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DETAILED CONCEPTUAL DESIGN OF
A HIGH TEMPERATURE CO₂ SENSOR
FOR GEOTHERMAL BRINE
FINAL REPORT - TASK II

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PREFACE

The investigation described in this report was authorized under prime Contract DE-AC06-76RLO-1830 for the United States Department of Energy, Division of Geothermal Energy. It was performed by the Research Department of Leeds & Northrup Instruments, a Unit of General Signal Corporation for the Pacific Northwest Laboratory, operated by Battelle Memorial Institute. This report covers work during the period March 26, 1981 to August 31, 1984; however, no work was performed from December 1981 to March 1983 due to lack of funds. The constructive guidance, provided by Dr. George A. Jensen, Project Officer for the Pacific Northwest Laboratory is gratefully acknowledged. The assistance of Dr. Robert Robertus, Senior Research Engineer, and his co-worker, Robert G. Sullivan, Technical Specialist, during the field trial of the sensors is also acknowledged with appreciation.

The authors are indebted to several members of the L&N research staff for their helpful assistance in completing this work. Special thanks are given to Mr. R.D. Baxter and Dr. J.G. Connery for their outstanding contributions in many technical areas, and to Mr. N.L. Bonatucci for his conscientious efforts in the preparation and execution of experiments.

SUMMARY AND CONCLUSIONS

The Task I $p\text{CO}_2$ sensor was evaluated in the laboratory and improvements incorporated. Of special note was the redesign of the internal reference electrode which offered greater stability, and improved reliability - a design both smaller and more simple. The ISFET sensor was improved by using a new sensing material which afforded better speed of response. The H_2S getter was redesigned to overcome seal problems encountered in early Task II tests.

The improved probe was thoroughly tested in the laboratory at both moderate and elevated temperatures. This version was also tested at the Magma Electric Company geothermal plant in California. Whereas the laboratory tests were encouraging, the field tests were disappointing, in part due to problems not directly attributable to probe design limitations. In both tests, however, evidence showed that the polymeric seal in the internal ISFET element limited probe life unacceptably in the hot aqueous environment.

Electrostatic bonding of silicon to glass for three critical seals is included in the Task II recommended design. The development required to perfect the seal technique and incorporate them into an acceptable design extended until late in the contract life. Testing of the improved assembly in the field was not possible. The extended development effort had exhausted contract funding and exceeded time limitations, and the Battelle-operated test facility was not readily available due to interruptions of power plant operation. Nonetheless, all elements of the design were tested successfully in the laboratory, and these results, coupled with earlier tests in the field, indicate that the Task II recommended design will meet the contract objectives for geothermal brine CO_2 measurement.

In addition to the CO₂ sensor effort, ISFET pH sensors were tested in the laboratory and in the field. The results indicate that a design incorporating electrostatic seals, as in the recommended CO₂ sensor, will meet all objectives for a geothermal pH sensor and significantly exceed the minimum lifetime requirement of 24 hours.

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I. INTRODUCTION

In-line sensing of solution chemistry in brines for geothermal power plants is desirable in order to adjust solute composition to reduce or eliminate scaling. At present solution chemistry is determined by downhole sampling and subsequent analysis. This process risks sample contamination, composition changes due to cooling and provides only intermittent information. A program has been undertaken by Battelle Memorial Institute, Pacific Northwest Laboratory (PNL), operated for the United States Department of Energy, to develop instruments for geothermal application. The PNL program is responsive to the recommendations of the National Materials Advisory Board (NMAB) of the National Academy of Science¹ and has initiated several investigations on the adaptation of electrochemical sensors to the corrosive high temperature, high pressure, environment of geothermal brines. The overall objective is to develop sensors for measurement of redox potential, conductivity, pH, corrosivity, sulfide content and carbon dioxide (CO₂). Significant progress has already been made on this challenging task. To date, PNL has successfully demonstrated a high temperature reference electrode, an electrodeless conductivity probe, a redox electrode and an instantaneous corrosion rate measurement.

Leeds and Northrup Company, a Unit of General Signal, has been contracted by PNL to develop both a pH and pCO₂ sensor in a configuration which would withstand the high temperature corrosive environment of geothermal brines. Information on the developmental work for the pH sensor can be found in references 2 and 3. The pCO₂ sensor under investigation was targeted to operate for a minimum of 24 hours, in brine at 5000 psi and 200 °C. In addition the brine could

contain hydrogen sulfide (H_2S) at concentrations up to 75 ppm. The feasibility of meeting these requirements with "solid state" pH sensing was demonstrated in Task I. Following the completion of Task I, a comprehensive report on solution chemistry, theory of sensor operation, probe component selection, testing and pre-production cost estimates was submitted in October 1980, to PNL under prime Contract DE-AC06-76RLO-1830. The interested reader is directed to this report⁴ for a thorough discussion of the electrochemical principles involved and the design philosophy of the device. A brief description of the probe design fundamentals is also given in Section II.

The objectives of the Task II program were to evaluate a fully assembled pCO_2 probe, based on the Task I recommended design, and to incorporate improvements as necessary to assure its successful operation in the geothermal brine environment. Field tests of the recommended design were also scheduled at a geothermal well site.

II. SUMMARY OF TASK I RESULTS AND PROBE DESIGN

The design of the carbon dioxide sensor proposed in Task I is a form of a Severinghaus electrode⁵. This measurement system consists of both a pH sensitive electrode and reference electrode in a solution which is isolated from the external sample by a gas permeable membrane. In the absence of any interferences, the pH of the internal solution is affected in a predictable manner by the concentration (fugacity) of the dissolved carbon dioxide in the sample. For operation in geothermal brines, two primary sources of interference have been shown to exist. These are dissolution of the pH sensing material and the presence of H_2S . The pH sensing element under ambient conditions may be a conventional glass electrode. However, under the high temperature conditions of the geothermal environment, pH glass tends to be dissolved. Since the design of the Severinghaus electrode allows only a thin film of solution between the pH sensor and the membrane, dissolution products of the glass are not easily dispersed, but instead are trapped within this thin liquid film. With the primary components of the pH glass being Li_2O and SiO_2 , dissolution products can be considered to be alkali silicates and as such, cause the electrolyte to become more basic. Large errors can result since the pH of the internal electrolyte can change dramatically from this glass dissolution alone. An alternative pH sensing element was proposed for use in this application and investigated in Task I. Called an ISFET (Ion Sensitive Field Effect Transistor), it is a solid state type, FET-based sensor which has been specifically tailored for hydrogen ion detection. Details of the ISFET are shown in Figure II-1. Its operation is depicted schematically in Figure II-2. Simply stated, the gate coating, through surface interactions with the ions in solution, produces a field which changes the channel conductance of the FET in proportion to the concentration of ions.

FIGURE II-1: STRUCTURE OF AN ION SENSITIVE
FIELD EFFECT TRANSISTOR (ISFET)

FIGURE II-2: SCHEMATIC OF ISFET OPERATION

The coating recommended was of a material (Al_2O_3) which was highly resistant to chemical attack and as such was not affected by the corrosive conditions of this application. High temperature test results using ISFET pH sensor components were very promising; therefore this sensor was recommended in the Task I proposed design. The internal electrolyte to be used with this sensor had the following composition: .001 M in both cesium carbonate (Cs_2CO_3) and cesium bicarbonate (CsHCO_3), .01 M in cesium sulfate (Cs_2SO_4) and 10^{-4} M in cesium chloride (CsCl). Use of the large cesium ion was specified to minimize its penetration into the pH sensing film. There was shown to be an inverse correlation between the cation size and its extent of migration into the film.

As with conventional glass pH sensors, a reference electrode is still required to complete the circuit and set the electrochemical potential. A simple silver/silver chloride (Ag/AgCl) system was recommended for this application. However, brines are known to have high concentrations of H_2S . Avoidance of H_2S in the internal electrolyte is required to prevent silver sulfide formation which would both perturb the reference potential and change the electrolyte pH (since it is an acidic gas). The problem was avoided by the incorporation of an H_2S "getter" system consisting of a "filter", soaked in a copper sulfate (CuSO_4) saturated solution and placed between two gas permeable membranes. H_2S passing through the first membrane was reacted in the following manner:

forming stable, insoluble copper sulfide (CuS). The other permeants (e.g., CO_2) could then pass through the second membrane unhindered. The efficacy of the system (at room temperature) was thoroughly tested in the Task I work, with excellent results.

Another integral part of this system, investigated in Task I, was the gas permeable membrane. After a thorough search of the literature, several polymeric membrane materials were chosen and experimentally evaluated for selective permeability to CO_2 , compression set properties, and finally thermal and chemical stability. Candidate polymers included several formulations of EPDM (Ethylene propylene [rubber with] diene monomer), Teflon FEP, Teflon TFE, Teflon PFA, Halar, Parylene C, Tefzel and Kalrez. The material recommended for the Task I design was EPDM #E692-75 from Parker Seal Company, Lexington, Kentucky, because of its superior compression set characteristics and permeability to CO_2 . Its thermal and chemical resistance to degradation, though not as good as Teflon, was definitely acceptable in the environment of interest. Figure II-3 shows the details of the completed Task I design.

