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DETAILED CONCEPTUAL DESIGN OF A HIGH TEMPERATURE GLASS
PH ELECTRODE FOR GEOTHERMAL APPLICATIONS

FINAL REPORT - TASK II

MASTER

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PREFACE

The investigation described in this report was authorized under Prime Contract DE-AC06-76RLD-1830 for the United States Department of Energy, Division of Geothermal Energy. It was performed by the Corporate Research Department of Leeds & Northrup Company, a Unit of General Signal Corporation, for the Pacific Northwest Laboratory, operated by Battelle Memorial Institute. This report covers work during the period of July, 1979 - February, 1980. The constructive guidance provided by Dr. George A. Jensen, Project Officer for Pacific Northwest Laboratory, is gratefully acknowledged, as well as that of Messrs. J. K. Ace, M. J. Danielson, L. D. Perrigo and D. W. Shannon, who reviewed an early draft of this report.

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I. INTRODUCTION

In order to control scaling or corrosion in a geothermal power plant, one must monitor and verify the solution chemistry. At the present time, the fluid chemistry is determined by sampling and subsequent analysis. Sampling processes introduce risks of sample contamination and changes due to cooling, and provide only intermittent information. A much better method would be the insertion of chemical sensors down-hole or in-line. In-line probes for high temperature geothermal environments are not available. Because of a variety of relatively new applications, including monitoring requirements in high pressure nuclear power plants, advances have occurred in many measurement technologies. A program has been undertaken by Pacific Northwest Laboratory (PNL), operated for the United States Department of Energy by Battelle Memorial Institute, to develop instrumentation for geothermal application. This is consistent with the recommendations of the National Materials Advisory Board (NMAB) of the National Academy of Sciences. The overall objective is to develop sensors including a high temperature reference electrode and redox potential, conductivity, pH, corrosivity, sulphide and $p\text{CO}_2$ probes. Significant progress has already been made on this challenging task. PNL has successfully demonstrated a high temperature reference electrode, an electrodeless conductivity probe, a redox electrode, and an instantaneous corrosion rate measurement.

Leeds & Northrup Company has attempted to develop a pH electrode for in-situ geothermal measurements under a subcontract to PNL. The sensor must be operable to at least 250°C and up to 5000 psi. According to the NMAB report, geothermal brines contain H_2S (up to 75 ppm), Na^+ (up to 87,000 ppm), CO_2 , K^+ , Ca^{++} , Cl^- , Mg^{++} , SO_4^{--} , silica and lesser constituents. The pH electrode must operate for several hours in this environment and be free of any chemical interference. The development of this pH sensor has been divided into two stages: Task I - Detailed Conceptual Electrode Design; and Task II - Fabrication and Test of Lead Units.

This report covers the work undertaken on Task II - Fabrication of Lead Units and Laboratory Tests. Task I effort was reported in detail previously; a summary of that work is reiterated in Section III of this report for the reader's convenience.

II. SUMMARY AND CONCLUSIONS

The performance of a pH sensor for use in hot geothermal brine was determined by laboratory tests simulating the expected conditions of use. Tests were conducted at temperatures from 21°C to 260°C and pressures from atmospheric to 5000 psi.

Probes were constructed according to the design recommended in Task I of this project. Deficiencies were found in the areas of seal, stem glass integrity and glass stability in hot simulated brine. Modifications of the design were made and tested, the improved versions overcoming the seal and stem glass cracking problems. A different pH glass formulation was used which improved sensor performance.

Test results of the final design show that the sensor survived hot brine exposure at temperatures up to and including 200°C, retaining its low temperature pH measuring capability. Exposure to 250°C brine resulted in irreversible probe changes which caused sensor deterioration and failure. Comparative results are shown in Table II-1.

TABLE II-1 COMPARATIVE PERFORMANCE OF pH ELECTRODE

Electrode	0-100°C	101-150°C	151-200°C	201-250°C
Existing Technology	Excellent	Good	Unacceptable	Unacceptable
B-13	Excellent	Excellent	Good	Unacceptable
B-19	Excellent	Excellent	Good	Unacceptable
B-17	Excellent	Excellent	Excellent	Poor

Probe performance at high temperatures could not be correlated to the Nernstian model because of unexpected changes to the sample pH inside the test vessel. The sample pH was considerably more basic at the end of each experiment, in spite of efforts to maintain a constant pH. The sensor did appear to track the drift of the sample pH and given its accurate response before and after exposure, it appears likely that accurate pH measurement at elevated temperature was achieved. Based on these results, it is recommended that this design be included in future tests, whether in the laboratory or in the field, to evaluate pH sensors for the measurement of hot geothermal brine.

