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R&D, FABRICATION AND TESTING OF pH AND CO₂ SENSORS FOR GEOTHERMAL BRINES

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PREFACE

The investigation described in this report was authorized under prime Contract DE-AC06-76RL01830 from the United States Department of Energy, Division of Geothermal Energy. It was performed under Subcontract B-P6530-A-P by the Research and Development 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 performed during the period April 1986 to March 1987. 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.

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SUMMARY

Reduction or elimination of scaling is a mandatory requirement for the operation of geothermal power plants. The use of downhole sampling and subsequent analysis for solution chemistry has many disadvantages. These disadvantages include composition change with cooling, risk of sample contamination, and non real-time indication.

The use of in-line sensing of solution chemistry avoids these drawbacks but requires sensors which can survive the extremely harsh environment of brine at high temperatures and elevated pressures.

Leeds & Northrup had previously undertaken a contract to develop sensors for pH and pCO_2 which would withstand these harsh environments. Detailed descriptions of this work were provided in four prior final reports (see References 2, 3, 4, and 5). At the conclusion of the research and development stage of this contract, a number of sensors were tested at a field site under actual operating conditions. Field test results which are addressed in the above report indicated that while we had made significant progress towards developing reliable sensors for both pH and pCO_2 , certain facets of the design were inadequate to give accurate long term measurement. The final report on contract DE-AC06-76RLO 1830 identified these weaknesses and recommended areas for further development to enhance the sensor operation.

At the request of Pacific Northwest Laboratory, Leeds & Northrup submitted a technical proposal, Q6410-41, dated March 27, 1986, to develop further these sensors with an option to assist in on-site field trials. Subsequently, subcontract B-P6530-A-P was awarded to develop the sensors according to the proposed improvements and to fabricate a small quantity for laboratory and field testing.

The primary areas addressed in the contract are replacement of polymeric seals with anodic bonding where possible, improved methods of lead attachment, improved sealing of the pCO₂ reference feed-through, H₂S getter optimization and improved passivation of the sensing head. Each of these areas is addressed in detail in the report along with laboratory test results pertaining to the particular phase.

In general, laboratory testing indicated that significant improvement had been achieved in most areas and results from the field trials conducted under actual operating conditions generally support this conclusion.

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1.0 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 sampling and subsequent analysis. This process risks sample contamination, composition changes due to cooling and gas release and provides only intermittent information. A program has been undertaken by Pacific Northwest Laboratory (PNL), operated by Battelle Memorial Institute, 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 Science (see Reference 1) 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 (CO_2). 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 & Northrup Company, A Unit of General Signal, has been contracted by PNL to develop both a pH and a CO_2 partial pressure (pCO_2) 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 pCO_2 sensor under investigation was targeted to operate in brine at 5000 psi and 200°C . In addition, the brine could contain hydrogen sulfide (H_2S) at concentrations up to 75 ppm (see References 4 and 5).

Leeds & Northrup has pioneered the development of the solid state Ion Sensitive Field Effect Transistor, known as the ISFET, for many years. Of particular importance in this application is the technology described in the Leeds & Northrup patent entitled ISFET Sensor and Method of Manufacture (see Reference 6).

In the approximately two years since the completion of work on the prior PNL contract, considerable advances have been made not only in the basic sensor (i.e., the ISFET technology) but also in bonding techniques and lead out technology.

In tailoring this sensor to the application, several critical aspects of its design had to be considered. The selection of a chemically inert pH sensing "oxide layer" which also showed excellent H^+ ion selectivity was of the utmost importance. Several candidate insulator film materials such as alumina, silica, silicon nitride, and tantalum were tested. In addition, the deposition and post treatment techniques were varied to obtain the optimum film properties. The development of special contacting and bonding techniques to eliminate polymeric components as primary bonds was also critical to the design.

The pCO_2 sensor developed for use in geothermal applications is a "Severinghaus" electrode system (see Reference 7). In its simplest form, it consists of a pH-reference electrode pair placed behind a gas permeable membrane in a carbonate/bicarbonate electrolyte solution. As CO_2 equilibrates with the internal solution, it determines its pH, which in turn is measured by the electrode pair. The pH sensor used in this design is the same as that described above, an ion sensitive field effect transistor (ISFET). (See References 8 and 9.)

In Section 3, Technical Approach, details of the R & D goals are presented along with a description of the actual work conducted and laboratory test results. The results of actual field testing are summarized in Section 5.

2.0 SUMMARY OF TASKS

The geothermal probe project was conducted in three phases as outlined in the Contract Statement of Work. A list of tasks performed in Phases I and II is shown in Table 2.1. Further, Leeds & Northrup provided technical support during field testing conducted by Battelle in Phase III.

TABLE 2.1. Work Breakdown Structure

Phase I - Research/Development and Final Design

Tasks:

- 1.1 Optimization of seals and bonds
- 1.2 Investigation of H₂S getter systems
- 1.3 Design finalization for pH and CO₂ probes
- 1.4 Design verification testing
- 1.5 Preparation of the final report

Phase II - Fabrication and Test of Probes

Tasks:

- 2.1 Acquisition of materials and parts fabrication
 - 2.1.a Mechanical parts
 - 2.1.b ISFET devices
 - 2.1.c Non-metallic parts
- 2.2 Probe assembly
 - 2.2.a Proof test units
 - 2.2.b Deliverable units
- 2.3 Laboratory Testing

Phase III - Field Testing

3.0 TECHNICAL APPROACH

This section on Technical Approach describes the research and development culminating in the final design of both the pH sensor and pCO₂ sensor. Further, the laboratory test results are presented and discussed. The section is divided into two major subsections: Section 3.1 relates to the pH sensor and Section 3.2 relates to the pCO₂ sensor.

3.1 pH SENSOR

The operation of an ISFET for pH sensing depends primarily on the development of an interfacial potential at the dielectric (membrane) - electrolyte interface, and the use of this potential to modulate the channel conductance of the underlying FET. Thus, the ISFET is a field effect transistor that responds to phenomena occurring at the insulator-electrolyte interface via the field effect (see References 8 thru 13). See Figures 3.1 and 3.2 which will be described in detail in Section 4.2.

A key element in the development of a practical pH ISFET is the availability of a suitable dielectric (membrane) material which has the required durability, selectivity, and sensitivity for the intended application (see Reference 14). Our work has shown Ta₂O₅ (tantala) to be an excellent choice with respect to all of these criteria (see Reference 5). This is illustrated by the results in Table 3.1. For comparison, the performance of Al₂O₃ gate ISFET's is also included in Table 3.1. Although either of these materials is adequate for the intended application, the Ta₂O₅ shows performance advantages in nearly every category.

A second key element is a suitable package which leaves the gate or sensing region exposed to the solution under test while protecting other sensitive regions (e.g., contacts, unpassivated chip edges) from the solution. Historically, packaging concepts have made liberal use of epoxy or other polymeric adhesives which deteriorate rapidly under the conditions of temperature and pH encountered in geothermal brine (see Reference 5).

FIGURE 3.1. Structure of an Ion Sensitive Field Effect Transistor (ISFET)

FIGURE 3.2. Schematic of ISFET Operation

	Al ₂ O ₃ gate	Ta ₂ O 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 14

** ΔmV in 1M NaCl or KCl solution at pH=7

TABLE 3.1 Summary of Chemical Characteristics of Al₂O₃
and Ta₂O₅ Gate ISFETs*

A more promising approach for such extreme environments is the use of anodic glass-to-metal bonding to form hermetic, durable seals. Earlier attempts to exploit the anodic bonding technique were only marginally successful. In the earlier design (see Reference 5), three anodically bonded seals were required, one in the fabrication of the header, a second to attach the chip to the header, and the third to attach the header to a support tube.

Although the first two bonds could be made reproducibly and with acceptable yields, the third (header to support tube) bond could only be accomplished with considerable difficulty and unacceptably low yields, due in part to the lead-out techniques employed to produce electrical connections between the ISFET chip and the external electronics. The approach, which employed conventional wire-bonding techniques between chip and header, and parallel gap resistance welding to attach the (.004 x .020") Au ribbons from header to lead-out wires resulted in a structure which was characterized by fragile bonds and was additionally difficult to fixture for the third and final bonding operation.

The improved design, as originally proposed for the present investigation, addressed all of these shortcomings of the earlier design. The salient features of the new design are highlighted in the following sections.

It is to be emphasized that the technical approach and detailed designs to be discussed looked very promising through the initial feasibility stage where the various subassemblies and procedures were tested independently, and indeed through some advanced assembly and testing stages of the investigation. It was only after it became clear that technical difficulties had precluded the possibility of obtaining laser drilled glass parts of the required quality and quantity to implement the proposed design that we redirected our efforts to the back-up design actually employed in the final laboratory and field tests. This back-up design is described in Section 3.1.7.

3.1.1 Edge Passivation

In previous assembly procedures, each chip was bonded to a Pyrex header individually after being diced from the processed wafer. Since only the back of the chip is bonded, the sides of the chip (essentially silicon with a thin layer of SiO_2) were exposed. In high temperature liquids, the SiO_2 layer dissolves and the exposed Si subsequently oxidizes and dissolves, resulting in corrosion of the chip. In addition to the physical consequences of such a situation, this corrosion process adversely affects the sensor's electrochemical performance.

In operation, the substrate and the source are electrically connected. In some cases, solution contact to the substrate can act as a shunt within the system, causing extraneous currents to flow. These effects perturb the gate voltage and yield erroneous readings.

One possible solution to this problem is to electrically bias the substrate to inhibit current flow. As shown in the voltammogram of an Si/ SiO_2 couple (see Figure 3.3) a bias too great in either direction will cause a current to flow (see Reference 5). However, there exists between the two extremes a "window" in which little current is produced and electrochemical reactions involving the substrate are minimal. The correct bias (normally around 0 volts) can be achieved, for example, by ion implantation in the gate region of the chip. The technique, however, is relatively empirical, and is thus subject to varied results.

With advanced processing technology at the wafer stage a more reproducible and cost efficient method of edge passivation appeared possible, obviating the need for ion implantation.

FIGURE 3.3. Typical Voltammogram of an Si/SiO₂ Couple in an Innocuous Electrolyte

In the preferred approach, anodic bonding of the Si (ISFET) to the Pyrex header is accomplished at the wafer stage, not at the chip stage. That is, a Si wafer containing many (potentially good) ISFET chips would be bonded to a Pyrex wafer having a like number of headers. The advantage of this approach is that the resultant Si/Pyrex laminate can be photolithographically patterned to produce an array of discrete Si islands or mesas, each containing an ISFET sensor. This structure permits subsequent passivation of the mesa walls by means of a sputter deposited inorganic insulating layer, such as tantalum. This chemically resistant coating thus protects the sidewalls in the test solution from corrosion and the formation of corresponding parasitic currents.

After suitable back side preparation (e.g., laser drilling and contact metallization), the Pyrex was to be diced to give a chip/header assembly ready for bonding to the selected support.

In practice, the viability of this wafer scale approach to bonding and edge passivation was readily established. Wafer level bonding was accomplished with acceptable yields, mesas were successfully etched on test wafers, and sidewall passivation was accomplished by sputter deposition of Ta_2O_5 . Figure 3.4 shows such a test structure after bonding, mesa etching, and Ta_2O_5 deposition.

3.1.2 Anodic 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 anodic bonding (also called electrostatic bonding and field assisted sealing) was therefore proposed in the assembly of the internal pH sensing element. This process permits the sealing of certain semiconductors and 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.

FIGURE 3.4. Photograph of Si Mesas on Pyrex Substrate

Anodic bonding involves the application of a high dc voltage across, for example, a silicon/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 2 microinches 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 follows. When the glass is heated to the proper sealing temperature, its resistivity is lower due to increase 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 approximately 3×10^6 volts/cm is generated, corresponding to a pressure of approximately 350 psi. The seal formation begins as the SiO_2 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 15-18.