DET.	DESCRIPTION
1	A _g REFERENCE
2	INCONEL HOUSING
3	INTERNAL ELECTROLYTE RESERVOIR
4	DIAL MEMBRANE
5	COVER
6	GAS IMPERMEABLE METAL FOIL
7	H ₂ S GETTER
8	PH ISFET

FIGURE II-3: TASK I PROPOSED DESIGN

III. TASK II pCO₂ PROBE DEVELOPMENTAL TESTS

All of the components for the recommended pCO₂ probe were tested in Task I for resistance to chemical attack, maintenance of seal integrity and electrical characteristics after brine exposure. Reported in this section are the results of testing the mechanical integrity of completely assembled probes in simulated brine at temperatures up to 200°C and pressures up to 1000 psi. Several design modifications were made in the outer housing in order to simplify the probe assembly process, reduce its overall size, improve the seals, and increase its corrosion resistance. In addition, the internal pH sensing chip was altered for better electrical and electrochemical operation. The sealing process of the chip to its Pyrex supports was optimized. Finally, the membrane-getter system was simplified and its expected lifetime increased.

3.1 Internal Element

The internal pH sensing element is defined as the solid state pH sensing chip (ISFET) and materials that are used to support it, adhere it to the supporting structures, isolate the electrical contacts from solution, and passivate surfaces which are less chemically resistant. Throughout the test period, several alternate designs were used as described below.

3.1.1 Ryton Body and Epoxy Seals

Electrostatic bonding is the recommended sealing method (see Section 3.1.2) for high temperature testing and use. Prior to the optimization of that process, the electrochemical performance of the sensors was observed at moderate temperatures (80°C) using an internal pH sensing element shown in Figure III-1 with a Ryton body and epoxy seals. The assembly procedure is described below.

FIGURE III-1: pH SENSOR WITH RYTON BODY AND EPOXY SEALS

Polyphenylene sulfide or Ryton is a molded, machinable polymer, with excellent chemical resistance. The particular compound used contained both a glass filler for added strength and a Teflon filler for increased machinability. The material was purchased from International Polymer Corp., Houston, Texas, in rod form and machined in-house to the required dimensions. Since Ryton is a difficult material to bond, the machining operation, which inherently roughens the surface, aided in effecting good adhesive seals. The ISFET chip was mounted onto an alumina header with a highly filled epoxy adhesive from Armstrong Inc., Warsaw, Indiana. Both substrates were silanized to achieve a true chemical bond for maximum adhesion.

After the attachment of leads, the chip header assembly was mounted into the Ryton tube and back filled with the low thermal expansion, chemically resistant epoxy potting compound, #CX-0954 from Castall Inc., East Weymouth, Mass. In contrast to the proposed design from Task I, the Ag/AgCl reference electrode was also a part of this internal element. The configuration is further discussed in Section 3.1.4. Since the electrostatic bonding technique was still under development at this time, several sensors with Ryton bodies were prepared and tested at moderately elevated temperatures (80°), to determine probe response time and potential corrosion problems. These test results are given in Sections 3.3.1 and 3.4.2.

3.1.2 Electrostatic Bonding

The required geothermal environmental conditions generally inhibit the use of epoxies as sealants and molded polymers as structural supports in the probe. The technique of electrostatic bonding (also called anodic

bonding and field assisted sealing) was therefore proposed in the assembly of the internal pH sensing element. This process permits the sealing of metals to glass and other insulators at temperatures significantly lower than the softening point of the glass. The electrostatically formed seals are extremely strong and resistant to chemical attack because the substrate bonds are of a chemical nature, similar to conventional fusion seals.

Electrostatic bonding involves the application of a high dc voltage, across a silicon/glass (e.g. Pyrex) interface, where the metal is at a positive potential with respect to the glass. Typical working voltages are in the range of 200-2000 V. During the application of this high voltage, the components are maintained at a temperature ranging between 300 and 600°C or typically 200-400 °C below the softening point of the glass used. The process also requires smooth, extremely clean surfaces which can mate intimately. A surface finish of 2μ in., and flatness of 3 wavelengths/in. will generally assure this. A convenient criterion for the required level of contact is the appearance of interference fringes at the glass/silicon interface. Electrical contact is made to each part by means of either microprobes which provide point contact, metal plates and/or specialized metal fixturing.

Bond formation occurs as described below. When the glass is heated to the proper sealing temperature, its resistivity is lower due to increased positive ion (cation) mobility. As the positive ions in the glass move towards the cathode, the region of the anode becomes depleted and acquires a space charge of negative ions. Ultimately the voltage distributes itself between the polarized glass and the gap between the glass and

metal. At the optimum temperature and voltage an electrostatic field of $\sim 3 \times 10^6$ V/cm is generated, which corresponds to a pressure of ~ 350 psi⁶. The seal formation begins as the SiO₂ oxidizes and forms a diffusion bond with the glass, initially in the region of the maximum electric field, and extending outwardly from there. For more detailed descriptions of the process see References 6-9.

The seals thus formed are perfectly hermetic and can withstand thermal cycling of the type required in the brine applications.

The "ideal" pH sensing element is assembled using three electrostatic bonding operations, and is as shown in Figure III-2. The assembly procedure is briefly described below.

The first bond is made between a silicon and Pyrex "header". This layered header subsequently undergoes a process whereby sections of the silicon portion are removed leaving three isolated contact pads, and an annular ring connected to a 4th contact pad.

The second bonding operation results in the attachment of the ISFET chip to the Pyrex/silicon header. Electrical contact is then made between the chip and header, followed by the third bonding operation, the sealing of the chip header assembly to a supporting Pyrex tube. As stated previously, the bonding process requires clean, highly polished and optically flat surfaces, and good electrical contact to the substrates. Though every effort was made to provide a clean environment, invariably microscopic particles of dirt, photoresist, or "oxide" were present on some of the mating surfaces, inhibiting the bond formation in that area. Since

FIGURE III-2: ELECTROSTATICALLY BONDED pH SENSOR

each part must be perfectly bonded to be used in a subsequent bonding operation, those parts with entrapped particles could not be further assembled but instead were discarded. In addition, if the etching operation produced any irregularities in the annular ring, these units too were discarded.

The first and second bonding steps, which result in a chip-header assembly, were accomplished with an acceptable yield of ~ 33%. The third bonding operation, the most difficult, resulted in an unacceptably low yield. Several factors were causitive. There is a relatively small seal area, so that cleanliness became even more critical. Electrical contact must be made to the tube extremely close to the sealing end and yet far enough away to avoid a short to the header, leaving little margin for misalignment of fixturing. Finally, the nature of the fixturing and the parts themselves did not allow the observation of the interference fringes to assure intimate contact between the substrates.

A helium leak detector was used to check bond integrity after the final operation and the yield was found to be unacceptably low at <10%. This number was even further reduced by failures in assembling the sensor into the outer housing. Time and funding limitations did not allow sufficient experimentation or the production of parts in the quantities needed to solve the yield problem. For the interim, therefore, another method of sealing the chip-header assemblies to the Pyrex tubes was used to complete high temperature testing.

4.1.3 Permatex Seal

Permatex is a one component, room temperature vulcanizing, polysiloxane adhesive, and a product of Loctite Corp., Newington, Conn.¹⁰ It is a sealant and gasketing compound, specifically formulated for high temperature applications up to 315°C. Since the wet, corrosive environment of the carbonate electrolyte is likely to degrade the adhesive bonds of any polymer, the material was selected for use primarily as a gasket seal between the Pyrex tube and chip-header assembly with the elastomeric EPDM membrane providing the necessary back pressure to assure that no leakage or movement of the chip-header assembly would occur.

The Pyrex tube support for the pH sensing chip was back filled with a silicone rubber potting compound, #730 RTV from Dow Corning, Midland, Mich. This material was chosen because it was found that epoxies, even those with extremely low thermal coefficients of expansion, caused cracking of the Pyrex tube when thermally shocked to temperatures as low as 150°C. Several "high" temperature, high pressure tests (150°C, 500 psi) were performed with CO₂ sensors having an internal pH sensing element assembled with a Permatex seal. An example of the output from a successful run is shown in Section 4.2.3. Though this sealant performed satisfactorily under conditions stated above, its reliability at higher temperatures (i.e. 200°C) is low, and the seal of choice in the long term is that made with the electrostatic bonding technique. It is this one which is recommended in the Task II design.

3.1.4 Silver/Silver Chloride (Ag/AgCl) Reference Electrode

A reference electrode is required to be in direct contact with the internal pH sensing element. A simple Ag/AgCl reference system is sufficient since the internal solution is of a known composition, the chloride content of the electrode is fixed and the H_2S content is negligible. The Task I design specified a silver rod in a ceramic/metal feedthru, which was brazed into the outer housing of the probe. This design was not completely satisfactory since the feedthrus were found to be mechanically unreliable. The brazing operation could not be successfully carried out without resulting in warpage of the outer housing, and the feedthru design contributed greatly to the overall size of the probe. An alternative design was therefore implemented whereby a silver wire was sealed into the Pyrex tube of the internal pH sensing element. This was done by conventional glass sealing methods prior to the attachment of the ISFET chip-header assembly. An insulated leadout wire was connected to the Ag wire on the inside of the tube. The excess silver wire on the outside was wrapped around the tube and electrochemically chloridized. This configuration is shown in Figure III-2.

Thus, all leadout wires originated from the internal pH sensing element, and this design change allowed the reduction of the outer housing to approximately 1/2 its original diameter.

3.1.5 Tantalum (Ta_2O_5) Gate ISFET and Ion Implantation

Of the several composite gate materials tested in Task I, the most promising was the silicon/silicon dioxide/alumina ($Si/SiO_2/Al_2O_3$) system.

After exposure to the internal electrolyte up to 200°C, wafers of this type showed no chemical attack. They also maintained the greatest selectivity to H^+ and gave the most stable and reproducible signal. For this reason, SiO_2/Al_2O_3 gate ISFET sensors were used in the initial Task II work. Confirming Task I experimental results, Al_2O_3 gate ISFET sensors were found to be highly chemically resistant, and to have excellent pH sensitivity and acceptable response times. Two of the sensors used in the field tests discussed in Section 3.2.4, were of this type.