III. SUMMARY OF TASK I RESULTS AND PROPOSED DESIGN

The feasibility of developing a pH sensor for use in hot geothermal brine was investigated by testing the essential components of proposed design alternatives in the laboratory.

A specific electrode design, shown in Figure III-1, was recommended as a result of earlier work based upon the testing of glasses, polymers, electrolytes, electrodes and seal materials. Of paramount importance was the formulation and testing of pH sensitive glasses which could survive exposure to the brine. Over 50 different formulations were tested in brine during Task I. The glass formulations which exhibited best durability in brine survived for 24 hours at 250°C. However, much of the pH response was lost by exposing the sensor to simulated brine at 250°C. The glass compositions are reported in detail, the most durable being lithia-silica glass of relatively low lithia content, with alkaline earth, lanthanum and other modifiers (e.g., Ti and/or Zr) added.

A specific formulation (B-13) was recommended for brine measurement, with two additional glasses (B-17 and B-19) recommended for testing should B-13 prove unsatisfactory. The compositions of these glasses are reported in Table III-1.

TABLE III-1
Glass Composition
Mole % (as oxides)

Glass Code	SiO ₂	Li ₂ O	Cs ₂ O	Na ₂ O	Ti	Zr	La	Ba
B-13	68	18	2	--	--	2	3	7
B-17	68	18	2	--	2	2	3	5
B-19	63	24	2	2	1	--	3	5

Polymeric materials were investigated for use in the probe as potting compounds. Two epoxies were identified which survived brine exposure well, as did several elastomeric compounds. The proposed design included one epoxy and one elastomeric encapsulant.

NOTE - PROBE END CAN BE TERMINATED IN ONE OF THE FOLLOWING WAYS:

- 1) "SWAGELOK" FITTING.
- 2) "CONAX" DISCONNECT FITTING.
- 3) THREADED TUBE/PIPE TO ELECTRONICS HOUSING.
- 4) CONTINUE PROBE JACKET TO ELECTRONICS HOUSING.
- 5) MINIMUM LENGTH OF PROBE ASSEMBLY IS 5 INCHES.

* BAL-SEAL #300-06 GC (GRAPHITE-CARBON FILLED TEFLON)

^ .247" O.D., .128" I.D., 1/32 THK.

FIGURE III-1: TASK I PROPOSED SENSOR DESIGN

Sealing configurations were tested, with a spring loaded polymeric seal (commercially available) recommended for sealing the glass sensing tube into an Inconel 625 housing.

Internal electrolytes and a reference electrode were tested with one aqueous recommended and one molten salt mixture proposed as an alternative with special advantages, but some unresolved limitations. A silver/silver chloride internal reference electrode was selected for inclusion in the recommended design, with a glass-to-platinum seal allowing lead connection to the electrode.

IV. HIGH TEMPERATURE-HIGH PRESSURE TEST APPARATUS

For high temperature-high pressure testing of the probe assembly, a test apparatus 4 1/2" in diameter and 6" high was fabricated from Inconel 625 for maximum corrosion resistance (see Figure IV-1). The assembly includes an upper and a lower chamber, each 1 7/8" in diameter and 1 3/4" deep. Separating the chambers is a 1/2" thick center plate, machined with two thru-holes to accommodate the sensors. Each thru-hole contains two O-ring seats. A flanged cap, with an O-ring seat machined into it, was fitted over the end of each sensor and secured to the center plate with four 6-32 cap screws. Thus, sealing of the sensor plate was accomplished via two radial and one facial seal.

A 1 1/4" diameter hole was machined in the center of the top chamber. It accepted a shouldered feedthru holder from underneath and was secured from above with a 1 3/4" clamp and four 8-32 cap screws. An O-ring seat machined into the holder provided a facial seal at this point. The holder was also tapped to accommodate four high pressure threaded feedthrus which were purchased from Alberox Corporation, New Bedford, Massachusetts 02745. The feedthrus, originally designed for use in oil field equipment, are rated for use up to 40,000 psi and 600°F. Supplied with the feedthrus were O-rings of nitrile rubber (Buna N) and 90 durometer hardness; however, Task I experimental results indicated that this material was not satisfactory in the brine system even with limited exposure. As a result, O-rings of the same type used throughout this assembly (EPDM, 75 durometer hardness) were substituted. In both the top and bottom "faces" of the chamber, a blind hole was bored to serve as a thermocouple well. Iron-constantan and chromel-alumel thermocouples were used for temperature monitoring. This dual monitoring system was used to check for thermal gradients and consequent errors during testing.