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

Two significant changes were proposed in the anodically bonded seals for the present design. First, as described previously, the silicon chip to header bonding was to be done at the wafer stage rather than at the chip

stage in order to permit passivation of the chip edges. The second essential change was that all anodic bonds would be formed between Pyrex and a deposited metal film (Al or Ta) instead of between Pyrex and Silicon.

In the case of the wafer level chip to header seal, the Pyrex was to be bonded directly to the back side chip metallization. In the case of the header to support tube seal, the metallization was to be deposited directly onto the support tube and the bond formed between this film and the Pyrex header. This approach offers the advantage that the bond areas can be observed directly through the Pyrex header during the bonding operations. The earlier approach did not permit such observation and precluded detection of faulty seals by visual inspection. In addition, this approach eliminates one anodic bond completely.

Finally, it was proposed to passivate the exposed metal (Al or Ta) by anodization as necessary.

During the exploratory stage of the project, it was established that wafer level anodic bonds could readily be made between Pyrex and Al chip metallization as illustrated by Figure 3.5.

In the case of the header to support tube bonds, it was found that the bond integrity was strongly influenced by the type of metal employed. Bonds to Al metallization were achieved more readily than to Ta metallization. It was often the case that Ta bonds which visually appeared adequate would spontaneously fail at some later time. However, it was also demonstrated that the Ta metallization was much more chemically resistant than the aluminum.

It is our suggestion that the phenomenon of decreased bond strength and increased chemical resistance for Ta are in fact related and are attributable to the fact that Ta oxidizes readily at modest temperatures. We have completely oxidized 2000 Å thick Ta film to Ta₂O₅ in 60 minutes at 550°C in Ar/O₂ mixtures. Moreover, the presence of a surface oxide could be detected

FIGURE 3.5. Photograph of ISFET Wafer Bonded to Pyrex Header Substrate

visually after only 10 minutes at 550°C, a time and temperature combination comparable to that employed in anodic bonding. Thus, it is likely that this rapid formation of a surface oxide was responsible for both the poor bonding and good chemical protection.

3.1.3 Glass to Glass Sealing

As an alternative to anodic bonding for attaching the chip-header assemblies to the support tube, a scheme was envisioned whereby glass-to-glass seals would be made utilizing laser welding techniques. It was thought for example that a defocused CO₂ laser beam could be used to produce a seam weld between pieces of Pyrex by melting and subsequent refusion in the seam area.

In subsequent discussion with various technologists who had direct experience with laser machining of Pyrex, we were unsuccessful in obtaining any enthusiasm, or even encouragement, for the approach, given the unknowns and contractual constraints.

3.1.4 Chip-Header Contacts

In previous designs, the electrical contacts between the ISFET chip and support structures (header) were accomplished by conventional wire bonding techniques using .001" gold wires. These wire bonds and the fragile wires themselves contributed significantly to the occurrence of electrical failures at subsequent stages of assembly.

The header design proposed in this work employed laser machining techniques to produce tapered via holes in the Pyrex header and a second level of metallization to coat the vias, thereby connecting the ISFET metallization to the header metallization pads (see Figure 3.6).

For the proposed scheme to work, four steps had to be successfully accomplished in order as follows:

FIGURE 3.6. Section View of Chip-Header Structure

1. Formation of a high quality anodic bond between the metallized ISFET wafer and the Pyrex header wafer.
2. Formation of laser drilled holes of correct geometry and sufficient smoothness to permit the formation of the conducting via by conventional metallization techniques.
3. Deposition of a well-adhering electrically continuous film to provide electrical connection between ISFET chip and Pyrex header.
4. Patterning of the deposited metal to isolate Source, Drain and Substrate contacts on individual dies as illustrated in Figure 3.6.

As discussed previously, step 1 was readily accomplished. Feasibility was also established and techniques developed to accomplish steps 3 and 4. However, step 2, laser drilling, proved to be the fundamental limitation on implementing the proposed design. This is discussed more fully in Section 3.1.5, Laser Drilling.

Because of our inability to solve the technological problems associated with the proposed design, an alternative contacting scheme was employed which used wire bonding to connect the chip to header but with an improved lead-out approach. This alternative approach, the one actually used in the field test and illustrated in Figure 3.7 thru 3.9, is described in Section 3.1.7.

FIGURE 3.7. Exploded View of Sensor Assembly

FIGURE 3.8. Photograph of Assembled Sensor

FIGURE 3.9. Photograph of Partially Assembled Sensor

3.1.5 Laser Drilling

Laser drilling was originally selected as a means to achieve electrical contact to the ISFET chip after it had been bonded to the Pyrex substrate. Under optimum conditions, this drilling method produces a tapered hole, which facilitates subsequent metallization by vapor deposition.

The type of laser used and the optimum operation parameters are determined by the substrate being drilled and the desired hole size. For Pyrex, a CO₂ laser with a 10.6 micron wavelength beam is well suited since the material is highly absorbing in this infrared region.

A common problem encountered with this technique is crack formation in the substrate. They can occur during the drilling process, or afterward, and are apparently a result of excess heat dissipation into the material. It is known that by operating the laser in a pulse modulated rather than continuous mode, cracks can be eliminated. Dwell time, or the amount of time the laser is off, and pulse width, or the amount of time the laser is on, can be varied to produce a cycle which minimizes drilling time, and subsequent overheating and stress inducement, maximizing yield.

Power density, or power/cm² is a parameter which determines the mechanism of the hole producing process. At lower power levels this hole formation occurs by melting. At a higher power level, the material is vaporized. The latter was believed to be the preferred mechanism in minimizing crack formation.

The final consideration in utilizing this technology was the formation of a via with a conical profile, without which continuous metallization is not readily achieved by vapor deposition techniques. It has been shown that the condition of the exit end of the hole is dependent upon the sequence in which drilling and bonding are performed. If the holes are drilled through a separate

glass wafer, the hole flares outward slightly, preventing this end from being metallized by a single deposition from the entrance side of the glass. By contrast, when the holes are drilled after anodic bonding to a metallized silicon wafer, the exit end of the hole curves inward and the Pyrex at the circumference of the exit end remains anodically bonded to the underlying metal pad. The latter procedure was the one used in the proposed design.

The metallization on the silicon wafer has a twofold purpose. First, it is needed within the metallization scheme to provide electrical contact to the ISFET chip. More importantly, if it is reflective at the wavelength of the laser, it serves to terminate the drilling process (see Reference 20). In this work, aluminum was the metal of choice.

As indicated previously, formation of the drilled holes was the primary obstacle to implementing the proposed design. The preferred sequence Bond-Drill-Metallize-Pattern (see Section 3.1.4) was abandoned roughly mid way through the contract after repeated unsuccessful attempts to achieve the required hole characteristics. Although drilling was shown to be effectively terminated at the reflective Al/Pyrex anodically bonded interface, a Pyrex residue always remained which precluded the formation of electrical contact to the underlying ISFET structure.

Subsequently, a second approach was employed, one in which the Pyrex plates were laser drilled prior to bonding. Then, after repolishing both surfaces, the laser drilled plates were aligned to the ISFET wafers so that the holes lined up with the ISFET wafer metallization and then anodically bonded.

Initially, this second approach seemed promising, and low resistance ohmic contact was successfully achieved on anodically bonded structures after metallization with 2 micrometers of sputter deposited Al and patterning.

Subsequently, 6 Pyrex plates (1.5" x 1.5" x .008") were drilled, polished, and bonded to 2" diameter ISFET wafers to produce the final parts for laboratory and field testing. Each of these plate/wafer laminates at 100% yield would have supplied 25 good units, for a total of 150 potentially good devices. However, after metallization and testing, only 4 good devices were found. In all the rest, the via metallization was not continuous. Moreover, 3 of the 4 good devices were on one substrate, and after dicing, only one of the three remained good.

The yield problem was ultimately traced back to the laser drilling procedures, which were not capable of maintaining the required hole profile and which also resulted in crack formation in the wall surface which formed the hole boundary. These cracks then propagated during subsequent processing steps (polishing, anodic bonding, metallization). (Refer to the photograph in Figure 3.10.)

In subsequent discussions with the vendor supplying the drilled plates, it became evident that no solution to these problems was forthcoming within the contractual period. It was at this point that the wafer scale bonding approach was abandoned and the back-up design described in section 3.1.7 was implemented.

3.1.6 Electrical Lead-Outs

As pointed out in section 3.1.3, one objective of the proposed research was the development of improved electrical leadout techniques to eliminate lead stress and consequent electrical failure. Three alternatives were considered as described below.

Pogo Contacts

This approach involves the use of an array of miniature spring loaded contacts whose construction is similar to a child's pogo stick, thus the

FIGURE 3.10. Photograph of Crack Formation
in Laser Drilled Holes

name pogo pins or pogo contacts. L&N has considerable experience with this technique, and employs it to contact the sensing element in its 2600 series Pressure Transmitter. The lead wires are attached to the end of the pogo pins using high temperature solder while the other end, containing the spring loaded contact, is connected to the pad areas on the ISFET headers by mechanical force. This technique was actually tried in earlier geothermal brine investigations but was unsuccessful because of the presence of the fragile gold wire bonds. Since the pogo contacts and the wire bonds were on common small pads, even slight movement of the pogo on the pad could destroy the wire bond, resulting in open circuit conditions.

The elimination of wire bonds would, of course, alleviate this difficulty. Also, in contrast to earlier attempts, the pogo was to be fixed in place by means of a machineable ceramic support block.

Using this approach, the stress resulting from thermal expansion mismatches are taken up by the pogo springs resulting in secure mechanical and electrical contact at the operating temperatures.

Flex Strip

A second option was the use of a polyimide flex strip. Although the oxidative stability of the polyimide is excellent, its hydrolytic stability at high temperatures is poor. However, the strip is in the back of the "sealed" tube, essentially a dry atmosphere in the absence of other bond failure.

The metallization pattern on the flex strip would be attached to the ISFET header pads by the use of high temperature conductive epoxy or solder bumps on the flex strip.

Direct Attachment to the Header Contact Pads

The third alternative was to directly attach the lead wires to the header pads using solder, high temperature conductive epoxy, or parallel gap resistance welding. The latter approach is nearly identical to that used in previous contracts but warranted reexamination in light of the new header configuration. In this case, the lead attachment must be performed prior to the final bond of the header to the support tube. It offers the advantage of eliminating the need for special fixturing to affix the contacts. Conversely, the approach complicates the fixturing requirements for the header support tube bond.

During Phase I, the trade-offs associated with the various alternatives discussed above were evaluated and a decision was made to employ the pogo pin approach.

Figure 3.7 shows an exploded view of the entire lead-out assembly. The assembly consists of the three spring loaded pins, A, a machineable ceramic (Macor) contact block, B, to locate the pogo pins, and a spring steel retaining clip, C, which maintains the contact block at a sufficient depth in the Pyrex support tube, D, to assure positive contact between the pogo contacts and the metallized header, E.

The concept was tested initially on sensor mock-ups consisting of anodically bonded header/tube assemblies and pogo pin lead-outs, but without any active devices attached to the header. Such mock-ups were successfully tested to 500 psi and room temperature and temperature cycled between room temperature and 200°C with no adverse effects. A silicone foam was used to seal the back end of the support tube.

The original design concept employed three pogo pins, one each for the ISFET source, drain, and substrate (bulk) contacts. In the back-up approach to be described in Section 3.1.7, only two pogos were required since the

Source and Bulk contact were shorted together at the header. Thus, the field trial units employed the same lead-out approach and structure illustrated in Figure 3.7, but with the omission of one of the pogo pins. As a practical matter then, the lead-out design employed in the field trials is essentially the one used in the original design verification studies.

3.1.7 Laboratory Test Results

The preceding sections have described the preferred design approach and identified the technological difficulties which prevented its implementation in toto. In this section, the modified design and construction actually employed in the field trial will be described along with the internal laboratory test results.

Whereas the pH sensor assembly is illustrated in the diagram of Figure 3.7, a photograph of an actual sensor final assembly is shown in Figure 3.8. A photograph of a partially assembled device is shown in Figure 3.9. In this photograph, the following essential elements may be identified: the chip header assembly, the metallized Pyrex support tube, and the pogo pins supported by the Macor contact block.