During the course of the Task II work, the ISFET chip was optimized in two ways. An improved gate material was deposited and a method of passivating the chip edges, which are subject to corrosion in this application, was instituted.

It was reported by Matsuo and Esashi¹¹ that tantala (Ta_2O_5) gate ISFET sensors were somewhat superior to their Al_2O_3 counterparts in response time, selectivity, pH sensitivity and hysteresis.¹¹ The first three parameters are basically self explanatory. The final parameter, hysteresis, is defined in Reference 11 as the offset voltage one hour after solution changes such as PH 7->4->7 or PH 7->10->7. Table III-1 shows the supporting data.

Ta_2O_5 gate sensors were prepared and evaluated in-house at room temperature for the parameters mentioned above with results confirming or surpassing those reported in the literature.¹²

TABLE III-1

Summary of Chemical Characteristics of Al_2O_3 and
 Ta_2O_5 Gate ISFETs*

	Al_2O_3 gate	Ta_2O_5 gate
pH range tested	1-13	1-13
pH sensitivity (mV/pH)	53-57	56-57
Na^+ sensitivity (mV)**	2	<1
K^+ sensitivity (mV)**	2	<1
Chemical response time		
95% (sec)	<0.1	<0.1
98% (min)	2	1
Hysteresis (mV)	0.8	0.2

* from Reference 11

** $\Delta_m V$ in 1M NaCl or KCl solution at pH=7

However, for use in the geothermal brine application, the chemical resistance of the new material had to be tested. In contrast to previous testing, the film was not tested in wafer form but on an ISFET with a gate area of $.011 \text{ cm}^2$ making detection of chemical attack more difficult. After 24 hours at 200°C in the internal electrolyte, the sensor showed no visible signs of film deterioration. Literature solubility data support this finding since Ta_2O_5 is reported to be soluble in only fused potassium bisulfate (KHSO_4) and hydrofluoric acid (HF).¹³ The majority of ISFET sensors used in the field tests had Ta_2O_5 gate insulation and again, after the test, no significant chemical attack was seen in the

gate area. In the field trials, some of Ta_2O_5 gate sensors were used to monitor pH, and they were exposed directly to a flowing stream of geothermal brine. Brine is known to have a high solids content and the physical survival of the chip surface also shows the film's satisfactory abrasion resistance.

A final consideration for the use of the ISFET chip was passivation of the potentially vulnerable areas of the chip, other than the gate area. The design of the sensor allows exposure of the sides of the chip (essentially silicon with a thin layer of SiO_2) to solution, in that only the back is bonded to the Pyrex header. (See Figure III-2.) In production, the sides cannot be passivated because planar microfabrication techniques are used. With this, many chips are processed on a single wafer and the wafer is later diced to separate the individual components; thus exposing the bulk silicon.

After the dicing operation, the first $\sim 20\text{\AA}$ ⁰ of silicon spontaneously oxidize in air forming, under normal circumstances, an acceptable passivation layer to further oxidation. For geothermal brine application, this is not sufficient. The SiO_2 layer dissolves in the internal electrolyte at elevated temperatures (similar to the dissolution of pH glasses) and the exposed Si subsequently oxidizes and dissolves, ultimately resulting in corrosion of the chip. In contrast to the pH glass dissolution, however, dissolved SiO_2 from the chip may not significantly affect the electrolyte pH. Only a relatively small amount is produced and it can dissolve into the bulk of the solution, its effect being diluted. It is not trapped in the thin layer between the chip and membrane, as are the pH glass dissolution products.

Importantly, this corrosion process does affect the sensors' electrochemical performance. Since the substrate is electrically connected to the source (see Figure II-2), under some conditions solution contact to the substrate can act as a shunt within the system, cause extraneous currents to flow which perturb the gate voltage and result in erroneous readings.

Several alternative protection methods were considered. A stable polymeric coating such as an epoxy or silicone rubber could be used to minimize the corrosion process. However, this would only work temporarily. The adhesive bonds would eventually deteriorate, allowing a thin solution layer to develop at the interface of the substrate with the predicted detrimental effect. A chemically vapor deposited (CVD) film of a noble metal, such as platinum, might be feasible. However, at the elevated use temperatures of the geothermal brine application, the metal is likely to react with the Si substrate forming complex, conductive silicides of unknown electrochemical characteristics.

Another alternative is to electrically bias the substrate itself to inhibit the current flow. As shown in the voltammogram for an Si/SiO₂ couple in Figure III-3, a bias too great in either direction will cause a current to flow. However, there exists between the two extremes a "window" in which little current is produced and electrochemical reactions involving the substrate are minimal.

FIGURE III-3: TYPICAL VOLTAMMOGRAM OF AN Si/SiO₂ COUPLE IN AN INNOCUOUS ELECTROLYTE

The reactions which do occur at the Si/SiO₂ solution interface have been investigated extensively.^{14,15} The cathodic current is reportedly generated as a result of a time dependent (cathodic) bias which produces a high, positive ion density in the SiO₂ ultimately causing it to become electrically conducting, and resulting in reduction of ionic species in the solution. In common electrolytes (e.g. KNO₃) this current has been observed at -1.7 to -3V.¹⁴ It occurred everywhere the Si/SiO₂ couple contacted the solution, but was seen principally at defect sites. With elevated temperatures, it is highly likely that this reduction process would be facilitated and would occur at an even less negative bias.

The anodic currents are generated when Si is oxidized to SiO₂. This reaction may be self limiting. When the insulating SiO₂ becomes thick enough, its high resistance prohibits further current flow. In corrosive media such as HF or a basic solution at elevated temperatures, the passivating layer dissolves as it forms and a continuously increasing current (concurrent with the erosion of the Si) is seen.

Experiments were carried out to identify the potentials where anodic corrosion currents occur in the solution proposed for this application, i.e. a cesium salt internal electrolyte at elevated temperatures. To illustrate the extreme cases, HF and KNO₃ were also used as the solution media. Since the ISFET devices used have n-type substrates, n-type Si wafers (with no FET structure) were used in this investigation. The composition of the electrolyte tested was .002 M CsCO₃, .1 M CsSO₄, .005 M CsCl, and .001 M H₂SO₄. The HF and KNO₃ solutions were 2.9 M and 1 M respectively. The elevated temperature testing was done at 85°C. The wafer was prepared with metallization on one side such that it could

be connected to a standard lead. Any metallization which might have contacted the solution was removed to avoid ambiguous results. A current-voltage scan was done within the range of +5V to -1.8V (depending on the substrate-solution system being evaluated) versus an Ag/AgCl reference electrode. The results are discussed mainly with regard to anodic currents, since the reaction, dissolution of the SiO_2 , is the same in each case. Cathodic currents are dependant on the electrochemical characteristics of the species in solution, and are not of interest here.

Figures III-4 to III-6 show the current-voltage curves generated for a Si wafer in various electrolytic media. In HF (Figure III-4), anodic current is seen at a potential of $\sim 0\text{V}$ and more positive. As expected, any anodic bias results in a current flow since the passivating layer of SiO_2 is not allowed to form. In the innocuous KNO_3 solution (Figure III-5), a fairly large anodic current is first seen in the range of +1.5 to +5V, however, with time and under a constant bias of +4V the current decreases to 5% of its original value, due to the passivating effect of the SiO_2 film being produced. Apparently the insulating layer is imperfect since there is still a small current present. In the carbonate electrolyte (Figure III-6) at room temperature, a stable anodic current begins at +1.0 V, suggesting that either a more soluble species than SiO_2 is being formed or the somewhat basic solution is dissolving the SiO_2 as with the HF, but not so extensively. Increasing the temperature of the carbonate electrolyte resulted in both an increase in the current and a shift in the anodic current wave to less positive values (+.8V), as would be expected. The data suggests that if the substrate bias could be kept at a potential near 0, the "corrosive" anodic current would be minimized

FIGURE III-4: VOLTAMMOGRAM OF AN Si/SiO_2 COUPLE IN HF

FIGURE III-5: EXPERIMENTAL VOLTAMMOGRAM OF AN Si/SiO_2 COUPLE IN KNO_3 , SHOWING TIME DEPENDENT SURFACE PASSIVATION

FIGURE III-6: VOLTAMMOGRAM OF AN Si/SiO_2 COUPLE IN CARBONATE ELECTROLYTE AT ROOM TEMPERATURE AND 80°C

if not completely avoided. This can be accomplished by suitable modification of the doping levels in the channel region. ISFET devices of the type shown in Figure II-3 have a "surface" Channel region located directly below the insulator. Such devices can have a substrate bias of (+) several volts, an unacceptable condition in this application. The following example shows how this condition can be remedied.

If "acceptor" atoms are introduced into the channel region in sufficient quantity to create a p-region to some depth below the surface, a so called "buried" channel structure is formed. The resulting FET may be either "normally-on" or "normally-off", depending on the dopant concentration in and extent of the p-region. Thus, the equivalent threshold voltage can be varied around the zero bias point. Ion implantation is a technique commonly employed to affect the desired control over the magnitude and content of the doped region. The concentration is controlled by the implant dose (ions/cm²) and the extent (junction depth) is controlled by the ion energy and subsequent thermal redistribution.

For use in the geothermal brine application buried channel devices are preferred. As an added precaution, the substrate can be electronically disconnected from the source and kept at ground potential (as opposed to the virtual ground potential of the source). This would prevent any small extraneous current flow occurring at the substrate from interfering with the device current and as a result causing an error in the measured pH.