An inlet port was drilled in the side of each chamber to allow for pressurization. Heavy wall tubing (316 stainless steel, 1/4" O.D.) and Swagelok type fittings of the same material were used to connect the high pressure N₂ tank with the inlet ports of the test apparatus (Figure IV-2). High pressure, corrosion resistant valves and gauges were also incorporated into this assembly to permit independent monitoring and venting of each chamber.

QTY	SYM	PART OR C.W.G. NO.	DESCRIPTION
1	1	B-RC-347-2-1	TOP CHAMBER
2	1	-2-2	CENTER CHAMBER
3	1	B	BOTTOM CHAMBER
4	1	-2-24	HOLDER, FEEDTHRU
5	1	-2-25	CLAMP FEEDTHRU HOLDER
6	2	-2-2	PROBE STOP, TOP
7	2	A	PROBE ASSEMBLY
8	8	A	BOLT, 5/8-11 X 6 1/2 LG
9	8	-2-18	WGT, 5/8-11
10	2	-2-20	MALE CONNECTOR
11	6	-2-7	O-RING #111
12	2	-2-8	O-RING #136
13	4	-2-10	FEEDTHRU
14	2	-2-6	BAND HEATER
15	1	-2-23	O-RING #127
16	4	-2-22	O-RING #008
17	4	304-854	1/2 X 8-32 HN 500 H CAP SCR
18	8	5043-0	7/8 X 3-32 HN 500 H CAP SCR
19	1000		BRINE SOLUTION
20	-	825210	STL 316 CRES TUBE .254-250 OD X .180 ID

Figure IV-1: High Temperature, High Pressure Test Vessel

Figure IV-2: Experimental Configuration for High Temperature, High Pressure Testing

Finally, eight 5/8-11, 6 1/2" long steel bolts, tourqued to 210 ft. lbs., were used to seal the vessel. The bolt circle and size were determined as a function of area under stress, and tensile strength of the bolt with an additional 20% safety factor calculated in. With the specified tourque, the bolts were tightened to almost their rated yield strength, which provided maximum clamping.

Probe output was continuously monitored and recorded with an L&N pH meter, on the millivolt scale, and an L&N Speedomax recorder. An electrometer was used for intermittent impedance measurements and to confirm the output signal of the pH meter. At low temperatures (100°C) and concomitant high source impedance, the electrometer was relied upon for all readings.

V. TEST RESULTS

The results of Task II testing of the recommended design and modifications thereof are reported in this section. The electrodes were subjected to response tests at moderate temperatures, exposed to simulated brine at a variety of temperatures and pressures and if they mechanically survived, were retested at moderate temperatures.

All high temperature tests were conducted in 25,000 ppm NaCl. In most of the tests, 0.01 M $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ was used to buffer the solution pH. In some tests, the buffer concentration was increased to 0.1 M, and one test was run in unbuffered NaCl.

The gas phase above the test solution was usually pressurized with pure nitrogen. In some tests, the solution was presaturated at room temperature with CO_2 to increase the system CO_2 content (and lower the pH).

Test temperatures ranged from 137°C to 250°C for periods of from 2 1/2 hours to 24 hours. Pressure was controlled from 50 psi (the steam pressure at the lowest temperature) to ~ 5000 psi. For elevated pressure tests, N_2 was introduced to increase the pressure in 500 psi increments after the test vessel had reached its desired temperature.

Considerations primarily relating to the mechanical integrity of the design are grouped and presented first, with the electrochemical test results following in Section 5.2.

5.1 MECHANICAL INTEGRITY AND DESIGN MODIFICATIONS

Probes were assembled, as specified in the Task I report, and tested. An additional copper lead wire was potted into the probe paralleling the electrode lead wire, but simply buried in the epoxy potting compound. The impedance measured between this wire and the electrode housing should be very high; a reduced impedance was taken as indicative of solution leakage and seal failure. The impedance between the sensing electrode lead and the housing (through the sensing glass) was also monitored, both as an important characteristic of the pH membrane glass and to verify the glass membrane integrity.