The chip/header assembly consists of the ISFET chip, anodically bonded to a Pyrex header. The ISFET chip itself, illustrated in Figure 3.11, is .100" x .100" x .008" thick. The front side of the chip is completely covered by the pH sensing Ta_2O_5 membrane. The back side contains the Al metallization which provides electrical contacts to the chip. The back side of each chip also contains an Al border for providing the anodically bonded seal to the Pyrex header.

The header shown in Figure 3.9 is a .250" dia. Pyrex disc, .020" thick, and containing a centrally located .080" x .040" rectangle cut-out. A sputter deposited Al metallization pad pattern was also provided to the back side of each header.

FIGURE 3.11. Back Side of ISFET Chip

The Al pads were connected to the chip contacts by wire bonding. These pads were also the points of contact with the pogo pins.

The notch in the Macor contact block, Figures 3.6 and 3.8, and pogo spacing provided clearance so that the pogo pins and contact block would not disturb the wire bonds. The rectangular cut-out in the Pyrex header precluded the use of the third pogo contact. Therefore, the ISFET source and substrate contacts were wire bonded to a common pad on the header yielding a two terminal device.

A total of 46 such chip header assemblies were anodically bonded in preparation for laboratory and field tests. After wire bonding, 30 of the 46 passed electrical tests and were available for the next stage of assembly, anodic bonding to the Pyrex support tube .250" O.D. x .150" I.D. x .750" long.

Anodic bonding to the support tube was accomplished through an intermediate metal film sputter deposited onto the sealing surface of the support tube. The anodic bond then occurred between the Pyrex header and this metal film. As indicated earlier, both Al and Ta were employed, with Al providing the more dependable bonds. Of the 30 good chip/header assemblies, 21 were successfully bonded to the support tube. Of the 21, 12 were pH sensors and 9 were CO₂ sensors, the distinction being that the CO₂ sensors had a Pt wire sealed into and through the wall of the support tube as described in Section 3.2.1. Only two of these had Ta metallization.

During the next stage of assembly, insertion of the Macor contact block, pogo pins and retaining clip (see Figure 3.7), and potting, only 3 sensors were lost, so that 18 sensors were available for functional test, 12 pH and 6 CO₂ sensors.

It should be pointed out that in fact the only losses incurred during this stage of assembly were associated with CO₂ sensors, and may be attributed to the greater fragility and difficulty of assembly of the CO₂ sensor because of the presence of the Pt wire feed-through.

The results of functional tests are presented in Table 3.2. Two of the 18 sensors failed functional test, one because of an electrical open circuit, and one with excess light sensitivity indicative of a bad substrate (bulk) contact. In two others, header-to-support bond failures occurred during temperature tests. The remaining 16 probes were then subjected to more detailed tests over the temperature range 0-95°C. Typical results are shown in Table 3.3.

From column one, it may be seen that a typical temperature run lasted about 24 hours. Parameters monitored during this run were temperature (col. 2), reference voltage; V_r , between reference electrode and ISFET source; a.c. pick-up (noise) in the V_r signal; drain current, I_d ; source drain voltage, V_d ; substrate voltage, V_b , which was equal to the source voltage hence $V_b=0$); the drift rate of V_r with time at temperature (col. 10); the leakage current, I_k , in the "gate" or reference electrode circuit (col. 12); the known pH of the buffer solution at the measured temperature; the pH value obtained from the sensor at that temperature; and the error (difference) between actual pH and pH indicated by the sensor output.

The more important of these quantities are leakage currents, I_k , which is related to package integrity; the pH error, which shows how well the sensors' temperature dependence can be predicted; and the closure or difference between the values of V_r at the beginning and conclusion of the 24 hour temperature cycle. For the example shown, the closure is approximately 2.8 mv or approximately .05 pH units.

SENSOR NO.	WAFER SERIES	TYPE (pH or CO ₂)	V _r	SENSITIVITY (mV/pH Unit)
681	11-7-85	pH	-1.6982	57.3
682	8-26-86	pH	-2.8620	58.8
683	8-26-86	pH	-2.2809	59.0
684*	11-7-85	pH	-1.4743	58.0
685	8-26-86	pH	-2.1635	59.0
686	8-26-86	pH	-2.6284	58.7
687	11-7-85	pH	-1.6902	58.7
688	11-7-85	pH	-1.6191	58.6
689	8-26-86	pH	-2.8771	58.6
690	8-26-86	CO ₂	-2.1756	57.6
691	11-7-85	CO ₂	-1.6139	59.5
692	11-7-85	CO ₂	-1.4452	59.1
693	11-7-85	CO ₂	-1.4447	58.8
694**	11-7-85	pH		
695	11-7-85	pH	-1.5183	58.0
696	11-7-85	pH	-1.5888	59.0
697	11-7-85	CO ₂	-1.2063	58.0
698	11-7-85	CO ₂	-1.4547	58.5

* device is light sensitive

** device has open circuit

TABLE 3.2. Laboratory Functional Test Data

SUMMARY OF ISFET PROBE # 693 TEST RESULTS 11/13/86
IN NBS KHP (185F) BUFFER

W ₁ DC REFERENCE TO SOURCE ENF														ANALYSIS				
AC IN W ₁ mV				SLOPE, mV/pH										FINAL VALUES				
TIME	TEMP	MEAN	σ	I _d , μ A	V _d , V	V _g , V	MEAN, W ₁	σ , mV	MEAN	σ	I _h , nA	I _b , nA	2nd REF	TEMP	TIME	NBS pH	PH	ERROR
16:04:15	25.02	0.01	± 0.01	-99.997	-1.5000	0.0000	-1.6032	± 0.03	-0.53	± 0.02	-1	0	16.54			4.006	3.997	-0.009
16:13:28	25.03	0.05	± 0.01	-99.997	-1.5000	0.0000	-1.6032	± 0.03	-0.35	± 0.02	-1	0	16.54	25.02	16:21:08	4.006	3.997	-0.009
16:22:48	25.03	0.67	± 0.01	-99.997	-1.5000	0.0000	-1.6032	± 0.02	-0.38	± 0.01	-1	0	16.57	25.02	16:30:28	4.006	3.997	-0.009
16:31:59	25.02	0.58	± 0.01	-99.997	-1.5000	0.0000	-1.6033	± 0.02	-0.43	± 0.01	-1	0	16.55	25.03	16:39:39	4.006	3.996	-0.010
17:29:06	0.06	0.96	± 0.01	-100.003	-1.5000	0.0000	-1.6358	± 0.00	0.05	± 0.00	0	0	18.51	0.04	17:36:46	4.006	4.049	0.043
17:38:19	0.04	0.94	± 0.01	-100.003	-1.5000	0.0000	-1.6358	± 0.00	-0.48	± 0.00	0	0	18.45	0.02	17:45:58	4.006	4.058	0.044
17:47:31	0.02	0.94	± 0.01	-100.002	-1.5000	0.0000	-1.6358	± 0.00	-0.15	± 0.00	0	0	18.40	0.01	17:55:11	4.006	4.051	0.045
17:56:44	0.01	0.95	± 0.01	-100.003	-1.5000	0.0000	-1.6358	± 0.01	0.42	± 0.00	0	0	18.31	0.01	18:04:24	4.006	4.051	0.045
18:37:39	9.96	0.88	± 0.02	-100.004	-1.5000	-0.0000	-1.6242	± 0.02	-0.45	± 0.00	0	0	16.53	9.96	18:45:19	3.999	4.005	0.006
18:47:03	9.98	0.88	± 0.01	-99.998	-1.5000	-0.0000	-1.6242	± 0.02	-0.58	± 0.00	0	0	16.44	9.99	18:54:43	3.999	4.005	0.006
18:56:33	9.99	0.69	± 0.02	-99.998	-1.5000	-0.0000	-1.6242	± 0.02	-0.07	± 0.01	0	0	16.37	10.00	19:04:13	3.999	4.004	0.005
19:05:45	10.00	0.98	± 0.01	-99.998	-1.5000	-0.0000	-1.6243	± 0.02	-0.31	± 0.01	0	0	16.33	10.00	19:13:25	3.999	4.004	0.005
19:46:58	19.98	0.84	± 0.01	-99.998	-1.5000	-0.0000	-1.6109	± 0.01	0.10	± 0.00	0	0	16.22	20.00	19:54:38	4.001	3.988	-0.013
19:56:14	20.00	0.84	± 0.01	-99.998	-1.5000	-0.0000	-1.6109	± 0.00	0.14	± 0.00	0	0	16.27	20.01	20:03:54	4.001	3.988	-0.013
20:05:27	20.01	0.86	± 0.01	-99.998	-1.5000	-0.0000	-1.6109	± 0.02	-0.52	± 0.01	0	0	16.24			4.001	3.988	-0.013
20:14:39	20.01	0.86	± 0.01	-99.997	-1.5000	-0.0000	-1.6109	± 0.02	0.29	± 0.01	0	0	16.22	20.01	20:22:19	4.001	3.988	-0.013
20:25:32	29.97	0.81	± 0.01	-99.997	-1.5000	-0.0000	-1.5962	± 0.03	0.16	± 0.02	-1	0	16.99	29.99	21:03:13	4.012	3.996	-0.016
21:04:45	30.00	0.81	± 0.01	-99.997	-1.5000	-0.0000	-1.5962	± 0.04	-0.46	± 0.02	-1	0	16.92	30.00	21:12:25	4.012	3.996	-0.016
21:13:58	30.00	0.68	± 0.01	-99.997	-1.5000	-0.0000	-1.5961	± 0.03	0.13	± 0.02	-1	0	16.92	30.00	21:21:38	4.012	3.996	-0.016
21:23:10	30.01	0.82	± 0.01	-99.997	-1.5000	-0.0000	-1.5961	± 0.02	0.25	± 0.01	-1	0	16.95	30.01	21:30:58	4.012	3.996	-0.016
22:03:57	40.01	0.77	± 0.02	-99.997	-1.5000	-0.0000	-1.5803	± 0.03	0.58	± 0.02	-1	0	17.73			4.031	4.021	-0.010
22:13:10	40.05	0.77	± 0.01	-99.997	-1.5000	-0.0000	-1.5803	± 0.02	0.27	± 0.01	-1	0	17.71	40.06	22:20:58	4.031	4.021	-0.010
22:23:14	40.04	0.78	± 0.01	-99.997	-1.5000	-0.0000	-1.5803	± 0.02	0.27	± 0.01	-1	0	17.72	40.05	22:30:54	4.031	4.021	-0.010
22:32:27	40.05	0.65	± 0.01	-99.997	-1.5000	-0.0000	-1.5802	± 0.02	-0.10	± 0.02	-1	0	17.76	40.05	22:40:06	4.031	4.021	-0.010
23:17:18	49.91	0.73	± 0.01	-99.997	-1.5000	-0.0000	-1.5641	± 0.01	0.05	± 0.01	-1	0	18.55	49.93	23:24:58	4.057	4.053	-0.004
23:26:31	49.93	0.63	± 0.02	-99.997	-1.5000	0.0000	-1.5641	± 0.00	0.10	± 0.00	-1	0	18.52	49.94	23:34:11	4.057	4.053	-0.004
23:35:44	49.94	0.73	± 0.01	-99.997	-1.5000	0.0000	-1.5641	± 0.02	-0.00	± 0.01	-1	0	18.56	49.94	23:43:23	4.057	4.053	-0.004
23:44:56	49.94	0.75	± 0.01	-99.997	-1.5000	-0.0000	-1.5641	± 0.00	-0.05	± 0.00	-1	0	18.59	49.94	23:52:36	4.057	4.053	-0.004
00:04:18	59.99	0.73	± 0.01	-99.996	-1.5000	0.0000	-1.5471	± 0.02	-0.02	± 0.02	-3	0	19.29	60.00	00:13:58	4.091	4.090	-0.001
00:13:49	60.00	0.71	± 0.01	-99.997	-1.5000	0.0000	-1.5471	± 0.03	0.04	± 0.02	-2	0	19.20	60.03	00:41:29	4.091	4.090	-0.001
00:43:26	60.03	0.71	± 0.02	-100.004	-1.5000	0.0000	-1.5472	± 0.03	-0.03	± 0.02	-2	0	19.32	60.03	00:51:06	4.091	4.088	-0.003
00:52:51	60.03	0.73	± 0.01	-99.997	-1.5000	0.0000	-1.5472	± 0.03	-0.29	± 0.02	-2	0	19.31	60.03	01:00:31	4.091	4.088	-0.003
01:30:03	70.04	0.71	± 0.01	-100.003	-1.5000	-0.0000	-1.5297	± 0.02	-0.09	± 0.02	-6	0	19.03	70.06	01:37:43	4.126	4.132	0.006
01:39:16	70.06	0.61	± 0.01	-100.003	-1.5000	0.0000	-1.5297	± 0.03	-0.36	± 0.02	-5	0	19.09	70.08	01:46:56	4.126	4.131	0.005
01:48:29	70.08	0.68	± 0.01	-100.004	-1.5000	0.0000	-1.5298	± 0.04	-0.66	± 0.02	-5	0	19.93			4.126	4.130	0.004
01:57:48	70.08	0.68	± 0.01	-100.003	-1.5000	0.0000	-1.5298	± 0.03	-0.68	± 0.02	-5	0	19.96	70.07	02:05:28	4.126	4.130	0.003
02:34:51	79.99	0.99	± 0.01	-100.002	-1.5000	-0.0000	-1.5119	± 0.00	-0.31	± 0.00	-11	0	20.35	80.01	02:42:31	4.164	4.179	0.015
02:44:04	80.01	0.68	± 0.01	-100.002	-1.5000	0.0000	-1.5120	± 0.02	-0.41	± 0.01	-10	0	20.39	80.02	02:51:44	4.164	4.178	0.014
02:53:16	80.04	0.68	± 0.01	-100.002	-1.5000	0.0000	-1.5120	± 0.00	-0.31	± 0.00	-10	0	20.52	80.04	03:00:56	4.164	4.177	0.013
03:02:29	80.04	0.68	± 0.01	-100.001	-1.5000	-0.0000	-1.5121	± 0.04	-0.74	± 0.02	-10	0	20.49	80.04	03:10:09	4.164	4.176	0.012
03:39:26	90.01	0.65	± 0.02	-100.001	-1.5000	0.0000	-1.4935	± 1.66	-3.60	± 1.06	-18	0	20.95			4.205	4.232	0.027
03:46:39	90.04	0.65	± 0.02	-100.002	-1.5000	-0.0000	-1.4937	± 0.04	-0.00	± 0.02	-17	0	21.02			4.205	4.229	0.024
03:59:36	90.06	0.64	± 0.01	-100.002	-1.5000	0.0000	-1.4939	± 0.04	-0.94	± 0.02	-16	0	21.07			4.205	4.226	0.020
04:00:48	90.04	0.65	± 0.01	-100.001	-1.5000	-0.0000	-1.4940	± 0.06	-1.44	± 0.02	-15	0	21.09	90.04	04:16:28	4.205	4.224	0.019
05:26:19	25.03	0.76	± 0.02	-100.002	-1.5000	0.0000	-1.6055	± 0.01	-0.54	± 0.00	0	0	20.36			4.006	3.999	-0.007
05:35:32	25.00	0.77	± 0.01	-100.002	-1.5000	0.0000	-1.6056	± 0.00	-0.19	± 0.00	0	0	19.00	25.00	05:43:12	4.006	3.998	-0.008
05:44:44	25.00	0.77	± 0.01	-100.002	-1.5000	0.0000	-1.6056	± 0.03	-0.72	± 0.02	0	0	19.39			4.006	3.997	-0.009