3.2 Membrane-Getter System

The gas permeable membrane primarily serves to isolate the internal electrolyte from the outside solution. The ionic composition and strength of the internal electrolyte can then be fixed, poisoning the reference electrode and allowing direct correlation of pH to CO_2 . Also large osmotic pressure can be avoided which might result in water vapor migration through the membrane and consequent alteration of internal electrolyte concentrations.

Though the membrane permeability varies with respect to the permeating gas, the membrane is not truly permselective. All gases dissolved in the brine will ultimately reach the internal electrolyte in the absence of other filtering means. The composition of geothermal brine is known to have appreciable quantities of H_2S , an interfering gas (see Section II), necessitating a gettering system for its removal from the other permeants.

The Task I proposed design specified a membrane-getter system, the operation of which was confirmed at room temperature. In Task II work, this system was optimized and further tested. A spacer was added between the membrane and internal pH sensing element to assure more reliable and uniform operation of the probes. To simplify the assembly operation and minimize the risk of contamination of the internal electrolyte, the liquid getter was replaced by a porous solid one. The entire system was characterized at elevated temperatures to evaluate the response time and to determine membrane diffusion coefficients. As a result of these tests, the membrane thickness was reduced to improve the response time.

3.2.1 Spacer

The Task I design assumed a thin layer of electrolyte solution between the pH sensitive probe and the membrane assured only by capillary action. Results of room temperature testing indicated that this solution layer was either very thin, non-existent or variable which was in any case unacceptable. Though a thin solution layer is desirable for a relatively rapid response time, probes which responded normally in a beaker of electrolyte solution would become erratic or give a signal which indicated an "open" circuit when covered with an elastomeric membrane under tension. This was attributed to the "squeezing out" of electrolyte by the pressure of the membrane. Steps were taken to correct this using a porous spacer, which defined the solution layer by its thickness and also served as a wick to keep the solution in contact with both the pH sensor and gas permeable membrane.

Several spacing materials were considered. Glass paper was unsuitable for this purpose since it was known to lose its mechanical integrity after long term exposure to the internal electrolyte at 200°C. In addition, the paper was likely to dissolve somewhat and change the solution pH, acting as an interference, similar to the pH glass discussed in Section II. Ceramic paper, (i.e. mostly alumina) with a greater resistance to chemical attack, could not be obtained in a suitable thickness of .015" or less.

Teflon paper and woven graphite cloth were both considered because they are very chemically inert. The latter, with its superior mechanical stability, was ultimately selected for use in the Task II recommended

design. The cloth, Pyron type PW-3 is .011" thick, and was procured from the Stackpole Fibers Co., Inc. in Lowell, Mass. It is prepared in the standard manner¹⁶ from the polymer fiber precursor, polyacrylonitrile (PAN) and is typically used to reinforce or strengthen various other molded, extruded or cast polymers.

3.2.2 Membrane Thickness and Permeability Measurements

The Task II program included an experimental verification of the high temperature permeability coefficients for CO_2 and H_2S (P_{CO_2} and $P_{\text{H}_2\text{S}}$) in EPDM. These values were predicted in Task I work from data gathered at room temperature. Because Task I results were in good agreement with the literature values available, the test assembly and procedure was felt to be reliable and therefore suitable for Task II experimentation. The theory upon which the test assembly is based, and the details of sample preparation are presented in Reference 4. Figure III-7 shows the experimental configuration, which was modified from the Task I design to allow heating of the membrane up to 150°C , and the use of H_2S as a permeant. All tests were done with .035" thick samples.

The membrane was cut to the proper diameter and placed in the sample holder, which was wrapped with heating tape and insulation. The holder was then heated to the desired temperature. The entire system was fully evacuated (valves #1 and 3 open) allowing time for the membrane to out-gass (up to 16 hrs.). One side of the chamber, on the right, as shown in Figure III-7, was raised to atmospheric pressure (valve #4 open) using the gas (CO_2 or H_2S) under test. A "leak rate" was obtained over a period of 15 minutes by observing the increase in pressure on the vacuum side of

FIGURE III-7: EXPERIMENTAL CONFIGURATION FOR EPDM PERMEABILITY DETERMINATIONS

the membrane. Assuming the diffusion through the membrane is negligible during the period, the pressure increase was due only to leaks within the system. The entire system was then filled with the permeating gas (valves #1, 3 and 4 open) which "soaked" the membrane for 16 hours to assure complete saturation. Finally, the chamber on the left was evacuated (valve #3 open) to a minimum, predetermined pressure reading, generally $\sim 24\mu$. In calculations this value is the intercept. At this level, it was felt that little or no outgassing of the membrane had occurred, but the chamber was fully evacuated. Upon completion of the evacuation, valve #3 was closed, and the flux rate was measured by noting the increase in pressure with time.

The value, after correcting for the leak rate and intercept, was the permeability, at the temperature of interest in terms of μ/minute . The permeability constant (P_{EPDM}) was computed by including corrections for thickness, area, pressure differential across the membrane and gas volume of the vacuum chamber. P_{EPDM} was measured at 6 different temperatures, using both CO_2 and H_2S as permeants. Sample calculations using data obtained with CO_2 at 25°C are given below:

Gross flux rate: 16.5 μ/min
Leak rate: 1.17 μ/min
Net flux rate: 15.33 μ/min

Sample thickness = 0.79 cm

Sample area = 2.7 cm^2

Pressure across the membrane = 76 cmHg

Vacuum chamber volume = 29.2 cm^3

Intercept = 24μ

$$[(15.33 \text{ } \mu/\text{min} \times 10 \text{ min}) - 24] \times 29.2 \text{ cm}^3 \times 1/76,000 \text{ } \mu \times 0.079 \text{ cm} \times 1/2.7 \text{ cm}^2 \times 1/76 \text{ cmHg} \times 1/600 \text{ sec} = 3.19 \times 10^{-9} \frac{\text{cm} \cdot \text{cm}^3}{\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}} \quad (1)$$

This compares well with the Task I experimental value of

$$2.39 \times 10^{-9} \frac{\text{cm} \cdot \text{cm}^3}{\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}}$$

and literature value of $5.2 \times 10^{-9} \frac{\text{cm} \cdot \text{cm}^3}{\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}}$.

Table III-2 gives the experimentally determined values of P_{H_2S} and P_{CO_2} at 25, 70, 90, 110, 130 and 150°C, in columns #1 and 2. Column #3 shows values for P_{CO_2} after exposure to this gas for 40 hours at 110-150°C. For the results shown in columns #1 and 2, a new membrane was used, and was evaluated starting at room temperature. Testing then progressed to successively higher temperatures, until a maximum temperature of 150°C was reached. The data in column #3 was taken in the reverse order, starting at 150°C and decreasing incrementally to the temperatures of interest. These data reflect the theory that elastomers (and to some extent all polymers) undergo an "aging" (or degradation) process of elevated temperatures. Tensile strength, elongation and hardness are the parameters in which changes due to aging are typically observed. However, because the mechanism of degradation is presumed to be an increase in crosslinking and a resultant increase in density, the permeability of the polymer should also be affected, i.e., it will likely decrease.

TABLE III-2

Experimental Permeability Data For CO₂ and H₂S in EPDM

Temperature °C (°K)	Permeability Coefficient $\frac{\text{cm} \cdot \text{cm}^3}{\text{cm}^2 \cdot \text{sec} \cdot \text{cmHg}} \times 10^8$		
	H ₂ S	CO ₂	CO ₂ *
25 (298)	.495	.316	.249
70 (343)	2.37	1.13	.829
90 (363)	3.56	1.65	1.15
110 (383)	4.60	2.12	1.42
130 (403)	5.11	2.74	-
150 (423)	5.52	3.53	-

*Data taken after exposure to CO₂ at 110-150°C for 40 hours.

Crosslinking can also be initiated in the presence of sulfur, as evidenced by the fact that sulfur is a common curing agent in the preparation of elastomers. In Task I, the P_{CO_2} for EPDM decreased to $\sim 1/3$ of its original value after exposure to simulated brine + H₂S at 250°C for 24 hours. It had been concluded that the reason for this decrease was only from the presence of H₂S. The more recent data suggest that the elevated temperatures also contributed to this decrease significantly.

In Figures III-8 and III-9 permeability coefficients versus temperature are plotted for the experimental data and that theoretically predicted from equation (2).¹⁷

FIGURE III-8: PERMEABILITY COEFFICIENT VERSUS TEMPERATURE FOR CO_2

FIGURE III-9: PERMEABILITY COEFFICIENT VERSUS TEMPERATURE FOR H_2S

$$\log P_2 = \log P_1 + E_p / .0046 (1/T_1 - 1/T_2) \quad (2)$$

where P_1 and P_2 are the permeability constants at $T_1 > T_2$ ($^{\circ}\text{K}$), and E_p is the activation energy of the diffusion process in the material.

Equation (2) is most accurate if ΔT is small, since it does not account for second order effects which are more likely to occur over large temperature ranges. The activation energy (E_p) of EPDM for H_2S or CO_2 permeation is not known. For most permeation processes this value lies between 5 and 16 K cal/mole. A value of 8 kcal/mole was used; it is the reported value of E_p for the diffusion of CO_2 in butyl rubber, a closely related system. The experimentally determined values are lower than the computed ones. The discrepancy at high temperatures is thought to be especially significant.

Again, the cause is thought to be a thermally induced initiation of cross-linking in the sample. This effect could lead to probe failure in the long term by causing extreme embrittlement. However, it is not expected to have significant impact on the probe operation within the 24 hour use period, except to lengthen the response time slightly.