Tests indicated that the original probe design recommended was deficient in two general ways. The glass sensing element could not withstand the higher test pressures reliably without implosion, and certain other probes developed solution leakage between the housing and the potting compounds. Furthermore, some glass elements developed cracks which permitted leakage paths shunting the electrochemical measurement cell. Modifications to overcome these problems were undertaken, and subsequent tests verified that the problems had been eliminated. Each design modification is discussed in turn below.

5.1.1 Membrane Glass Configuration

The membrane glass in the recommended Task I design was conical. This shape resists end-on impact well, impact such as might arise from dropping the sensor onto its exposed sensing tip. While this design is desirable in a laboratory device, the protective housing of the brine pH sensor protects the sensing glass from such damage. Although the probe survived well below 1000 psi and 200°C, at most elevated temperatures and pressures implosion occurred. The cause of the problem was identified as relatively thin walls and high stresses located on the side of the conical shape. Even though the wall in certain regions was quite thick, cross sections of glass membranes revealed that the glass was only 0.005"-0.007" thick in the relatively thin sidewalls of the cone. Despite the fact that end-on impact resistance of this probe is good, this design does not resist hydrostatic pressure well.

As a result of these tests, the probe design was modified to include a hemispherical pH glass membrane tip. Figure V-1 shows this modified tip design. The pH glass membrane was made approximately .030" thick to further increase implosion resistance. The greater compressive strength of the hemisphere, along with the increased wall thickness, resulted in a design which repeatedly survived high temperature, high pressure use up to 250°C and 5000 psi.

Figure V-1: Sensor Subassembly with Hemispherical Glass Membrane

5.1.2 Potting Compound Modification

The location of the spring loaded polymeric seals results in the portion of stem glass located between the first seal and the pH sensing glass being easily accessible to brine. In Task I of this project, a room temperature vulcanizing adhesive, Dow Type 730, was successfully used to minimize brine contact in this exposed region. Also, the polymeric seals rely somewhat on their thermal expansion properties, reaching maximum efficiency at elevated temperatures. The adhesive, therefore, when placed so that it completely fills the space between the internal glass element and stainless steel housing, also serves as a temporary pre seal during the initial heat-up period of a test.

At elevated temperatures and high pressures (greater than 2500 psi), the portion of stem glass surrounded by the fluorosilicone sealant failed. Longitudinal cracks were discovered in the stem glass over its entire length. It was felt that forces at the ends of the stem glass were acting in concert to put the stem glass in the region surrounded by silicone elastomer under tension. The glass is much less strong under tension than under compression. Compressive forces counteracting this are readily provided by the Bal-Seals and rigid epoxy at the platinum feedthrough end of the probe, but not by the fluorosilicone elastomer. The probe design was modified by first reducing the thickness of the fluorosilicone coating to a minimum. The resultant space between the adhesive and stainless steel housing was then filled with the same low expansion epoxy used at the opposite end of the probe, affording similar compressive forces as are present in all other parts of the probe. When tested up to 5000 psi in hot brine, the modification was successful in preventing stem glass failure, and no adverse effects were seen from the reduction of the amount of fluorosilicone protective sealant.

5.1.3 Spring Loaded Seals

The design of the sealing mechanism of the probe employs a spring loaded polymeric seal in a labyrinth configuration. The seals specified in the Task I probe design were purchased from Bal-Seal Engineering Company for further testing and verification of suitability in Task II. The body of the seal consists of graphite-carbon filled Teflon. Higher operating

temperatures and pressures are possible than with graphite filled or unfilled Teflon. However, the material has a moderate amount of rigidity which results in less sealing ability. This is compensated for by a heavier spring loading. Partially embedded inside the Teflon body is a 302 stainless steel spring with a .008" wire diameter. According to the manufacturer's specifications, seal integrity is maintained in water and steam up to 550°F and with 3000 psi differential pressure. Task II test results initially indicated that the seals did not meet the minimum requirements of 24 hours at 250°C. However, another factor, the inner wall finish of the housing, was eventually found to be the primary cause of the leakage observed (see Section 5.1.4). Once this problem was corrected, the seals performed satisfactorily for 24 hours at 200°C, as determined by membrane impedance measurements before and after the test. At temperature, variables such as volume resistivity of the potting compounds and the proximity of the copper wire used for leak detection to the platinum feedthrough wire, made impedance measurements somewhat ambiguous.