TABLE 3.3. Detailed Laboratory Functional Test Data

The results of functional tests are presented in Table 3.2. From these data it may be observed that although the two different wafer processing series yielded somewhat different values of V_r , $-2.8 < V_r < -2.1$, for the 8-26-86 series versus $-1.7 < V_r < -1.4$ for the 11-7-85 series, both series yielded comparable near-Nernstian responses.

Finally, based on these measurements, 11 sensors were deemed appropriate for final assembly into probes, 7 pH and 4 CO₂. The pertinent data for these sensors are found in Appendix A.

Probe assembly, that is incorporation of the sensor into a housing appropriate for the field test site, was accomplished according to the original design as discussed in Section 3.2.3.

One of the completed pH probes was subsequently tested at rated temperature and pressure as indicated schematically in Figure 3.12 using the following test sequence.

1. pH 4, 7, 10 buffers at 50°C and 150 psi.
2. brine at 65°C and 465 psi.
3. pH 4, 7, 10 buffers at 170°C and 150 psi.

Accurate measurements of pH could not be obtained during these tests because there was no provision for a reference electrode. Instead, V_r was measured against a metallic counter electrode whose potential was, of course, not independent of pH. Nevertheless, V_r did respond qualitatively to pH changes, becoming more positive with increasing pH. In this manner, the pH sensor operated well at 170°C, 150 psi in pH 4, 7, and 10 buffers (see Table 3.4).

At the conclusion of this test, and while the sensor was still at 170°C, an attempt was made to replace pH 10 buffer with a brine solution.

FIGURE 3.12. Block Diagram of High Temperature Laboratory Test

TEMPERATURE	PRESSURE	SAMPLE	COUNTER ELECTRODE VOLTAGE (V_r)	ELAPSED TIME (HOURS)
°C	PSI			

24.5	AMBIENT	pH 4.0 Buffer	-2.89	0
50.2	150	pH 4.0 Buffer	-2.77	0.6
50.4	150	pH 6.8 Buffer	-2.73	1.6
50.6	150	pH 9.9 Buffer	-2.69	2.6
65.2	150	Brine	-2.78	3.6
65.0	465	Brine	-2.79	3.8
170.0	150	pH 4.2 Buffer	-2.69	6.0
170.2	150	pH 6.8 Buffer	-2.61	6.5
171.1	150	pH 9.8 Buffer	-2.47	7.2
*170				

*NOTE: Test concluded due to pump failure (see text).

TABLE 3.4. ISFET Survival Data

During this process however, a pump failure resulted in a pressure spike which fractured the ISFET chip, driving half the header into the mounting assembly, thereby destroying the sensor and terminating the test. Observation of the pressure gage reading just prior to its failure indicated a peak pressure of ≥ 2000 psi. This is at least consistent with earlier pressure results in which the modified chip/header design used in the field trial had been successfully tested up to pressure of 1700 psi without failure.

Therefore, it was concluded that the backup design was suitable for the pressure and temperature conditions expected during the field test.

3.2 pCO₂ SENSOR

The CO₂ sensor developed for and tested in this phase is a form of a Severinghaus electrode. The measurement system consists of both a pH sensitive electrode and a 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. A primary source of interference in geothermal brines is hydrogen sulfide. Avoidance of this acidic gas in the internal electrolyte is required, since its presence would change the electrolyte pH as well as result in silver sulfide formation on the reference electrode perturbing the reference potential. The problem is overcome by the incorporation of an H₂S getter system, which selectively removes the gas prior to its entry into the internal electrolyte.

Prior to this effort, the design of this sensor has been shown to be satisfactory overall for operation in geothermal brines. However, field testing indicated weaknesses, and by utilizing new technologies which have since become available, several aspects of the design were improved. These

include the reference element feedthrough, the H₂S getter and its incorporation into the sensor, the housing seals, and the membrane thickness. These are discussed in detail below.

3.2.1 Reference Element Feedthrough

To complete the measurement circuit, the internal pH sensor must have a reference element in contact with the internal carbonate electrolyte. A silver/silver chloride (Ag/AgCl) electrode is used, since in this closed system, the chloride content can be fixed, and H₂S incursion into the system is prohibited by the getter. In the current design, the silver reference electrode is wrapped around the Pyrex support tube and welded to a platinum feedthrough wire. Due to the low melting point of silver, it is not possible to seal the silver wire into the Pyrex directly. The lead wire is then 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. Early attempts to heat seal the platinum lead wire into the Pyrex tube were only moderately successful. Due to the high temperature, difficulty was encountered in maintaining the roundness of the Pyrex tube, as well as the flatness of the polished end. These features are essential for assuring uniform contact of the Bal Seals (see also Figure 3.13 and Section 3.2.2), and for achieving a continuous seal at the header-support tube interface, respectively. In this contract period, these concerns were both addressed.

The distance of the seal from both the critical areas was maximized by locating the feedthrough hole midway between the polished end of the tube and the position of the first Bal Seal.

The size of the hole was significantly reduced, to about one-sixth the earlier size, resulting in a hole which was approximately 15% larger than the feedthrough wire. This was achieved by laser drilling (see section 3.1.5) the holes instead of the conventional drilling method used earlier. Though uniformity and precision in hole placement are easily accomplished by

FIGURE 3.13. Exploded View of pCO₂ Sensor

this technique, several iterations were required to acceptably minimize the hole taper and blow out or amount of debris accumulated at the exit end of the hole.

As expected, the relatively close sizes of the feedthrough hole and the platinum wire significantly reduced the sealing difficulty. However, problems with distortion at both the circumference and the polished end of the Pyrex tube were encountered to some extent. The distortion in the O.D. of the tube was inconsequential with regard to the sealing of the system, since it ended well below the position of the Bal Seals. Distortion in the I.D. of the tube resulted in assembly difficulties, since the ceramic support block for the Pogo contacts could not be properly placed at the bottom of the tube. The distortion was accommodated by machining a flat in the ceramic block large enough to clear the distended area. This treatment was not found to affect the mechanical strength of the ceramic block in any way. The distortion at the polished end of the tubes was so small that in most cases, it did not become evident until the tube was metallized. However, it was sufficient to prohibit the anodic bonding of the chip header assembly. To correct this, the original manufacturer was able to repolish the tubes with negligible loss of overall length, allowing the metal housings to be used unmodified.

Though these changes resulted in a satisfactory feedthrough, it was found that in further assembly, several problems were encountered which rendered the reference or entire probe unuseable. First, the wire at either end of the feedthrough was somewhat brittle, and it tended to break with very little bending or stress. Second, though the tubes were fully annealed after being sealed, spontaneous crack formation initiating at the seal was seen in at least one case.

For the field tests, a Ag/AgCl reference in a slightly different configuration was used, since in assembly into the metal housings, the Pt wire or entire internal element was at some point destroyed for the reasons stated above or in Section 3.1.2. It was prepared by first silver plating

the inside of the housing in all areas which came in contact with the internal electrolyte. The plating solution used was 0.05M potassium silver cyanide ($\text{KAg}(\text{CN})_2$), adjusted to a pH of 4.6. Plating was carried out for a minimum of 4 hours at a current density of 0.5 mA/cm^2 . This was followed by a thorough wash in deionized (DI) water, a short soak in concentrated ammonium hydroxide and a final wash in DI water. Contact was made to the reference by attaching a lead with conductive epoxy in the small cavity between the two housing parts. To assure stability of the reference at elevated temperatures, excess silver chloride was added to the internal fill solution.

3.2.2 Housing Seal

In the current design, there are two critical seals. The first seal is in the dual membrane assembly, which contains the H_2S getter, and is fully assembled prior to its attachment to the body of the probe. The second seal, a gasket, is used in attaching the membrane assembly to the remainder of the probe (see Figure 3.13). In prior contract work, the optimum material for both applications was determined to be EPDM (a copolymer of ethylene and propylene with diene monomer). This material, when properly formulated, offers chemical durability comparable to perfluorinated polymers. Since it is also an elastomer, its compression set properties make it an ideal candidate for use as a gasket material. In this contract phase, a critical evaluation of the housing seals was made. In particular, the available options with regard to sealing area, compression requirements, machining tolerances, and assembly procedures were explored. When each was optimized, several tests were performed to verify the results.