The time constant of the probe response was experimentally determined to be ~ 9 hours at 150°C , using two .035" thick EPDM membranes, and the porous silver getter described in Section 4.2.3. This was the thickness recommended in the Task I design for use in operating conditions of 250°C and 5000 psi. With the incorporation of the ISFET, the maximum use temperature of the pCO_2 probe was reduced to 200°C for reasons detailed in Reference 4. The apparent stress on the EPDM membrane is now also

reduced, primarily because the aging process is retarded at lower temperatures. Given the need to improve the response time, and the fact that the gas permeable membrane is thought to be the limiting factor at this temperature, the membrane thickness was reduced by one-half in the Task II design to .017". The advantage obtained was that of a corresponding improvement in response time, to one fourth its original value. A disadvantage introduced is the lowering of the overall membrane strength, increasing the risk of membrane rupture under high pressures.

Membranes of this thickness were not commercially available and had to be prepared from the .035" thick membranes. A machining process similar to lapping was used in which excess material was slowly and uniformly abraded away until the desired thickness was reached. The membranes were then ultrasonically washed to remove all loose particles. In use, the membrane functioned satisfactorily. No difficulties were encountered up to a differential pressure of 500 psi. A question of paramount importance was the maintenance of permeability characteristics similar to the thicker counterparts after this treatment. Though permeability measurements of the thin membranes were not made, useful information can be gained by comparison of a permeability parameter of this membrane with a known value from the literature. As stated above, butyl rubber is the material for which permeability parameters are well characterized and which most closely approximates EPDM. The permeability parameter which can be evaluated by analysis of the CO₂ response curves generated using this membrane is the diffusion coefficient or diffusivity, D.

The rate of transfer of CO₂ through the membrane is assumed to be controlled by the resistance of the membrane; all other resistances to the gaseous transfer being negligible. If the electrode responds to the influx of gas in a known, direct manner, the rate of transfer prior to arrival of the steady state condition can be evaluated and related to the diffusivity of the membrane. This relationship is expressed as:

$$D = L^2/t \text{ at time } t \text{ when } \frac{C-C^0}{C'-C^0} = 0.89 \quad \text{where} \quad (3)$$

C⁰ = Initial concentration of the gas

C' = Final concentration of the gas

C = Concentration of the gas at time t

D = Diffusion coefficient of the membrane

L = Thickness of the membrane

Diffusivity is related to permeability by $P = D \cdot S$ where S is the solubility constant of CO₂ in the membrane. In Figure III-10 the response curve of the pCO₂ probe with one .017" thick membrane, is shown. By solving for C in equation (2), t can be obtained and subsequently, D. The calculated values of D obtained from several response curves at 80°C, are shown in Table III-3. The literature value of D for butyl rubber at 25°C is also shown.

Direct comparison of these values is not possible, as temperature effects must be accommodated. Diffusivity exhibits an Arrhenius dependence on temperature.

FIGURE III-10. $p\text{CO}_2$ PROBE RESPONSE AT 80° USING ONE .017" THICK MEMBRANE

$$D = D_0 \exp(-E_D/RT) \quad (4)$$

where E_D is the activation energy for the diffusion process, and R and T are the gas constant and the absolute temperature. Using this equation and the literature value of D for butyl rubber at 25°C, the diffusion coefficient at 80°C was calculated and is listed in Table III-3.

TABLE III-3
Diffusion Coefficients for CO₂
in EPDM and Butyl Rubber

Material	Temperature °C	D x 10 ⁶ cm ² sec ⁻¹
EPDM	80	1.6
	80	0.9
	80	1.4
	150	0.6
Butyl Rubber	25	0.058
	80*	1.35
	150*	23

*Predicted value of $D_{\text{butyl rubber}}$ using literature value given at 25°C.

It compares closely with the average value of D for EPDM at 80°C (1.30×10^{-6} cm² sec⁻¹). It was concluded that the machining of the EPDM to reduce the thickness had little or no effect on its transport of CO₂.

A final comment must be added in reference to the value of D for EPDM at 150°C. It is considerably lower than predicted. This corresponds to a longer response time than would be expected from extrapolation of the data at lower temperatures. Primarily it was felt that one aspect of the test procedure contributed most to the observed slow response. The closed pressure vessel did not permit as rapid a CO₂ concentration change

as the jacketed cell used in the 800°C work. Also, previous permeability data indicated that some "aging" of the membrane did occur at 1500°C. Whereas the transient response characteristics were affected, these conditions do not affect the steady state results.

3.2.3 Hydrogen Sulfide (H₂S) Getter

Task I work included a thorough investigation of the efficacy of the H₂S getter system. The recommended configuration from Task I, shown in Figure II-3, uses saturated copper sulfate (CuSO₄) on a porous filter support. Task II experimentation, while confirming the operation of the completed probe assembly at elevated temperatures, showed that copper metal was deposited in between the dual layer membrane due to reduction of the CuSO₄ getter solution. This was postulated to be a result of a galvanic reaction with a component of the stainless steel housing, probably nickel, at the elevated temperatures used.

Though copper metal can combine chemically with H₂S, and also act as a getter, its efficiency is significantly lowered since the copper is in the form of large aggregates and has a decreased overall surface available for H₂S uptake. Even more undesirable is corrosion of the housing. This problem was eliminated by the selection of an alternative H₂S getter, one with a more negative reduction potential than that of Ni⁺⁺, i.e. Cd⁺⁺. The reduction potentials of each metal are given below¹³:

	E. Volts vs. SHE	
$\text{Cu}^{++} + 2\text{e}^{-} \longrightarrow \text{Cu}^0$	+0.377	(5)
$\text{Ni}^{++} + 2\text{e}^{-} \longrightarrow \text{Ni}^0$	-0.250	(6)
$\text{Cd}^{++} + 2\text{e}^{-} \longrightarrow \text{Cd}^0$	-0.403	(7)

It can be seen that copper ions are more likely to be reduced by nickel than are cadmium ions. Qualitative testing with a cadmium chloride (CdCl_2) getter solution confirmed this prediction. The corrosion of the housing was eliminated and H_2S was removed by the following reaction:

An added advantage to the CdCl_2 system is its increased solubility over CuSO_4 by 2 times. Thus, the getter capacity was also doubled. This system was used successfully in several probes which underwent high temperature testing, but was abandoned when modifications in the housing design caused getter solution leakage into the electrolyte during the probe assembly. This was unacceptable since it lowered the getter capacity and changed the pH of the internal electrolyte. The extent of these changes could not be controlled or known readily. The incorporation of a "solid" getter, in the form of a porous silver (Ag) disc, solved the leakage problem and facilitated the probe assembly process markedly. This system is shown in Figure IV-2.

The reaction by which H_2S is consumed is shown below.

The porous Ag was purchased from Selas Corp., Flotronics Division, Huntington Valley, Pa. Each disc was 1.11 cm in diameter, was matched to the diameter of the EPDM membrane material exposed to the brine. As with the liquid getter system, it was sandwiched between the two EPDM membranes covering the pH sensor. To assure unhindered permeation of the CO_2 , while at the same time maximizing the surface area for reaction with

H₂S, a 0.005 cm thick disc with a 0.8 μ (8×10^{-5} cm) pore size was selected. A test performed at 80°C with a disc of the same thickness but with 5 μ diameter pores showed no noticeable change in response time to CO₂ variations. The decrease in pore size of the disc recommended for use is not expected to affect the CO₂ response time, but yet will significantly increase the getter capacity. The membrane of the recommended pore size could not be evaluated due to time limitations.

The capacity or lifetime of the getter was determined theoretically using a simplified model.

The volume of the disc and the volume of the silver in it are 4.94×10^{-3} and 2.65×10^{-3} cm³ respectively. By subtraction, the volume of open space in the disc is found as 2.29×10^{-3} cm³. Assuming that this space is in the form of spheres 0.8 μ in diameter, each with a volume of 2.68×10^{-13} cm³, the number of spheres can be approximated by

$$\frac{2.29 \times 10^{-3} \text{ cm}^3}{2.68 \times 10^{-13} \text{ cm}^3} = 8.54 \times 10^9 \text{ spheres} \quad (10)$$

The surface area of the 0.8 μ diameter sphere is 2.01×10^{-8} cm², therefore the total surface area of the spheres in the disc is

$$(8.54 \times 10^9) \times (2.01 \times 10^{-8} \text{ cm}^2) = 172 \text{ cm}^2, \quad (11)$$

and is taken to be equal to the area of the surface silver in the porous disc. To determine the molar quantity of silver that this defines, the amount of silver per unit of surface must be calculated.