Some seal failures were encountered at 250°C and prolonged brine exposure. This led to investigation of another possible alternative, utilizing the same spring loaded type sealing mechanism. "Omniseals" were procured from the Fluorocarbon Company, Los Alamitos, California 80720, which differed from the Bal-Seal in spring design, spring material and composition of the polymeric body. The spring was a helical wound flat wire of the corrosion resistant steel, Elgiloy. The outer cover consisted of 80% virgin TFE, 15% glass and 5% Moly Disulphide. The seal was specified for use up to a maximum of 550°F or 10,000 psi, with sealing capabilities under pressure decreasing with increasing temperature. At 500°F, the seal was rated for use up to 1000 psi differential pressure. When tested in a brine solution, the seals appeared to begin to fail at temperatures as low as 137°C, the impedance measured through the glass membrane being 10^7 versus an expected value of 10^8 . At 250°C, the membrane impedance was 5×10^4 . Since the Bal-Seal specified gave the better results, improvements on other sealing factors, such as greater smoothness of the sealing surfaces and closer attention to tolerances on the various probe parts, were employed to improve performance and meet the temperature and pressure requirements of this application.

5.1.4 Finish on Inside Surface of Housing

According to the manufacturers, the sealing capabilities of the spring loaded polymeric seal are directly proportional to the smoothness of the surfaces it contacts. Design specifications for the housing followed the manufacturer's recommendation, calling for at least a 32 rms finish to achieve effective sealing.

Several alternative machining processes may be used to prepare this surface, including reaming, boring and grinding. In the fabrication of the housings used in early Task II tests, a stainless steel rod was reamed to the correct ID with no further treatment to effect surface smoothness. Visible flaws on the inner wall surface were not deemed critical if they were not in the seat region of the Bal-Seals. They were, in fact, expected to be beneficial in aiding the adhesion of the epoxy potting compound by providing increased surface area and roughness.

In high temperature tests, the probes so constructed showed evidence of leakage which, after the integrity of the glass element was confirmed, was attributed to poor sealing. Leakage was indicated during the test by comparing the measured "membrane" impedance with the expected value. If the measured impedance was more than a decade lower than anticipated, leakage was presumed. Apparent leakage problems were encountered at temperatures as low as 173°C with "reamed" housings.

Consultation with Bal-Seal Engineering Company resulted in a further recommendation that the inside wall be honed to produce an 8-16 rms finish. Such surface treatment was employed and greatly reduced the leakage problem.

5.1.5 Stem Glass Flow

In use there are significant compressive forces imposed upon the stem glass of the spring loaded polymer seals and associated spacers. This is essential to maintain a good seal and to prevent incursion of geothermal brine.

During the Task II effort, sensors were taken apart after use and examined. It was observed that the forces encountered in use had caused the stem glass to flow and develop ridges between the component parts of the compression seals.

Figure V-2 is an SEM photomicrograph (15x) of the polymer seal and a section of the stem glass. An enlarged view (86x) of the glass-seal interface (Figure V-3) shows glass flow on the outer surface of the stem glass tube as the glass exits from the polymer band. Similar glass flow occurs between the steel washers separating the end polymer seals. Figure V-4 shows the stem glass exiting through a steel washer (15x magnification). A ridge of glass had been formed as the glass flowed into the space adjacent to the washer. An enlarged view (89x) is shown in Figure V-5. A clearer view of the ridge formed is shown magnified 230x in Figure V-6.

This ridge formation has not caused problems during Task II testing. It is described here to point out the irreversible changes which occur in the probe which could affect its longevity. Furthermore, this particular glass flow would likely cause seal failure if temperatures were cycled in use. The thermal contractions on cooling will likely open leakage paths which will jeopardize probe performance. If probe life proves otherwise sufficiently long so that reuse is feasible, an alternative seal arrangement might be preferred. At the present time, it seems unlikely that glass pH sensors will have sufficient life to justify reuse after removal from down-hole applications.

5.1.6 Stability of pH Sensing Glass

A significant portion of the Task I work examined alternative pH glasses, resulting in specially formulated compositions better able to survive extended exposure to hot brine. The three formulations recommended (Table III-1) have been found to survive brine exposure without physical alteration.