In Task II, several improvements were made in the housing design by tightening the tolerances on machined parts, adding lock washers to all screws to prevent their loosening during the test. In order to maximize precision and reproducibility of the screw holes in the EPDM gasket and membranes a special cutting tool was manufactured. The hole diameter was also decreased to increase the available seal area. In the current work, these

alterations were readdressed by a design engineer to ascertain whether or not further improvements could yet be made, especially with regard to dimensional changes which would serve to maximize seal area.

However, due to the limitations listed below, this was not deemed possible. First, as dictated by field test conditions, the O.D. of the housing is at its maximum. Second, the dimensions of the pH sensing element are defined by the internal parts used, and the assembly process (including yield) and are not reducible. Finally, the I.D. of the housing is at its minimum, being constrained by the solution volume required in the system, as well as the assembly process itself. This conclusion does not prohibit the success of the design since, on a preliminary basis, it had been demonstrated as leak free in prior contract work.

The emphasis in this phase was then placed on improving and simplifying the assembly procedures, with the ultimate objective of increasing the yield. To this end, the following changes were made. Prior to final sealing of the membrane/getter assembly, it was placed in the getter solution under vacuum for about five minutes, to assure complete wetting of the getter support disc, as well as the removal of all air pockets. The assembly was then sealed while still in solution. Similarly, the internal chamber of the housing was vacuum filled with electrolyte, however, the orientation of the housing was found to be important in this process. Whereas vacuum filling in an upright position could result in air gaps under the membrane, the same procedure with the probe in a horizontal position was found to be more reliable in removing all air gaps. A special fixture was made which permitted vacuum filling in this orientation, and final sealing with the probe in an upright position, while still maintaining a solution cover. This fixture was also used in the field tests.

Finally, in order to increase the reliability of the intermediate seals positioned between the Pyrex tube and the outer housing (Bal Seals) a change was made in the material used in the area which precedes them (see Figure

PART	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	1	HOUSING (PYREX)
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

FIGURE 3.14. Final pCO₂ Probe Design

3.14). The suitability of the Bal Seals for the geothermal brine application was tested and verified by L&N during the developmental program for a high temperature pH sensor (see Reference 2). However, the optimum performance temperature of the seals is somewhat higher than room temperature, necessitating a "preseal". Due to the relative fragility of the glass tube, the anterior section was previously filled with a compressable fluorosilicone compound which offered protection from solution leakage past the Bal Seals prior to reaching the recommended use temperature of the seals. The adhesive properties of this RTV were known to be only marginally acceptable in geothermal conditions. Also, at a minimum of 24-48 hours, it has an inconveniently long cure schedule. Based on earlier work, epoxies were felt to be unsuitable for this application due to their rigidity and high thermal coefficient of expansion relative to the Pyrex tube which tended to crack it in use. With the increase in wall thickness, and resultant increase in compressive strength of the Pyrex tube, the feasibility of replacing the fluorosilicone compound with a suitable epoxy was tested and confirmed. The epoxy used was produced by Castall, Inc., East Weymouth, Mass. It was developed specifically for the geothermal brine environment, and for use with glasses, ceramics and other low thermal expansion materials. This material offers the advantages of a short cure schedule, and enhanced adhesive properties over the fluorosilicone compound. The latter property was particularly useful in the current work since extended testing below the use temperature for the Bal Seals was frequently called for.

3.2.3 Membrane Thickness

The gas permeable membrane used in this probe is EPDM, the same material used for the gasket seal discussed above. The permeability coefficients of this material have been experimentally determined for CO₂ and H₂S up to 150°C and calculated theoretically up to 200°C. The probe was originally designed to operate at pressures up to 5000 psi and temperatures to 200°C. As such, the total membrane thickness (two membranes are actually used) was optimized at .034". This allowed for some flexing to equilibrate

pressure differentials, and liquid thermal expansion yet sufficient mechanical strength was maintained to avoid rupturing. A reasonable probe response time was seen at 200°C; however, at more moderate temperatures, it became unacceptably slow. For example, at 80°C and atmospheric pressure, the probe response time would be approximately 6 hours.

. With pressures now limited to a maximum of 800 psi, the option of reducing the membrane thickness to improve the response time at lower temperatures is a viable one, and it was explored at length in this contract phase. A reasonable target was felt to be a reduction of 1/2 in the total thickness, which would translate to a fourfold decrease in response time (i.e. 90 minutes for the same conditions listed above). This would increase the H₂S permeability as well and must be accounted for in terms of getter capacity. (See Section 3.2.4).

EPDM is only available in sheet thicknesses of .034"; therefore, the desired thickness of .0085" was obtained by machining. The same method as that used in previous work was used here. It is described in Reference 5 and it has already been shown to have no adverse effects on the EPDM permeability coefficient. In order to determine whether the required pressure and temperature could be accommodated using membranes of this thickness, several tests were performed. This work is outlined below.

The probe was first fully assembled as shown in Figure 3.14. For tests done before the internal pH sensing elements were available, a stainless steel plug of the same dimensions was used. In place of the internal electrolyte, a 1M solution of cadmium chloride (CdCl₂) was used. The sensor was then placed into a solution of 1M sodium sulfide (NaS). Since the two solutions will react to form the bright yellow, highly insoluble compound, cadmium sulfide (CdS), this configuration served to indicate any leakage in the system during the test. The test apparatus used was the same as that used in previous contract work, and is shown in Figure 3.15. In use, it was found that some refinements were required in both the temperature regulation and pressurization systems.

DET.	QTY	PART NO.	DESCRIPTION
1	1	B-RD-847-2-1	TOP CHAMBER
2	1	B-RD-847-4-1	CENTER CHAMBER
3	2	A-RD-847-2-8	"O" RING #136
4	-		STL 304 CRES TUBE .065 O.D. x .045 I.D.
5	2	A-RD-847-4-2	MALE CONNECTOR - SWAGELOCK
6	1	B-RD-847-2-3	BOTTOM CHAMBER
7	8	A-RD-847-2-12	BOLT, $\frac{5}{8}$ -11 x $6\frac{1}{2}$ LG
8	8	A-RD-847-2-13	LOCKNUT $\frac{5}{8}$ -11
9	-		STL 316 CRES TUBE .250 O.D. x .120 I.D.
10	1	A-RD-847-2-20	MALE CONNECTOR - SWAGELOCK
11	1	B-RD-923-2	CO ₂ /BRINE SENSOR ASS'Y

FIGURE 3.15. Test Apparatus for High Temperature,
High Pressure Experimentation

For temperature control, the original configuration used only two thermocouples, controlled separately and placed in drilled wells at the top and bottom of the test apparatus. During the initial heating stage, the bottom half of the test bomb (as a result of its additional mass) was observed to lag the top by as much as 20°C. Since the heat loss from the bottom also contributed to a heat gain at the top of the apparatus, overheating at the top of the apparatus was frequently seen. With no reading being taken at the sensor itself, the temperature at this critical point could only be inferred. With the new configuration, two additional thermocouples were placed in the system: one directly in the sensor, and the second on the outside of the lower half of the bomb. The progress of all four was monitored continuously, and the main temperature control was dictated from the sensor thermocouple. This effectively avoided overheating. At times, it also served to indicate a leak in the test system which could be inferred by the corresponding (temporary) cooling effect.

The membranes were initially tested under elevated conditions only. It was recognized that at elevated temperatures, some steam pressure does exist, however, it was deemed to be of no consequence since it does not result in a differential pressure on the membrane. At elevated temperatures only, the membranes survived, but at times leakage around the screw holes was observed. The problem was solved by shortening the screws slightly to allow more compression on the (thinner) membranes, and thus a tighter seal.

In pressurizing the system, two different methods were used. The first utilized a high pressure gas, usually air or nitrogen. The pressure of the system was measured both at the inlet, by the gas tank regulator guage and again at the outlet by a second guage. In order to minimize any detrimental effects on the sensor from rapid pressurization, a "buffer" chamber filled with water was inserted between the gas tank and the inlet of the test apparatus. This simplistic method functioned reliably however it had the disadvantages of being a "closed" system (in that solution changes could not be made while the pressure was engaged) and a somewhat "energetic" one, posing a potential danger in the event of a sudden leak.

In an effort to overcome these disadvantages, an alternative pressurization system using solution and a High Pressure Liquid Chromatography (HPLC) pump was used in some of the tests, particularly those in which actual sensing elements were being evaluated. The pump used had been selected for its high degree of corrosion resistance. In spite of this, however, test runs were frequently delayed or interrupted due to pump failure often traceable to corrosion of parts, limiting the usefulness of this system during this contract period.

When the "thin" membranes were evaluated using a combination of high temperature (180°C) and pressure (500 psi), consistent failures were encountered when pressurizing with the HPLC pump. The reason for this was hypothesized as an overpressure acting on the membrane, created as a result of high pressure pulses from the pump. Quantitative evaluation of these pulses showed that they were generally in excess of 2000 psi. The thinner membranes did, however survive this combination of test parameters when the gas pressurization method was used, and as such, they have been incorporated into the final design. These results were obtained after the field trial, and thus could not be acted upon for the field test sensors.

3.2.4 H₂S Getter System

In previous contract work, two types of getter systems have been investigated. The first was a liquid system. Initially, saturated copper sulfate (CuSO₄) was used, but was replaced by saturated cadmium chloride (CdCl₂) when electrochemical corrosion of the housing was noted. Ultimately, the liquid system was abandoned in favor of a porous solid (Ag) disc when solution containment problems were encountered and could not be addressed within the time limitations of the contract (see Reference 5). For convenience, the reaction by which each of these removes H₂S from the permeant is shown below:

The liquid system offers several advantages over the porous solid. As versus the solid system, it has been shown to have no effect on probe response time. Also, within the dimensional constraints of the housing, the liquid getter capacity is inherently greater than the solid one. As calculated in Reference 5, the effective lifetime of the porous silver getter is 14.7 hours at 200°C, whereas in the same "worst case" situation with respect to H₂S concentration, the lifetime of the liquid getter was shown to be 22 hours at 250°C, and therefore would be even greater at 200°C. For these reasons, the primary effort in this contract phase focused on overcoming the containment problems of the liquid system thereby permitting its reincorporation into the design.

As discussed in sections 3.2.2 and 3.3.3 above, the housing seal and membrane integrity with respect to incursion of the outside solution have been verified over the temperature range of interest. Following this, another test was performed to assure that the assembly techniques used for the probe did not result in inadvertent mixing of the two internal solutions: i.e., the carbonate internal electrolyte and the cadmium chloride getter solution. A similar experimental approach was employed here, whereby two solutions (CdCl and NaS), which react to form an insoluble precipitate, were used to detect any internal leakage. The CdCl was placed between the membranes in a porous support, and the NaS was placed in the internal electrolyte chamber. Using normal assembly procedures, including prolonged evacuation of each section in the housing, no internal leakage was detected. Within the constraints of the contract schedule, only a limited number of high temperature tests could be performed. As such, it was not possible to test the assembled probe over the entire temperature range of interest, only up to 70°C. However, given the success of the related testing done on the housing and membrane seals, problems in this area are not expected.

Finally, it is necessary to recalculate the getter capacity, accounting for the change in various test parameters, as well as the membrane thickness. Experimentally, the permeability coefficient of H₂S in EPDM (PEPDM) at 150°C has been determined to be:

$$5.52 \frac{\text{cm} \cdot \text{cm}^3}{\text{cm}^2 \cdot \text{sec} \cdot \text{cm Hg}} \times 10^8$$

It is possible to estimate the permeability constant at a second temperature if a value has been established at one temperature (see Reference 19).

$$\log P_2 = \log P_1 + \frac{E_p}{.0046} \frac{1}{T_1} \frac{1}{T_1}$$

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. Although the activation energies for most permeation processes lie between 5 and 16 kcal/mole, that of H_2S permeation through EPDM is not known. A value of 8 kcal/mole is used since it is the reported value of E_p for the diffusion of CO_2 in butyl rubber, a closely related system. Using this value, P_{EPDM} for H_2S at 200°C is calculated to be $1.48 \times 10^{-7} (\text{cm}^3)(\text{cm})(\text{cm}^2)^{-1}(\text{sec})^{-1}(\text{cmHg})^{-1}$. Ellis (see Reference 20) reports that the maximum level of H_2S ever measured on geothermal wells was 0.2 bars (15 cm Hg), and another source (see Reference 5, pg. 47) 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 now .021 cm and the effective membrane area is 0.97 cm^2 . The design includes a total getter solution volume estimated to be 10^{-2} cm^3 . A saturated getter solution contains approx. 8 M/L of CdCl . The number of moles of available Cd^{++} , and therefore the number of moles of H_2S which can be trapped is approximately 8×10^{-5} . The volume of 8×10^{-5} moles of H_2S at standard temperature and pressure is 1.8 cm^3 .