The density of elemental silver is 10.5 g/cm^3 , therefore,

$$.095 \text{ cm}^3/\text{g} \times 107.87 \text{ g}/\underline{\text{M}} = 10.240 \text{ cm}^3/\underline{\text{M}} \quad (12)$$

Since 1 mole = 6.02252×10^{23} atoms, a 4.72 cm^2 surface of silver, i.e. $(10.25)^{2/3}$, would contain $(6.02252 \times 10^{23})^{2/3}$ or 7.13×10^{15} atoms of silver. A 1 cm^2 surface would therefore contain 1.511×10^{15} silver atoms. Multiplying by the total surface area in the disc, (equation 10), the total amount of "surface" silver can be found.

$$1.51 \times 10^{15} \text{ atoms} \times 171 \text{ cm}^2 = 2.583 \times 10^{17} \text{ cm}^2 \quad (13)$$

$$2.58 \times 10^{17} / 6.02252 \times 10^{23} \text{ atoms}/\underline{\text{M}} = 4.29 \times 10^{-7} \text{ M} \quad (14)$$

This is the amount of surface silver available for immediate reaction with H_2S and it is $\sim 0.17\%$ of the total amount of silver in the disc. The actual amount which can react, however, is much greater than the first monolayer on the surface since Ag_2S is non passivating and will allow Ag migration through it. Thus available silver metal can exist even after the first monolayer has been reacted. Since the kinetics of such a reaction are generally increased at elevated temperatures, such as in the geothermal brine environment, an even greater amount of unreacted silver may be available than is at ambient temperatures. Perhaps as much as 500 times the predicted value is available, or $2.2 \times 10^{-4} \text{ M}$. With this, and the knowledge of the permeability constant for H_2S in EPDM, it is possible to estimate the capacity or lifetime of the porous silver H_2S getter in geothermal brine at 200°C and 1000 psi. For consistency, a worst case situation will be used as in the Task I report.⁴ The accuracy of the calculation is improved since experimental H_2S permeability values

for EPDM at elevated temperatures are known, as reported in the previous section. The permeability constant, P_{H_2S} , of EPDM at 150°C was experimentally determined to be $5.52 \times 10^{-8} \text{ (cm}^3\text{)(cm)(cm}^2\text{)}^{-1}\text{(sec)}^{-1}\text{(cmHg)}^{-1}$. For the purposes of this calculation, P_{H_2S} at 200°C can be estimated by equation (2) to be $1.48 \times 10^{-7} \text{ (cm}^3\text{)(cm)(cm}^2\text{)}^{-1}\text{(sec)}^{-1}\text{(cmHg)}^{-1}$. Ellis¹⁸ reports that the maximum level of H_2S ever measured in geothermal wells was 0.2 bars (15 cm Hg), and another source¹ reports a maximum value of 5.7 cm Hg. Ellis' value will be used in the computations, recognizing that it is a "worst case value", and typical H_2S levels to be encountered will be much lower.

The membrane thickness through which H_2S must diffuse to reach the getter is 0.046 cm and the effective membrane area is 0.97 cm². The number of moles of available silver is 2.2×10^{-4} M, however, since 2 moles of silver are required to react with 1 mole of H_2S , only 1/2 of this amount of H_2S or 1.1×10^{-4} M will be precipitated as Ag_2S . The volume of 1.1×10^{-4} M of H_2S at standard temperature and pressure is 2.47 cm³. Using the permeability coefficient estimate for 200°C, one can compute the effective lifetime of the porous silver H_2S getter, t :

$$t = \frac{(2.48) (0.046)}{(0.97) (15) (1.48 \times 10^{-7})} = 103,650 \text{ sec} = 14.7 \text{ hours} \quad (15)$$

Again, this estimate presumes the highest H_2S level reported in geothermal brine. Also, it must be noted that in Task I experimentation, it was found that the permeability of EPDM to H_2S decreased to 1/3 of its original value after exposure to simulated brine plus H_2S for 22 hours at 250°C. The decreased permeability, attributed to crosslinking of the

elastomer initiated by the H_2S would, in use, extend the getter lifetime beyond the estimated value. It is therefore believed that the getter system will effectively limit H_2S incursion for at least 24 hours in most geothermal applications.

3.3 Housing

The outer housing for the pH sensing device must meet several criteria for use in the harsh environment of geothermal brine. It must maintain mechanical strength at high temperatures and pressures. It must be chemically inert, primarily to avoid contamination of the internal electrolyte, but also to minimize the occurrence of pitting which could ultimately lead to mechanical failure of the housing. Precision machining, with close tolerances on mating surfaces and o-ring seats, is mandatory in such a design where high performance, leak proof seals are essential. Finally, it is desirable to have a simple design for low cost and ease of assembly and installation.

One modification, previously discussed in Section 3.1.4, was the repositioning of the Ag/AgCl reference electrode, which not only simplified the housing design considerably but enabled a reduction in the diameter to 1/2 of its original size. Two further design modifications which resulted in improved performance and increased long term reliability, are discussed below.

3.3.1 Gold Plating

Recognizing certain advantages of stainless steel over Inconel, namely increased machinability, quick availability and lower cost, the former was used as the housing material in the production of all Task II sensor housings. The fact that the material is not as chemically inert as Inconel was overcome by gold (Au) plating. Without it, evidence of chemical attack was seen in the form of pitting and greenish discoloration of the internal electrolyte solution when placed in simulated geothermal brine conditions. Pitting is extremely undesirable since it can ultimately lead to mechanical failure of the part by stress induced cracking initiated at the pitting sites. The discoloration of the internal electrolyte was felt to be from the formation of soluble nickel compounds. Contamination of internal electrolyte composition in this manner can adversely affect the probe operation and must be eliminated.

An electroplated gold coating with minimum porosity was applied to the housing. The plating was accomplished in a buffered acid bath, containing complexed $\text{Au}(\text{CN})_2$ as the gold source. Complexed cobalt compounds were also present to obtain maximum hardness and resultant abrasion resistance. A coating thickness of 0.0001", double the normal thickness, was applied. Prior to immersion in the plating bath, all parts were treated to maximize adhesion of the coating by micro glass ball blasting for the removal of adherent soil and to increase surface roughness, followed by submersion in an alkali cleaner to eliminate any loose soil. In all high temperature tests, the coating provided the necessary protection as evidenced by the absence of electrolyte contamination or pitting.

3.3.2 Seal Refinement

In initial Task II experimentation the cadmium chloride getter solution served as an indicator by detecting leakage around the EPDM gasket and membranes. Refinement of the sealing system was necessitated and accomplished by tightening of the tolerances on machined parts and gasket seal dimensions. Specifically, tests were performed whereby a fully assembled pCO₂ probe with a CdCl₂ solution either between the EPDM membranes in the internal electrolyte chamber, or both, was subjected to 200°C temperatures and pressures up to 1000 psi. Externally, a simulated brine solution with added sulfide was used. In post-test examination, leaks in the outer housing could be pinpointed by the presence of cadmium sulfide, a yellow to orange powdery precipitate. As a result, several improvements in the housing design were made.

The diameter of the screw holes in the EPDM membranes and gaskets (details 8 and 9 in Figure IV-1) was decreased to increase available seal area.

A special cutting tool was manufactured to give added precision and reproducibility to hole spacing as well as to provide a cleaner cut hole. Lock washers were added to all screws to prevent their loosening during the test. All of these changes resulted in a leak-free housing which effectively isolated the internal electrolyte and pH sensor from all but gaseous components of the brine.

For improved sealing of the internal pH sensing element, Bal Seals™ were incorporated into the design. These are spring-loaded polymeric seals in

a labyrinth configuration, purchased from Bal-Seal Engineering Co., Santa Ana, Cal. Their suitability for geothermal brine application was tested and verified by L&N during the developmental program for a high temperature geothermal pH sensor.⁴ As shown in Figure IV-1, 2 seals were used, separated by stainless steel spacers. By experimentation, it was found that using seals of varied polymeric compositions resulted in maximum sealing capability over the greatest temperature range.

The first seal, consisting of a graphite-Teflon composite, was rated for optimum performance at low temperatures i.e. room temperature to ~ 150°C. The second seal, consisting of a graphite-carbon-Teflon composite, allowed an increase in the maximum use temperature to ~ 250°C. The addition of carbon, however, results in increased hardness of the polymer, and as such, does not permit satisfactory sealing at more moderate temperatures. A preliminary seal of Dow-Corning RTV #730 fluorosilicone sealant (detail #7 in Figure IV-1) simply served to minimize contact of the internal electrolyte with these components and thus avoid potential contamination.

3.4 Electrochemical Performance in House

The operation of the pCO₂ probe was evaluated both in the lab and in field tests conducted at Magma Electric Co. in Holtsville, Cal. Lab tests were performed at room temperature, 80°C and 150°C. The lower temperature tests were done in a temperature controlled flow cell at atmospheric pressure. These tests mainly provided information about the stability of the reference electrode, and gave an indication of the probes response time. The high temperature tests simulated the actual

environment in which the probes were to be used, and confirmed the integrity of all seals within the system. These test results are presented below, along with experimental evidence which led to the alteration of the internal electrolyte composition.

3.4.1 Internal Electrolyte

The Task I recommended composition of the internal electrolyte included 10^{-4}M CsCl, for poisoning of the Ag/AgCl reference electrode.

With this Cl^- concentration, sensors could operate and give a stable output for up to 2 hours. However, they would begin to drift severely after that. Fresh internal fill solution would correct the problem in most cases. With some sensors, the reference electrode also had to be cleaned. The problem was successfully eliminated by several changes, all aimed at better stabilizing of the reference electrode potential.

The Cl^- concentration in the internal electrolyte was increased to $5 \times 10^{-3}\text{ M}$ and excess AgCl was added to the solution to assure an AgCl saturated solution at all times. The solubility of AgCl increases with temperature and it was felt that there may not have been enough to maintain a saturated solution during the elevated temperature tests. At 10^{-3} M concentration, the solubility of AgCl from the formation of soluble chloride complexes is at a minimum; thus there is further assurance that excess AgCl is always present.

In some cases, where cleaning of the reference electrode was required, contamination from reactive metal ions in solution was suspected. These ions were thought to have originated from the housing, or spacers used in

the sensor. Plating onto the reference electrode could have occurred as a result of a cathodic current. In theory, this current should not exist if all leads are perfectly insulated from one another. Should solution leakage occur, a current could flow. In order to minimize the adverse consequences of solution leakage, the reference electrode area was increased significantly, resulting in a greater distribution of the current and a lower current density. In most cases, solution leakage was not a major problem. However, in the event that it did occur, normal probe operation was not significantly affected.