During Task II some probes were fabricated using a commercially available glass recommended for moderately high temperature use, i.e., up to 105°C. This glass was included in this study to provide a performance norm in terms of resistivity and selectivity. It was valuable to have a well-

Figure V-2: Polymer Seal and Section of Stem Glass (15x)

Figure V-3: Glass-Seal Interface Showing Glass Flow (86x)

Figure V-4: Stem Glass Exiting through Steel Washer (15x)

Figure V-5: Stem Glass at Steel Washer Showing Glass Flow (89x)

Figure V-6: Ridge Formation from Stem Glass Flow (230x)

characterized glass fabricated into the brine pH configuration to facilitate evaluation of design criteria and test instrumentation and procedures.

When these probes were exposed to simulated geothermal brine, however, marked physical deterioration of the pH glass occurred. Figure V-7 shows the sensing tip at 15x magnification. Significant glass attack had caused cracking and ablation of the outer surface. The mechanism is believed to involve the dissolution of the alkali content, leaving a high silica residue which cracks and flakes off as the temperature varies. Figure V-8 shows a cross-section of the glass (150x) with the inside and outside layers both appearing dark while an inner region remains apparently unattacked. Note that the glass appears similarly reacted, whether exposed to simulated brine or the 1M HCl internal electrolyte.

These results emphasize the desirability of formulating a pH glass especially for this application rather than employing what might seem to be a desirable alternative selected from among commercially available glasses.

5.2 ELECTROCHEMICAL PERFORMANCE

The test results on the electrochemical performance of the various probes have been grouped for presentation into three categories: sensor impedance, pH response at low temperature before and after exposure to hot brine, and pH response at elevated temperatures. The results for each type of pH glass tested are reported below.

5.2.1 Sensor Impedance

The test apparatus used for high temperature testing is described in Section IV. An electrometer with shielded cables was used to measure the impedance from the sensor's internal reference element through the sensing glass to the solution and its container. At lower temperatures the test system shown in Figure V-9 was used. The high impedances encountered, up to $\sim 3 \times 10^9 \Omega$, were measured by briefly introducing a known incremental voltage in addition to the "zero" current cell voltage and measuring the resultant current. It is then possible to compute the system impedance.

Figure V-7: Deteriorated Membrane of Commerical pH Glass after Brine Exposure
(15x)

Figure V-8: Cross Section of Commercial pH Glass after Brine Exposure
(150x)

Figure V-9 : Experimental Configuration for pH Membrane Testing

The impedance for sensors having 0.03" thick pH membranes is shown as a function of temperature in Figure V-10. As expected, the impedance of glass B-13 is highest and B-19 lowest. A conical sensor with a membrane thickness of only 0.005" in places was also tested with the results shown in Figure V-10. All the sensors showed the expected linear relationship between the logarithm of the resistivity and $1/T$. The impedance of each sensor was below 10^9 ohms at temperatures above 130°C , low enough to facilitate measurement with relatively simple electronics. For comparison, the resistance-temperature relationships for several commercially available pH glasses are shown in Figure V-11 with the results for glasses B-13, B-17 and B-19 shown as dotted lines.

The relatively high resistivities of the low lithia glasses, developed during Task I, make low temperature pH measurement difficult. This is only a problem in that calibration at moderate temperatures is desirable. However, we were able to measure pH even at 22°C without the use of a Faraday cage. It is believed that by operating at slightly elevated temperatures, such as 50°C , it will be possible to calibrate sensors fabricated from any of these glasses.

5.2.2 Low Temperature pH Measurement

In order to check the pH response of the new glass formulations and to determine how well they survived high temperature brine exposure, pH measurements were made at low temperatures and repeated after the probes had been exposed to high temperatures. Due to the high source impedance involved, special care had to be exercised in the experimental design to minimize electrical noise pickup. When proper shielding of circuit components and leads was used, it was possible to make measurements of the sensor emf without the use of a Faraday cage. The measurement scheme employed is shown in Figure V-9. When the switch shown was closed, the battery was shunted and the measured voltage indicated sample pH. Standard buffer solutions of known pH at the controlled temperature were used.

In general, when the mechanical problems described in Section 5.1 had been eliminated, all three glass formulations could be employed in the

Figure V-10: Membrane Resistance versus $1/T$ for Experimental pH Glasses

Figure V-11: Membrane Resistance Versus $1/T$ for Experimental and Commercially Available pH Glasses

recommended configuration to measure pH. These low lithia glasses showed a slightly less than Nernstian response at all temperatures tested, usually 90-95% of theoretical. The cell voltage before brine exposure was measured versus a standard calomel reference electrode and is shown for B-13 and B-17 glasses in Figure V-12. Although B-19 glass also responded well before brine exposure, it lost pH response to a greater degree and at lower temperatures in hot brine and for that reason is not recommended for elevated temperature use (at temperatures greater than 175°C).