Using the permeability coefficient estimate for 200°C and other values derived above one can compute the effective lifetime of the getter solution, t .

$$t = \frac{(1.8) (.021)}{(0.97) (15) (1.48 \times 10^{-7})} = 17,600 \text{ sec} = 4.88 \text{ hours}$$

Again, this estimate presumes the highest H_2S level reported in geothermal brine. Also, it must be noted that in prior contract work, 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 by the H_2S would, in use, extend the getter lifetime beyond the estimated value.

Alternative actions could be taken to increase the getter lifetime in certain situations, if necessary. For example, in place of a dual membrane system of the same thickness (.0085"), the thickness of only the first membrane could be doubled which corresponds to doubling the getter lifetime. This 33% increase in total thickness would also double the response time. Whether or not this increase would be acceptable would depend upon the actual use temperature, and other environmental conditions.

Another alternative would be to reduce the overall area of the membrane through which H_2S could permeate. This could be accomplished by placing a barrier (e.g., a thin metal foil) between the first membrane and the getter support pad with a small hole positioned directly in line with the active portion of the ISFET. In this case, response time would not be compromised, and the getter lifetime would be increased in proportion to the effective decrease in membrane area. It is required that the barrier specified be gas impermeable, chemically and thermally stable, somewhat flexible, and be incorporated into the design such that the relatively thin membrane material is not damaged by it in use (e.g., by cutting, etc.)

Finally, the getter lifetime could be extended by increasing the solution volume. An increase in the thickness of the getter support pad would be required to accommodate the additional volume. While it is known that the presence of the current liquid getter system does not add measurably to the probe response time, the effect of this variation would have to be fully evaluated.

3.2.5 Laboratory Test Results

During this contract phase, laboratory testing of the pCO_2 sensor was limited to characterization of the pH sensing element in terms of response to temperature and pH, identification of any anomolous behavior within these areas, and verification of the seal integrity of the sensor over the temperature range of 0 to 90°C . Data for one of these sensors, in particular that used in the field test, are presented in Table 3.5. All column headings are fully described in Section 3.1.7, but for clarity some are briefly reiterated below.

Columns 3 and 4 refer to the a.c. pick up or noise in the V_r signal (voltage between the reference electrode and the ISFET source). I_d , V_d and V_b denote the drain current, the source-drain voltage and the substrate voltage respectively. Column 10 (MEAN) indicates the drift rate of V_r with time at temperature. The last three columns, NBS pH, pH and ERROR give the known pH of the buffer solution at the measured temperature, the measured pH value and the relative difference between the two. The values for all of the parameters described above are within the normal range for the pH sensors used in this work.

The values given in column 12 (I_k) deserve somewhat closer attention. I_k is an indication of the leakage current in the "gate" or reference electrode circuit and is related to package integrity. It can be seen that in this sensor, after temperature cycling to 90°C , the leakage current was significantly higher than that measured initially, corresponding to some level of degradation in the package integrity prior to the field trial. Overall, however, the probe's performance was still deemed to be acceptable for use in the field test. Its performance in this environment is discussed in more detail in section 5.2.

In-house testing of a fully assembled $p\text{CO}_2$ sensor was not achieved during this phase, primarily due to the shortage of functioning sensors and problems noted earlier with the HPLC liquid pump, which were not solved within the time limitations of the contract. In prior contract work, the probe response to a step change in CO_2 concentration of one decade was measured and found to be in good agreement with theoretical predictions at both moderate (80°C) and higher (150°C) temperatures. Figures 3.16 and 3.17 show these results.

SUMMARY OF ISFET PROBE # 608 TEST RESULTS
IN NBS KHP (1857) BUFFER

10/29/86

Vr, DC REFERENCE TO SOURCE EMP												ANALYSIS		
TIME	TEMP	AC IN Vr, mV		Id, pA	Vd, V	Vs, V	NEAR, Vr	e, mV	SLOPE, mV/pH		IK, nA	NBS pH	LINEAR	
		MEAN	e						MEAN	e			pH	ERROR
12:24:15	25.01	0.58	± 0.03	-100.003	-1.5001	0.0000	-1.7814	± 0.00	0.19	± 0.00	-1	4.006	3.983	-0.023
12:33:39	25.01	0.59	± 0.02	-100.003	-1.5000	0.0000	-1.7814	± 0.02	-0.30	± 0.01	-1	4.006	3.983	-0.023
12:42:52	25.01	0.58	± 0.02	-100.003	-1.5000	0.0000	-1.7814	± 0.02	-0.35	± 0.01	-1	4.006	3.983	-0.023
12:52:04	25.01	0.57	± 0.02	-100.003	-1.5000	0.0000	-1.7814	± 0.00	-0.06	± 0.00	-1	4.006	3.983	-0.023
13:00:59	0.00	0.62	± 0.01	-100.003	-1.5000	0.0000	-1.0078	± 0.02	0.74	± 0.00	0	4.006	4.069	0.063
13:08:12	0.04	0.58	± 0.01	-100.003	-1.5000	0.0000	-1.0077	± 0.03	0.27	± 0.02	0	4.006	4.072	0.066
14:07:36	0.02	0.58	± 0.01	-99.996	-1.5000	0.0000	-1.0077	± 0.03	-0.16	± 0.02	0	4.006	4.072	0.066
14:16:55	0.02	0.60	± 0.02	-99.997	-1.5000	0.0000	-1.0077	± 0.03	0.19	± 0.02	0	4.006	4.072	0.066
14:27:44	9.93	0.59	± 0.01	-99.996	-1.5000	0.0000	-1.7905	± 0.00	0.24	± 0.00	0	3.999	4.013	0.014
15:07:14	9.98	0.62	± 0.13	-100.003	-1.5000	0.0000	-1.7906	± 0.03	-1.00	± 0.00	0	3.999	4.011	0.012
15:16:26	9.99	0.59	± 0.02	-100.003	-1.5000	0.0000	-1.7906	± 0.00	-0.28	± 0.00	-1	3.999	4.010	0.011
15:25:39	9.99	0.59	± 0.01	-100.004	-1.5000	0.0000	-1.7906	± 0.02	-0.99	± 0.00	0	3.999	4.010	0.011
16:06:36	19.95	0.60	± 0.02	-100.003	-1.5000	0.0000	-1.7878	± 0.02	-0.26	± 0.01	-1	4.001	3.982	-0.019
16:15:49	19.98	0.59	± 0.02	-100.003	-1.5000	0.0000	-1.7878	± 0.02	0.18	± 0.01	-1	4.001	3.982	-0.019
16:25:01	19.99	0.60	± 0.03	-100.003	-1.5000	0.0000	-1.7878	± 0.03	-0.51	± 0.01	-1	4.001	3.981	-0.020
16:34:13	20.00	0.60	± 0.01	-100.003	-1.5000	0.0000	-1.7878	± 0.03	0.12	± 0.02	-1	4.001	3.980	-0.021
17:15:06	29.94	0.58	± 0.01	-100.003	-1.5000	0.0000	-1.7750	± 0.00	-19.00	± 0.29	-1	4.012	3.975	-0.037
17:24:21	29.98	0.55	± 0.01	-100.002	-1.5000	0.0000	-1.7750	± 0.06	-1.36	± 0.02	-3	4.012	3.973	-0.039
18:18:23	29.98	0.57	± 0.03	-100.004	-1.5000	0.0000	-1.7759	± 0.02	-0.83	± 0.00	-2	4.012	3.972	-0.040
18:27:47	29.99	0.58	± 0.01	-99.997	-1.5000	0.0000	-1.7762	± 0.02	-0.83	± 0.01	-2	4.012	3.971	-0.041
19:02:42	40.00	0.60	± 0.02	-99.998	-1.5000	-0.0000	-1.7605	± 0.00	4.01	± 5.71	-2	4.031	4.020	-0.011
19:51:30	40.06	0.61	± 0.02	-99.998	-1.5000	-0.0000	-1.7605	± 0.07	19.35	± 3.88	-2	4.031	4.013	-0.018
20:00:35	40.04	0.53	± 5.51	-99.998	-1.5000	-0.0000	-1.7596	± 7.49	-63.53	± 4.60	-2	4.031	4.033	0.002
20:10:07	40.05	2.37	± 3.81	-99.998	-1.5000	-0.0000	-1.7615	± 3.62	-0.94	± 2.33	-1	4.031	4.003	-0.028
20:55:01	49.93	0.60	± 6.95	-99.997	-1.5000	-0.0000	-1.7570	± 9.06	149.05	± 5.38	-2	4.057	3.981	-0.076
21:26:46	49.96	3.63	± 1.46	-99.998	-1.5000	-0.0000	-1.7513	± 6.05	19.95	± 3.87	-1	4.057	3.965	-0.090
21:35:55	49.95	3.30	± 4.76	-99.998	-1.5000	-0.0000	-1.7470	± 3.37	-9.74	± 2.16	-1	4.057	4.036	-0.020
21:45:07	49.95	4.47	± 7.11	-99.999	-1.5000	-0.0000	-1.7447	± 3.19	75.30	± 2.88	-1	4.057	4.072	0.016
22:22:03	60.00	2.01	± 1.96	-99.997	-1.5000	-0.0000	-1.7314	± 0.59	-7.54	± 0.34	-3	4.091	4.002	-0.089
22:31:16	60.06	0.57	± 0.01	-99.997	-1.5000	0.0000	-1.7317	± 0.22	-0.91	± 0.14	-2	4.091	4.076	-0.015
22:40:28	60.06	0.57	± 0.02	-99.996	-1.5000	0.0000	-1.7318	± 0.04	-0.09	± 0.02	-2	4.091	4.074	-0.017
22:49:50	60.06	0.57	± 0.01	-100.002	-1.5000	0.0000	-1.7317	± 0.13	1.47	± 0.00	-2	4.091	4.076	-0.016
23:26:55	69.97	0.55	± 0.02	-100.003	-1.5000	0.0000	-1.7199	± 0.04	-0.21	± 0.03	-4	4.126	4.124	-0.002
23:36:07	70.00	0.58	± 0.02	-100.003	-1.5000	0.0000	-1.7157	± 0.10	1.37	± 0.05	-4	4.126	4.127	0.001
23:45:20	70.03	0.62	± 0.07	-100.003	-1.5000	0.0000	-1.7156	± 0.05	-0.93	± 0.02	-4	4.126	4.127	0.001
23:54:33	70.00	0.57	± 0.02	-100.003	-1.5000	0.0000	-1.7157	± 0.04	0.39	± 0.02	-4	4.126	4.127	0.001
00:32:25	00.02	0.56	± 0.02	-100.003	-1.5000	0.0000	-1.6909	± 0.04	-0.57	± 0.02	-7	4.164	4.184	0.020
00:51:04	00.07	0.56	± 0.03	-100.004	-1.5000	0.0000	-1.6909	± 0.03	-0.02	± 0.02	-6	4.164	4.183	0.019
01:00:23	00.10	0.54	± 0.02	-100.003	-1.5000	0.0000	-1.6909	± 0.03	0.25	± 0.02	-7	4.164	4.183	0.018
01:09:35	00.10	0.55	± 0.02	-100.003	-1.5000	0.0000	-1.6909	± 0.04	0.35	± 0.03	-10	4.164	4.184	0.019
01:42:33	09.95	0.48	± 0.02	-100.003	-1.5000	0.0000	-1.6817	± 0.25	-0.91	± 0.16	-330	4.205	4.247	0.042
02:11:34	90.01	0.53	± 0.06	-100.002	-1.5000	0.0000	-1.6818	± 0.36	-1.34	± 0.23	-166	4.205	4.243	0.038
02:21:39	90.01	0.55	± 0.03	-100.003	-1.5000	0.0000	-1.6821	± 0.23	-2.18	± 0.14	-294	4.205	4.240	0.034
02:30:52	90.01	0.53	± 0.06	-100.003	-1.5000	0.0000	-1.6822	± 0.34	-1.24	± 0.22	-200	4.205	4.239	0.034
03:48:11	25.00	0.53	± 0.01	-100.004	-1.5000	0.0000	-1.7824	± 0.04	-1.04	± 0.01	-40	4.006	3.966	-0.040
03:57:36	25.00	0.55	± 0.02	-99.998	-1.5000	0.0000	-1.7824	± 0.17	0.03	± 0.11	-73	4.006	3.967	-0.039
04:06:49	25.01	0.55	± 0.02	-99.998	-1.5000	0.0000	-1.7824	± 0.02	-0.69	± 0.00	-60	4.006	3.966	-0.040