3.4.2 Low Temperature Performance

As stated earlier, several tests of the pCO_2 sensor were done at the low temperature of $80^\circ C$ using a pH sensing element with a polymeric (Ryton) body and epoxy seals (see Section 3.1.1). The Task II recommended design including a pH sensing element electrostatically bonded to Pyrex, was still in the developmental stages at the initiation of the tests. Ryton body probes were readily available, not degraded by testing at more moderate temperatures, and provided valuable information for predicting the operational characteristics of the pCO_2 probe at $200^\circ C$.

Tests were performed in a temperature controlled flow cell at atmospheric pressure. CO_2 concentration changes were made by purging the solution with a gas of known CO_2 partial pressure.

The probe was tested in three stages of assembly. In the first assembly stage, the pH sensing element was sealed in the stainless steel housing, but no membranes were used. The test vessel contained the carbonate/bicarbonate electrolyte used in the probe. Also present, as a referee

probe, was a fully characterized glass pH sensor. This test verified the proper (Nernstian) functioning of the ISFET probe and reference element as well as confirmed the predicted chemical response of the electrolyte to variations in CO₂ concentration (Reference 4). Also, information relating to the temperature coefficient of the probe was obtained.

In the second phase of testing, a single .017" thick EPDM membrane was added to the probe assembly and the response time was evaluated. The external solution used was "simulated" geothermal brine, the composition of which is described in Reference 4. An example of a typical response curve is shown in Figure III-10 (p. 41). It is noted that, for a decade step change in CO₂ concentration, the time constant of this probe is ~ 15 minutes. In this test sequence, data was also obtained which aided in optimizing the configuration of the Ag/AgCl reference element to maximize its stability with minimum required electrode area. This work is further detailed in Section 3.1.4. Generally the tests showed that the basic system was operational and well characterized as evidenced by the agreement of the experimental data and theoretical calculations.

In the third phase of testing, a second EPDM membrane (the same thickness as the first) was added and the probe response was evaluated. Theoretically, doubling the thickness (of a single membrane) should result in a fourfold increase in the probes time constant, or one hour. However this was not seen. Instead, the time constant was generally several times the expected value, and was inconsistent from run to run. Also, even though the signal was steady, the response curve no longer had a simple exponential shape, but indicated the presence of two rate determining processes

with differing time constants. The causes of this behavior are complex and are undoubtedly related to the fact that the thickness of a single membrane was not doubled, but a second identical membrane was added. In order to have the two membranes act as one, one must presume that there is no slow absorption/desorption at the membrane surface. Furthermore, the membranes must either be in intimate contact or be separated by a thin medium which limits CO₂ flux less than the membrane itself. Our assembly process was not fully optimized when these test probes were fabricated. It is possible that an air gap was created between the two membranes which caused a lag in sensor response and gave rise to the complex response curve observed. Moreover, at times the sensors with two membranes failed to respond with theoretical (Nernstian) sensitivity, and this too might be explained by complex phase equilibration occurring between the two membrane layers. The sub-Nernstian response observed in these tests is not expected to be a problem in field use because probe assembly tested later at elevated temperatures (~ 150°C) did not evidence this problem.

3.4.3 High Temperature Performance

Figure III-11 shows the response of a fully assembled pCO₂ sensor to a step change in CO₂ concentration of one decade, i.e. 0.5 to 5%. The temperature and pressure during this test was 150°C and 500 psi, respectively. The design of the probe used in this particular test as shown in Figure IV-1, with three exceptions. The Permatex seal was used in place of electrostatic bond #3 (see sections 3.1.2 and 3.1.3). As previously stated, time and parts limitations did not permit the perfection of the

FIGURE III-11. p_{CO_2} PROBE RESPONSE AT $150^{\circ}C$ USING TWO .035" THICK MEMBRANES AND POROUS A_g GETTER

electrostatic seal. The porous Ag getter for H_2S had a 5μ diameter average pore size as versus the 0.8μ diameter average pore size in the recommended design. The EPDM membrane thickness was 0.035" instead of the recommended 0.017". It is thought that the limiting factor in the response time of the sensor was the membrane thickness. Therefore this time would be reduced to about 1/4 of that seen in this test, i.e. a time constant of approximately 2 hrs. at $150^\circ C$. At higher temperatures, a faster response is anticipated.

The Inconel high pressure test vessel, as well as the entire test assembly used in all high temperature experiments was the same as that used in the Task II developmental program for the geothermal pH sensor.³ A new center plate with a threaded hole to accept the pCO_2 sensor was made. After the probe was securely assembled into the test vessel, the testing was initiated with the filling of the chamber with simulated geothermal brine (see Section 3.4.2) equilibrated with .5% CO_2 . Care was taken to fill the entire chamber with liquid, leaving no air pockets into which CO_2 could outgas. After filling, the system was pressurized to 500 psi then heated to $150^\circ C$. After a stable reading was reached, the CO_2 concentration was changed by pumping in simulated geothermal brine equilibrated with 5% CO_2 .

Given the decade change in CO_2 concentration, the theory of operation discussed earlier predicts a change of one pH unit of the internal electrolyte. Since the Nernstian response of the pH sensor is temperature dependent, a change of 84 mV is predicted at $150^\circ C$. The test results confirm this.

It is noted that the noise level in the probe output increases with time. Two problems were encountered during the test, which are believed to have contributed to this noise. The Permatex seal was somewhat degraded in test allowing solution behind the chip. This results in an electrical short between the source, drain, substrate and/or reference leads. The more significant problem which ultimately led to the test being shut down before the 24 hour time limit, failure of the pump. An embrittled spring had broken, causing the metered flow of the brine to be increased, prematurely emptying the solution reservoir, and the pressure vessel. Since the noise level was a partial function of the pumping action, an increase in the flow rate caused an increase the noise level, as shown. When the solution chamber was emptied, probe dryout apparently occurred leading to its failure.

Despite the difficulties encountered, the test successfully demonstrated the proper functioning of the pCO_2 probe in the measurement of CO_2 in geothermal brine. The theoretically predicted response was seen as well as the typical exponential shape of the response curve. Further information about the properties of the EPDM membrane (i.e. diffusion coefficient) was also gained. This aspect was discussed in Section 4.2.2. Though additional tests at 200°C and 1000 psi were planned, they could not be carried out without the incorporation of the third electrostatic bond. Given these test results, however, no problems with the probe operation at 200°C are anticipated.

3.5 Field Tests

In October, 1983, field tests were performed on an interim design of the geothermal CO₂ sensor at the Magma Electric Company in Holtville, California. Battelle Pacific Northwest Laboratories had developed a comprehensive sensor test facility. The required pumps, piping, etc. had been installed previously. The bulk of the test instrumentation, including data logging capability, was in two trailers adjacent to the test site. A complete description of the geothermal field test capability developed by PNL and provided for use in these tests is included in Reference 20.

The comprehensive test facility permitted testing sensors under a variety of conditions and was found to be extremely valuable, even critical, to successful geothermal sensor development. High temperature brine from the plant inlet (at ~ 165°C) could be routed through the test facility and past its sensors. Alternately, brine at ~ 65°C from the plant outlet, i.e. after the heat exchangers but before the reinjection wells, could be monitored.

Of special importance was the ability to pass standard samples, e.g. pH buffers, through heat exchangers and subsequently to measure the heated standards for sensor calibration. This proved very valuable in testing brine pH sensors. However, it was not possible to expose the pCO₂ sensors to known concentrations of dissolved CO₂ in the field. This inability proved to be inconsequential because other problems severely limited pCO₂ sensor life such that comprehensive testing was impossible during the one field trial accomplished.

A second field trial near the close of the contract period had been planned, but delays caused by the development effort required for electrostatic seals limited the potential test date to a time period during which the Magma Electric Company plant experienced frequent problems causing plant shutdown. Further tests proved impossible before the test facility itself was removed from the site per agreement between PNL and Magma Electric Company.

Two types of sensors were tested in the field. An intermediate design of the dissolved CO₂ sensor was used. It had a polymeric body and seals, and is described in Section 3.1.1. Two CO₂ sensors were to be tested concurrently. Accordingly, four sensors were assembled, laboratory tested, and brought to the field site; two were available as backup in case of unforeseen problems.

In addition, at the suggestion of George Jensen, Project Officer for Pacific Northwest Laboratories, Leeds & Northrup agreed to construct and field test solid state (ISFET) pH sensors. The results of tests of each type of probe are reported.

3.5.1 Field Tests of pCO₂ sensors

Four pCO₂ sensors were available for testing. By mid-day of the first test day two were installed at the test site. It became clear immediately that one had an open lead, eventually determined to be the lead to the ISFET drain. This occurred before the probe temperature had exceeded 70°C. Since the probe had been checked in the laboratory the previous day and was functioning well, it may be that mechanical damage occurred in transit.

The second probe was placed on-line at noon in low temperature brine, and remained in this stream, at $\sim 67^{\circ}\text{C}$, until 2:46 p.m. During this period the probe showed a slight apparent decrease in sample CO_2 . The system was then flushed briefly with pH 7.85 buffer and later with pH 3.27 buffer to calibrate the pH sensors being tested concurrently. It was necessary to interrupt the test, and reduce the temperature to $\sim 30^{\circ}\text{C}$, to repair a valve. Finally, high temperature brine was passed through the test system at $\sim 159 \pm 1^{\circ}\text{C}$ overnight. The sensor worked well in this environment from 6:26 p.m. until about 1:45 a.m. the following morning. During this period the indicated pCO_2 changed only slightly, remaining constant to within $\pm 10\%$.