After measuring low temperature pH response, the probes were used in the high pressure, high temperature tests using the autoclave described in Section IV. Upon retesting after brine exposure, two of the three test glasses had virtually the same pH response as before exposure if the use temperature did not exceed 200°C. Figure V-13 shows the response of B-13 glass at 55°C after exposure to brine at 150°C, followed by further exposure at 200°C. There does not appear to be irreversible change in the B-13 glass as a result of brine exposure at these temperatures. However, when B-13 glass is exposed to brine at 250°C, a change in the glass occurs which degrades pH measuring capability. The exact nature of this change is not clear but appears to be a chemical alteration of the glass similar to that observed when a less stable glass is exposed to lower temperature solutions. The degradation occurs at 250°C reasonably independent of the brine pH or ionic strength, even if distilled water is used in place of the brine. The only variable which is observed to affect this deterioration of pH response is temperature. The B-13 glass maintains its pH response after 24 hours at temperatures below 200°C, but has significant lessening of response at 250°C for as little as four hours.

Figure V-14 shows similar results (at 40°C) for B-17 glass before and after brine exposure. The sensor maintained its pH measuring capability very well after exposure to 150°C and 200°C brine. As was found to be the case for B-13 glass, however, the sensor performance deteriorated after 250°C exposure. As little as four hours at 250°C reduced the sensitivity from about 93% of the Nernstian to about 60%. This would cause uncertainty in the measured pH values of greater than one pH unit at 250°C.

Figure V-12: Membrane Potential Versus pH Before Brine Exposure

Figure V-13: Membrane Potential Versus pH for B-13
Before and After Brine Exposure

Figure V-14: Membrane Potential Versus pH for B-17
Before and After Brine Exposure

Examination of all test results on B-13 and B-17 glasses indicates that the response of B-17 to pH more nearly approaches theoretical Nernstian behavior, has better precision before and after brine exposure, and has slightly lower resistivity. Because of these attributes, it is the recommended glass formulation. Although it functions after 24 hours at moderately high temperatures, however, relatively brief exposure to brine at greater than 220°C causes an irreversible change and performance deterioration.

5.2.3 Probe Performance at Elevated Temperatures

Impedance measurements at elevated temperatures have been reported in Section 5.2.1. In this section, attempts to correlate sensor signal versus a reference electrode at known sample pH over the temperature range of 150-250°C will be reported.

In order to monitor pH with the glass electrode, it is necessary to employ a high temperature reference electrode. A suitable reference electrode has been designed and tested at PNL¹. A significant effort was made to avoid interference effects from H₂S which may be present in geothermal brines. For the purpose of Task II testing of the glass pH sensor, it was decided to exclude H₂S from the sample. The materials had previously been tested for resistance to H₂S attack during Task I. Inclusion of H₂S in Task II tests would have confused the results because H₂S would presumably affect the sample pH, but in a manner difficult to predict quantitatively due to the complex equilibria involved and the paucity of reliable thermodynamic data in the literature. If H₂S is omitted from the sample, it further allows the use of a simple Ag/AgCl reference unprotected from H₂S interference. Such a reference electrode is shown in Figure V-15.

The reference electrode and the pH sensor to be tested were mounted in the apparatus described in Section IV. Simulated brine at a known pCO₂ and pH was placed in the vessel and the chamber sealed. The system was heated to the test temperature and pressurized to a known total pressure.

* BAL-SEAL #300-06 GC (GRAPHITE-CARBON FILLED TEFLON)
 Δ .247^{±.001} O.D., .128^{±.001} I.D., 1/32 THK.

Figure V-15: Silver Reference Electrode

From the relative liquid and gas volumes, known temperature, total pressure, Henry's Law constant and dissociation constants of the carbonate system, the approximate pH could be computed (within ~ 0.2 pH unit).

A significant problem was encountered when this experiment was attempted. In spite of the expectations, when the solution was cooled, the pressure released and the pH of the solution measured, rather than be the same or close to the initial pH, the solution was now basic, at times by more than 2 pH units. For example, an initial pH of 6.8 increased to 9.0 during 4 hours at 200°C . Given the uncertainty of sample pH, it was not possible to correlate sensor output with pH accurately.

