.