After 1:45 a.m. the sensor drifted significantly. This problem did not coincide with any identified event. Subsequent evaluation of this sensor showed leakage of the internal electrolyte into the "sealed" compartment housing the ISFET sensor leads. This is the likely cause of the drift and it indicated a seal lifetime of only about seven hours at 160°C , less than that demonstrated in the laboratory. It is speculated that the action of vibration on the softened polymeric seal may have caused failure of the seal prior to the laboratory findings carried out without vibration of the sensor.

Two new probes were installed on the morning of the second day. High temperature brine was run through the test facility, raising the temperature to about 135°C , at which point an unfortunate failure occurred. Another contractor, testing a new geothermal reference electrode system, experienced a catastrophic failure of his electrode. Its core element was

not satisfactorily contained and it blew out, across the test facility, landing about thirty feet away. The resultant leak in the system caused an immediate pressure drop and flash evaporation of a large quantity of brine. The rapid loss of pressure external to our CO₂ sensors caused the internal electrolyte to boil, rupturing the two EPDM membranes. Since the sensors would no longer operate as CO₂ sensors, the remainder of their membranes and getter system were removed and they were operated as additional pH sensors. The devices were not designed to withstand rapid loss of system pressure, and their early failure does not indicate that they would not have been acceptable had they been operated in the environment anticipated.

Analysis of all four probes after they were returned to the laboratory showed that each had suffered some degree of seal failure. This had occurred after at least five but not more than 12 hours of exposure to hot geothermal brine. Clearly improvements in sealing the ISFET sensing chip to its support tube were necessary. Electrostatic seals later proved to eliminate the high temperature polymeric seal failures encountered in the field, but this improved design was not field tested.

3.5.2 Field Test of pH Sensors

Four ISFET pH sensors were assembled, tested, and taken to the field site for test. These were identical to the pCO₂ sensors tested during the same period with the following exceptions:

1. The two EPDM membranes and the H₂S getter system were omitted, thereby directly exposing the internal pH sensing element to the geothermal brine. Rather than sense the pH of the internal electrolyte, the sensor would monitor the brine pH directly. Because the membranes and getter were omitted, the probe housing diameter on the pH probes was reduced.
2. The internal Ag/AgCl reference electrode used in the CO₂ sensor is not suitable for use directly in geothermal brine. It requires a constant chloride concentration in the solution to which it is exposed. Whereas this is the case when bathed by the internal electrolyte of the CO₂ sensor, it would not be the case in uncontrolled samples of brine. An alternative and physically separate reference electrode was used and the built-in reference electrode was omitted.

One of the four pH sensors was found to have a defective pipe-thread such that it could not be securely fitted into the field test assembly. Two of the remaining three were installed by noon of the first test day. They were operated until 2:46 p.m. in low temperature brine at about 67° C. The upstream sensor indicated a pH of about 4 whereas the second, relatively downstream, showed a pH of 6. It is felt that this difference may be real, caused by reaction of the brine with the test system plumbing.

At about 2:56 the sensors were exposed to preheated buffer adjusted to a pH of 7.85. Each sensor read within $\pm .05$ pH of this value. The devices were then exposed to buffer adjusted to a pH of 3.27. Both sensors read an apparent high value, the upstream one 3.60 and the downstream device read 3.65. Given the stability of these sensors in the field, and the

accuracy experienced in the lab, the discrepancies from the expected value of 3.27 pH were perplexing. The pH of the prepared buffer was verified to be 3.27. Dr. Robertus sampled the standard buffer coming out of the test assembly and found it to be 3.65! The pH of the buffer was increasing significantly after only one brief pass through the test plumbing. This confirmed that the sensors were monitoring the pH of the sample accurately. Other pH sensors based on a different principle and provided under contract by others did not note the extent of change of the standard buffers.

At 5 p.m., high temperature brine (at 150° C) was passed into the system and remained under test overnight. The "upstream" pH sensor failed almost immediately. It later was shown that the polymer seal had failed, allowing brine to short the sensor leads.

The second pH sensor continued to operate into the night. It is difficult to determine the measured brine pH since the sensor output was not temperature compensated. The pH was constant within ± 0.2 pH units from 7:26 p.m. until at least 1:26 a.m.

At approximately 1:30 a.m. a failure of the mechanical solution pump associated with the geothermal brine reference electrode terminated the test. This reference electrode, developed at PNL by M. J. Danielson, had functioned without problem to that point. It assures that its reference element, silver, is contacted by solution of known chloride content by pumping a reference solution over the silver electrode and into the brine. The pump failed, brine flowed into the reference electrode, and its potential shifted tremendously. That the error was due to reference

electrode shift is clear in that all sensors being measured versus this one common reference showed a signal change of like magnitude at the same time. This was true for our sensors and for several of a different type from another contractor. The failed pump was discovered and repaired the following morning.

The sensor still running after overnight brine exposure was left in place, and the final available pH sensor was installed in the upstream test port. As indicated in the CO₂ test description, shortly after the day's test was begun, a sudden decompression occurred which burst the CO₂ sensor membranes. After recovery and repair, pH buffers were checked and the system switched to high temperature brine. We now had four ISFET sensors under test as pH sensors. The final two pH sensors were operable and the two damaged CO₂ sensors had been converted for pH sensing. After only a few hours in hot brine, all four developed shorts, later identified to be due to brine wetting the ISFET leads.

Again, we had conclusive evidence of seal failure, and the necessity of redesign. Electrostatic seals of the ISFET to its support tube cured the seal failure as it did with the CO₂ sensors which exhibited like failures in field test.

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IV. TASK II DESIGN

The finalized probe design includes the essential components whose functions have been described in Reference 4, all modifications of the Task I design required as a result of testing described in other sections of this report were incorporated. The Task II probe design is shown in Figures IV-1 and IV-2, and its component parts are described below.

4.1 pH Sensing Element

The ISFET pH sensor has a Ta_2O_5 pH sensitive gate, selected for its superior speed of response, selectivity and stability characteristics. The chip is mounted onto a silicon/Pyrex header, which is subsequently supported on a Pyrex tube. All elements are joined by electrostatic bonding. Ohmic contact is made through the back of the chip. The sensor is shown in detail in Figure III-2.

4.2 Reference Electrode

A simple Ag/AgCl reference is used, since H_2S incursion into the internal electrolyte is negligible and the chloride content is fixed. The silver reference element is wrapped around the Pyrex support tube of the pH sensor, and welded to a platinum lead wire. The platinum lead wire had been fed through a hole in the tube and heat sealed in place, allowing it to exit through the center of the tube, along with the ISFET chip leads. This configuration is not only more simple and reliable than that used in the Task I design, but it also allowed a considerable reduction in the overall probe diameter. After the reference element was assembled, it was electrochemically chloridized in a KCl solution.

DET	QTY	DESCRIPTION
1	1	CONNECTOR (CRES)
2	1	O-RING #906 (E.P.D.M.)
3	1	HOUSING (CRES)/Au PLATED
4	-	EPOXY POTTING COMPOUND
5	2	BAL SEAL
6	2	WASHER
7	-	FLUOROSILICONE POTTING COMPOUND
8	1	GASKET (E.P.D.M.)
9	2	MEMBRANE (E.P.D.M.)
10	1	pH ISFET
11	-	H ₂ S GETTER SOLUTION
12	1	Ag REFERENCE
13	1	INTERNAL ELECTROLYTE RESERVOIR
14	1	HOUSING (PYREX)

FIGURE IV-1: TASK II pCO₂ PROBE DESIGN

FIGURE IV-2: EXPLODED VIEW OF TASK II pCO_2 PROBE DESIGN

4.3 Internal Electrolyte

The internal electrolyte has a low carbonate/bicarbonate content to minimize response time. A higher concentration of a "inert" salt is included to increase the ionic strength, more nearly matching that of the sample. This results in the stabilization of internal activity coefficients Henry's law constant and dissociation constants, as well as the reduction of osmotic pressure differences. A solution .001 M in both cesium carbonate and cesium bicarbonate, and 0.1 M cesium sulfate was used. CsCl is also added (10^{-3} M) for reference stabilization.

Excess solid AgCl is placed in the solution chamber to assure a saturated solution at the elevated temperatures. During assembly of the probe, the electrolyte chamber is filled under vacuum to avoid the entrapment of air.

4.4 Membrane-Getter System

Two EPDM membranes are positioned in the probe as shown in Figures IV-1 and IV-2. Each membrane is .017" thick. This allows a reasonable probe time constant and still assures that pressure gradients across the membranes can be accommodated by membrane distention.

A porous silver disc is placed between the membranes to serve as a getter for H_2S . To provide a continuous electrolyte layer at the chip-membrane interface, a spacer of non-conductive woven graphite fiber cloth is used. As shown in Figure IV-2, sizes of both the spacer and getter are such that neither interferes with the sealing capabilities of the EPDM membranes.

4.5 Housing

The stainless steel housing is comprised of 3 major sections. The terminal section, through which the leads exit, is threaded to match the installation ports of various field sites. The central section which houses the ISFET pH sensor is gold plated for maximum corrosion protection and avoidance of contamination of the internal electrolyte. The pH sensor is secured in place in this section with 2 spring loaded polymeric seals called Bal Seals. The seals differ from one another in their temperature and pressure related sealing capabilities such that, in tandem, sealing will be accomplished over the entire range of use conditions. To conform to the design specifications for use of these seals, each must be separated by a washer, which is in this case stainless steel. In order to minimize solution contact with these components, an RTV plug (Dow Corning Fluorosilicone #730) is potted in front of them, as shown in Figure IV-1, detail 7.

The final section consists of 2 gold plated stainless steel rings, between which the EPDM membranes and silver disc are secured. In final assembly onto the midsection, the rings serve to equally distribute tension on the membrane as it is stretched over the pH sensing element.

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