Several explanations for the increased pH of the electrolyte were investigated. Normal correction factors employed when using an autoclave⁴ could not explain a change of this magnitude. The possibility of CO_2 loss via leakage in the system was explored but although at 5000 psi some pressure drop was noted in overnight tests, it was too small to be significant (assuming the pressure drop was not due to selective loss of CO_2 rather than nitrogen). Another possibility exists and has been cited by Niedrach in high studies on a zirconia sensor for geothermal pH monitoring⁵. Corrosion of the container could cause an increase in pH by either the oxidation of metallic components to their oxides (e.g., by oxygen) or directly by the consumption of CO_2 if CO_2 oxidizes the vessel itself. Finally, glass dissolution could cause an increase in solution pH. Given the sample volume and buffer capacity and the extremely slight attack (if any) on B-13 or B-17 glass, this explanation is unlikely. No satisfactory explanation of the increase in solution pH has been verified and no corrective action, for example increased buffer capacity, significantly lessened its magnitude.

In spite of this, the data from tests could still be used to indicate the pH changes occurring at temperature. After design modifications had been implemented to correct problems discussed in Section 5.1, tests of probes fabricated from either B-13 or B-17 glass showed a general increase in

signal (versus the silver reference), corresponding to a gradual increase in pH occurring over several hours. Probes exposed to brine at temperatures up to and including 200°C showed similar output changes. Since they retained their pH response when tested subsequently at moderate temperatures, it is believed that they were indicating pH trends occurring at elevated temperatures during the test. Except for an increased sodium ion interference, it is anticipated that a sensor which functions well before and after hot brine exposure also functioned during the test. The magnitude of the sodium ion interference was not possible to determine accurately due to the pH uncertainty at high temperatures. However, given the observed changes in output indicating pH increases during the test and the confirmation of the increase at test completion, the sodium ion error was apparently sufficiently slight so that it did not affect the pH measurement at room temperature equivalent of pH 6 and not more than 0.3 pH unit at the final pH reached during the experiment.

A concern raised by Dr. George Jensen of Battelle was that problems might be encountered with the silver reference electrode, problems which might give rise to the sensor drift observed. Precision of silver reference electrodes in the AgCl-saturated brine was good, giving rise to the belief that the electrode was behaving as a reversible reference electrode. Furthermore, checking the potential of a silver reference versus the Inconel container showed that there was little relative drift. If the container is acting as a pseudo-reference electrode due to its large area and the stability of the oxidation-reduction chemistry at its surface, this indicates that the silver reference potential is quite stable, and the observed pH signal drift is indeed arising from an output change of the glass pH sensor.

VI. TASK II RECOMMENDED DESIGN

Figure VI-1 shows the recommended design based on Task I and Task II efforts. It is the same as the design after the Task I investigation with the following alterations:

1. B-17 sensing glass is recommended, replacing B-13.
2. The pH sensing bulb is hemispherical rather than conical.
3. The epoxy potting compound is used to encapsulate the full length of the stem glass with only a thin layer of silicone sealant around the stem glass at the sensing end of the probe.
4. The finish on the inner and outer surfaces of the metal housing is specified at the tighter tolerance of 16 rms inside and 32 rms outside.

One additional feature has proven useful and could be included at no extra cost: a second copper lead, embedded in the epoxy at the rear of the probe, can be used to check for leakage of solution past the polymeric seals. Should the impedance between this test wire and the metal housing drop below ten times the membrane impedance (corrected for temperature), the readings are being influenced by a shunt path and must be disregarded. Monitoring circuitry could be readily incorporated into test electronics.

The estimated price for probes per the recommended design is \$5,880 for 10 units, \$11,760 for 20 units, and \$14,700 for 25 units.

NOTE - PROBE END CAN BE TERMINATED IN ONE OF THE FOLLOWING WAYS:

- 1) "SWAGELOK" FITTING.
- 2) "CONAX" DISCONNECT FITTING.
- 3) THREADED CRES TUBE/PIPE TO ELECTRONICS HOUSING.
- 4) CONTINUE PROBE JACKET (CRES) TO ELECTRONICS HOUSING.

* BAL-SEAL #300-06 GC (GRAPHITE-CARBON FILLED TEFLON)

Δ .247^{+0.001} O.D., .128^{+0.001} I.D., 1/32 THK.

Figure VI-1: Modified Sensor Design

VII. REFERENCES

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