TABLE 3.5. In House Evaluation of Internal pH Sensing
Element Used in pCO₂ Sensor

FIGURE 3.16. pCO₂ Probe Response at 80°C Using One 0.017" Thick Membrane

FIGURE 3.17. pCO₂ Probe Response at 150°C Using
Two 0.035" Thick Membranes

4.0 ELECTRONIC CIRCUITRY

4.1 CONCEPT

The sensing element common to both the pH and CO₂ electrode is an Ion Sensitive Field Effect Transistor (ISFET) (see Reference 10). This FET based solid state sensor has been specifically tailored for hydrogen ion detection by the substitution of the normal gate electrode in a MOSFET with an insulating oxide coating which interacts with ions in a solution. A typical structure is illustrated in Figure 4. There are a number of modes in which to operate the ISFET, but invariably the gate coating, through surface interaction with the ions in solution, produces a field which tends to change the channel conductance in proportion to the concentration of ions. If a voltage is applied to the drain and source terminals, a current will flow with a magnitude which is controlled by the channel conductance. The channel conductance is related to the interfacial potential of the gate which is in turn a function of the ion concentration, and thus the drain-source current is related to pH. The chosen measurement mode for this application utilizes a constant current, variable gate voltage. In the constant current mode, an electrical voltage is applied at the gate via an electrode immersed in the liquid, which in concert with the interfacial potential due to the ion concentration, controls the drain-source current by modulating the channel conductance. If the hydrogen ion concentration changes, modifying the interfacial potential at the gate region, an equal and opposing electrical voltage is substituted to maintain the channel conductance and the drain source current. The change in voltage then is directly related to the change in hydrogen ion concentration in the solution and hence the pH.

The characteristics of a FET are such that as the drain-to-source voltage is increased, the source current first increases in a linear fashion followed by transition into a "saturated mode". In the saturation region, typically above 1 volt, the current remains essentially stable with further

increases in source-to-drain voltage. By choosing to operate in the saturation region, minor changes in the drain-source voltage will not affect the current which is the controlled parameter.

4.2 BASIC CIRCUIT

The basic circuit schematic is shown in Figure 3.2. The ISFET used in this application is a "P" channel device requiring a negative potential at the drain with respect to the source. The amplifier controls the source at the signal common potential by driving the reference electrode which controls the drain to source conductance. The constant current level is predetermined by the potential across the resistor which is held constant. Under steady state conditions, the amplifier will output a fixed negative voltage, which combined with the interfacial potential at the gate electrode, will control the drain source current to the level set by the resistor.

In operation, as the pH increases (due to a decrease in hydrogen ion concentration), the amplifier reduces the negative potential at its output to maintain the channel conductance and keep its input at the signal common level. The output of the amplifier is thus directly related to the hydrogen ion concentration, the sensor responding in a Nernstian fashion giving a linear pH response.

In order that the amplifier output truly represents the necessary applied potential, the driving electrode must have a stable reference potential. In this application, a flowing Ag/AgCl reference junction was utilized. The flowing junction reference guarantees a constant chloride level which results in a stable half cell potential at the junction. For typical pH applications, after calibration in a known buffer, the output is suppressed and additional gain is added as necessary to achieve the required scaling. For the field test, it was decided that the basic output of the control amplifier was the appropriate data to record.

The reference electrode or ISFET base current was monitored to determine the integrity of the sensor. Reference to the laboratory data indicates that a good sensor will have leakage or gate current in the single digit nanoamp range at room temperature and double with every 10°C increase in temperature. If the oxide membrane is damaged or sample incursion occurs through failed seals, the sensor is essentially bypassed and will indicate gate current in the microamp range.

5.0 FIELD TEST RESULTS

Field testing was performed in January 1987 at the San Diego Gas and Electric Binary Cycle Geothermal Plant in Heber, CA. Battelle Pacific Northwest Laboratories had previously installed a comprehensive test facility having four mounting locations for the Leeds & Northrup sensors.

The test facility enabled testing of the sensors under a variety of conditions ranging from the feed brine, nominally at 200°C and 200 PSIG, to the return brine at 60°C and 500 PSIG. With the use of heat exchangers and a city water supply, any temperature liquid between 200°C and 25°C could be achieved. The test facility included a means for circulating temperature controlled buffers and the addition of CO₂. This test facility was similar to that described in Reference 21 but with many improved features.

Data logging instrumentation at the test stand was interfaced to a computer in a nearby trailer for data reduction, graphics, etc., plus data transmission to Battelle in Richland, Washington.

Electronics for interfacing the sensors to the data logging facility had been shipped to the site. Five pH sensors and one CO₂ sensor were hand carried to the site. Additional CO₂ membrane assemblies and electrolyte were shipped two days later. A second CO₂ sensor had not passed final testing in the laboratory prior to the start of the field trial. During the field trial period, extensive effort was devoted in the Leeds & Northrup laboratory to repair the second CO₂ sensor without success. The premature failure of this CO₂ sensor was later found to be due to a crack in the Pyrex tube at the egress of the reference wire. The reference wire for the CO₂ sensor is fed through a laser drilled hole in the Pyrex tube and subsequently fused in place. This process apparently resulted in residual stress around the reference egress and subsequent fracture with temperature cycling.

The internal Ag/AgCl reference used in the CO₂ sensor is not suitable for the pH sensor which is exposed directly to the brine. The Ag/AgCl system requires a constant chloride level to maintain a stable potential. In the case of the CO₂ sensor, the reference is bathed by internal electrolyte solution of fixed chloride content plus protection from H₂S. For the pH sensors, a single reference electrode having a flowing liquid junction, developed by M. J. Danielson (see Reference 22) at PNL, was used as a common point of reference. This electrode, in addition to having a stable chloride level, has a special frit which in conjunction with the reference electrolyte flow assures protection against H₂S ingress.

In order to avoid interaction between the pH units, particularly if one failed due to high electrical leakage current, each sensor housing was connected to the gate input of its associated electronics (see Section 4.0). By using the pH sensor housing as a counter electrode, the reference is protected from potential changes due to sensor leakage current. This arrangement proved very beneficial in practice as sensors were tested in parallel and failed units did not affect the readings of the remaining sensors.

5.1 pH SENSOR TESTS

On January 12, 1987 two pH sensors were installed in the test rack, sensor #686 in point 21 and sensor #697 in location 22. At 1300 hours, these two sensors were exposed to the return brine at 60°C and 400 PSIG. After running for 30 minutes, sensor #686 indicated a pH in the correct or expected range whereas sensor #697 indicated a lower pH than expected (see Table 5.1). The expected data at this time was based on results using a different reference element; therefore, only estimates of the expected signal could be made.

At this time, before calibration, the estimated value was based on a standard pH probe immersed in a cooled sample. Knowing the temperature and approximate pH, the expected signal level was extrapolated from the computer printouts of the individual ISFET characteristics. Samples of the laboratory test data are included at the end of this section. Sensor #697 in

DATE	TIME	TEMP. °C	PRESSURE PSIG	TEST POINT NUMBER	SENSOR NUMBER	VOLTAGE REF TO SOURCE	SOLUTION	COMMENT
1-12-87	1300	60	400	21	686	2.41	LOW TEMP	
1-12-87	1300	60	400	22	697	2.50	BRINE RETURN	
1-12-87	1330	60	400	22	693	4.01		EXCHANGED WITH 697
1-12-87	1430	60	400	21	686	2.34	"	
1-12-87	1500	60	400	21	686	2.23	"	
1-12-87	1530	60	400	22	685	1.725	"	EXCHANGED WITH 693
1-12-87	1600	60	400	22	685	1.770	"	
1-12-87	1600	60	400	21	686	2.176	"	
1-13-87	0800	60	400	21	686	2.240	"	
1-13-87	0800	60	400	22	685	1.815	"	
1-13-87	0830	14.8	60	21	686	2.371	4.2 BUFFER	BEGIN CALIBRATION
1-13-87	0830	14.8	60	22	685	1.927	"	
1-13-87	0940	62	60	21	686	2.338	"	
1-13-87	0940	62	60	22	685	1.927	"	
1-13-87	1050	115	150	21	686	2.299	"	
1-13-87	1050	115	150	22	685	1.854	"	
1-13-87	1140	162	159	21	686	2.204	"	
1-13-87	1140	162	159	22	685	1.786	"	
1-13-87	1334	23	56	21	686	2.226	7.0 BUFFER	
1-13-87	1334	23	56	22	685	1.766	"	
1-13-87	1404	67	75	21	686	2.164	"	
1-13-87	1404	67	75	22	685	1.709	"	
1-13-87	1500	117	49	21	686	2.104	"	
1-13-87	1500	117	49	22	685	1.669	"	
1-13-87	1540	158	158	21	686	1.995	"	
1-13-87	1540	158	158	22	685	1.558	"	
1-13-87	1550	162	160	21	686	1.986	"	27 HRS RUNNING TIME
1-13-87	1550	162	160	22	685	1.550	"	24 HRS RUNNING TIME

TABLE 5.1. pH Sensor Field Test Data (page 1 of 2)

DATE	TIME	TEMP. °C	PRESSURE PSIG	TEST POINT NUMBER	SENSOR NUMBER	VOLTAGE REF TO SOURCE	SOLUTION	COMMENT
1-13-87	1600	HIGH TEMP BRINE ON						
1-13-87	1625	176	180	21	686	2.116	HIGH TEMP BRINE	
1-13-87	1625	176	180	22	685	1.668		
1-13-87	1630	66	400	RETURN TO LOW TEMP. BRINE				
1-13-87	1700	66	400	21	686	>5		GATE CURRENT 2.9uA
FLOW OFF OVERNIGHT								
1-14-87	0800	66	400	22	685	2.8		GATE CURRENT 1.15uA
1-14-87	0800	FLOW OFF			23	697		INSTALLED #697
1-14-87	0800	DURING INSTALLATION			24	693		INSTALLED #693
1-14-87	0800				21	682		INSTALLED #682
1-14-87	0900	110	500	21	682	2.5		GATE CURRENT 1.2uA
1-14-87	0900				22	685		AMPLIFIER SATURATED
1-14-87	0900				23	697		LEAKING BRINE
1-14-87	0900				24	693	4.4	DRIFTING UP SCALE
1-14-87	1040	240	180	SHORT (5 MIN.) EXPOSURE TO HIGH TEMP BRINE				
1-14-87	1045	240	180	24	693	0		DOWN SCALE TO ZERO
1-14-87	1045	240	180	21	682			REVERSE VOLTAGE
1-14-87	1055	110	500	21	682			RETURNED TO CORRECT POLARITY
				24	693			RETURNED TO CORRECT POLARITY

REMOVED SENSORS FOR ELECTRICAL LEAKAGE TEST

SENSOR	GATE CURRENT
693	4.0 microA
697	5.2 microA
682	4.2 microA
685	1.35 microA
686	3.2 microA

TABLE 5.1. pH Sensor Field Test Data (page 2 of 2)

in location 22 was replaced by sensor #693 at 1300 hours. After a baseline was established, and data recorded, sensor #685 was installed in the same location at about 1400 hours.

The two sensors #686 and #685 were then allowed to run overnight on the 60°C, 400 PSIG brine. At 0800 hours on January 13, the overnight data was analyzed. The two sensors had operated very well, with deviations being less than ± 0.5 pH units, typical of the brine excursions.

At 0830 hours pH 4.2 buffer was recirculated through the system starting out at 15°C and 60 PSIG. The buffer was then heated to 62°C at the same pressure and data was recorded. From mid morning until 1300 hours, the pH 4.2 buffer was circulated at increasing temperature and pressures, while data were taken, reaching a maximum of 162°C at 160 PSIG.

At 1330 hours this procedure was repeated using pH 7 buffer. At 1600 hours return brine exposure and calibration was completed, sensor #686 having a total running time of around 30 hours and sensor #685 about 4 hours less.

These two sensors were then exposed to high temperature brine at 176°C for 30 minutes under a pressure of 180 PSIG and followed by exposure to low temperature brine at 66°C and 400 PSIG. At 1700 hours on January 13, just before the overnight run was initiated, the gate potential of sensor #686 (in position 21) went positive approximately 2 volts and a high leakage current was suspected. A possible explanation for this is that the integrity of one of the seals or the passivation had failed. A test for leakage in the counter electrode lead confirmed this finding, showing that the gate current had increased by three orders of magnitude over the original data. The brine flow was turned off overnight.

At 0800 hours on January 14, sensor #686 was removed from location 21 and replaced by sensor #682. Sensor #685 was left in location #22, having accumulated 40 hours of running time. Sensor #697 was installed at position 23 and sensor #693 was installed at position 24. These two sensors had previously been run in low temperature brine for about one hour.

All four sensors were then exposed to 66°C brine at 400 to 500 PSIG for one hour followed by high temperature brine at 349°F or 176°C. During the transition from 66°C to 176°C, sensor #697 developed a liquid leak around the lead out wires. Sensors #682 and #693 went below zero and sensor #685 at location number 22 caused the fault light to come on in its associated electronics. These major changes in signal were attributed to brine leakage with subsequent shorting of the sensor connections.

After exposure to high temperature brine approximately one hour, the test stand was valved for low temperature brine flow. Cooling with low temperature brine caused sensors #682 and #693 to return to the correct polarity but with an incorrect amplitude. The higher pressure of the low temperature brine possibly reestablished the seal and pogo-pin connections, the residual brine inside the sensor housings causing the excess signal.

At this point, all five pH sensors indicated electrical leakage beyond the level warranting further site testing, i.e., 1.3 to 5 microamps. A notable difference between the laboratory tests and the field test was the cycling of both temperature and pressure. A further observation is that, with the exception of sensor #697, no leakage occurred at the outer housing indicating that the "BAL" seals held up well.

5.2 CO₂ SENSOR TESTS

Late on January 14, the test stand was modified for CO₂ injection. CO₂ sensor #688 was installed and run on a mix of city water and low temperature brine. There was no significant difference in signal between the level of CO₂ in the city water and brine due to the low temperature differential and the long time constant of the sensor at low temperatures.

The test stand was then valved such that low temperature brine at 60°C and 500 PSIG could be spiked with a liquid CO₂ cylinder. The spiked brine caused the sensor signal to respond in the correct polarity, rising about 20 mV in one hour. This corresponds to an increase of CO₂ level of 2.3 times the brine baseline.

In order to improve the response time of the CO₂ sensor, which approximately halves with each 10°C temperature increment, a high temperature brine (176°C) baseline was established. The sensor output stabilized after 15 minutes exposure and remained steady for 30 minutes. Before the brine could be spiked with CO₂, the sensor output started to drift slowly upscale indicating a malfunction. A test for electrical leakage indicated that the basic pH sensor was operating and it was assumed that the membrane system was leaking. A liquid leak either through or around the membrane system would result in the internal electrolyte being diluted with the lower pH brine and a subsequent increase in signal similar to a CO₂ concentration increase. Mixing of the brine with the internal electrolyte will also alter the chloride level resulting in a reference electrode potential shift and, if H₂S is present, will eventually poison the reference.

On January 16, the CO₂ sensor was rebuilt using a new membrane assembly and installed in test stand location 21.

At 1100 hours, high temperature brine was introduced at 168°C with a pressure of 200 PSIG. The signal was noisy but with a baseline exactly matching the previous reading for this condition before the membrane system failed. The noise was attributed to outgassing of the electrolyte. When the electrolyte is installed or replaced at the factory, it is first deaerated to avoid outgassing as the temperature increases, in this case the electrolyte was at approximately 4°C during the recharging operation and thorough outgassing in the field was not accomplished.

The rebuilt CO₂ sensor was run for two hours in high temperature brine to establish a steady baseline and then the brine was spiked with CO₂. The signal from the sensor increased by about 50 millivolts, indicating an eight-fold increase in CO₂.

After four hours running time in high temperature brine, the CO₂ injection was increased significantly and the sensor output rose 250 mV above the baseline, indicating greater than three orders of magnitude increase in CO₂. The CO₂ system was then turned off and the sensor set to run overnight in high temperature brine.

On January 17, the overnight trace was analyzed and showed that the sensor did not return to baseline but instead drifted upscale. A measurement of the leakage current led to the conclusion that the basic pH sensing portion of the CO₂ sensor had become inoperative.

At the conclusion of the field tests, electrical leakage tests were performed on all the sensors. The magnitude of the leakage current suggested that, in each case, a seal had failed such that the connections to the ISFET sensing element were being shunted by a salt solution. Subsequent laboratory analysis addressed in Section 6 confirms this finding.

In summary, data from the field test indicated significant improvement was made in field operation in comparison to the previous trial. Of particular note is the performance of pH sensors #685 and #686 which continued to give reliable data after 24 hours exposure to return brine. Data from the calibration run following brine exposure has been extracted from the field trial results and summarized in Table 5.2. By normalizing the actual data at pH 4.2 to pH 7, using the Nernst equation and correcting for temperature using field data at the same pH, any offset due to different reference potentials is eliminated. Reference to the right hand columns in Table 2 indicate that true Nernstian response was obtained, over a temperature range of 14.8 to 162°C, having an average difference less than 0.2 pH units from the stated buffer pH values.

ACTUAL READING VOLTS	SAMPLE pH	SENSOR NUMBER	TEMPERATURE °C	ACTUAL NORMALIZED TO pH7 USING NERNST EQUATION AT TEMP °C	CORRECTED FOR TEMP. FROM FIELD DATA	ACTUAL DATA pH7 AT TEMP °C
2.371	4.2	686	14.8	2.211 @ 14.8°	2.208 @ 23°	2.226 @ 23°
1.927	4.2	685	14.8	1.767 @ 14.8°	1.765 @ 23°	1.766 @ 23°
2.338	4.2	686	62.0	2.152 @ 62.0°	2.448 @ 67°	2.164 @ 67°
1.927	4.2	685	62.0	1.741 @ 62.0°	1.738 @ 67°	1.709 @ 67°
2.299	4.2	686	115.0	2.083 @ 115°	2.079 @ 117°	2.104 @ 117°
1.854	4.2	685	115.0	1.683 @ 115°	1.623 @ 117°	1.669 @ 117°
2.204	4.2	686	162.0	1.962 @ 162°	1.962 @ 162°	1.986 @ 162°
1.786	4.2	685	162.0	1.544 @ 162°	1.544 @ 162°	1.555 @ 162°

TABLE 5.2. Selected Field Trial Data

6.0 POST FIELD TRIAL ANALYSIS

Upon return from the field trial site, the five pH and the pCO₂ sensors were subjected to analysis to determine the most likely cause of failure.

The following sequence was followed in order that the most information could be gathered before destructive disassembly masked any significant evidence.

6.1 VISUAL INSPECTION

The active gate or oxide layer area was studied microscopically to determine if the brine had caused any deterioration. The results of this inspection were very encouraging, as four of the six units had gate areas indistinguishable from new devices. The ISFET chips for sensors 693, 697, and 688 were from a common wafer; number 688 was the sensor finally used for the pCO₂ sensor, the other two were originally designated for pCO₂, but due to reference wire difficulties were used as pH sensors. These last two were the units that had evidence of pitting.

Based on the evidence, it was concluded that a slight manufacturing defect in this wafer was exacerbated by brine exposure, whereas sensor chip number 688 from the same wafer was protected by the pCO₂ sensor membrane.

6.2 ELECTRICAL LEAKAGE

A measurement of the gate circuit electrical leakage indicated levels typically three orders of magnitude higher than that recorded in the laboratory data. These readings matched closely those taken in the field, and indicated shorting or shunting of current due to salt bridging.

The high leakage current is indicative of effect rather than cause, but is an excellent way to determine the integrity of the overall package.

6.3 CURVE TRACER ANALYSIS

Analysis of the semiconductor function indicated that the typical diode, or drain-substrate PN junction characteristic (see Figure 6.1) was absent. All units exhibited mainly ohmic behavior with varying amounts of capacitive response evidenced by a skewed Lissajous display. The sensors were then dried in an oven overnight, and the leakage and curve trace analysis was repeated. After drying, two units appeared to be open circuit, while the remaining four units exhibited similar results to the previous test. These results were consistent with the electrical leakage findings.

6.4 PASSIVATION INSPECTION

The chip to header, and header to support tube bonds are accomplished by first metallizing with subsequent anodic or electrostatic bonding. Any exposed metal is anodically treated, and the anodised areas then covered by epoxy for additional protection.

In order to evaluate the bonds the epoxy was softened and broken away to expose the metallizing. The ISFET chip to Pyrex header bonds showed slight deterioration in some areas, but not enough to account for the significant increase in gate leakage current.

The Pyrex header to Pyrex tube bonding area, which is visible through the header, indicated that significant corrosion of the aluminum metallizing had taken place allowing brine ingress. The etching of the tube metallizing was such that it was considered to be the primary cause of failure in all six units.

FIGURE 6.1. Curve Tracer Results, Drain-Substrate Diode

After visual inspection the headers were physically removed from the support tube for inspection of the pogo pin contacts and the mating metal pads on the rear of the header.

The pogo pins were electrically and mechanically inspected and found to be in operating condition but the mating metal pads were completely etched away. As this area is normally sealed, the etching of the contact pads is considered "effect" rather than cause of failure.

Evaluation of sensors 693 and 697, which failed prematurely, indicated that an additional failure mode may have preceded the header bond failure. The support tubes of these sensors, originally designated for pCO₂ sensing, had been laser drilled and resealed around a platinum feed-through wire which was to have supported the internal reference. The drilling and sealing had apparently weakened the tube at that point resulting in a crack after thermal cycling at the field trial site. The additional testing of these units, later in the trials, resulting in failure of the header bond, precluded absolute conclusion as to the original failure cause.

6.5 pCO₂ MEMBRANE

Inspection of the membrane assembly indicated that its integrity was still intact. Failure of the sensor bonding was due to the high temperature brine leakage around the first membrane assembly, which failed, or the combination of high temperature exposure and its own internal electrolyte.

6.6 SUMMARY OF POST FIELD TRIAL ANALYSIS

The most probable cause of failure at the conclusion of the field testing was erosion or corrosion of the metallizing at the header-to-support tube bond. This caused failure of the anodic bond, allowing incursion of electrolyte or brine which rendered the ISFET inoperable. An exception may be that for sensors 693 and 697 a support tube crack could have contributed to the premature disfunction.

7.0 SUMMARY AND RECOMMENDATIONS

7.1 SUMMARY

In March 1986, Leeds & Northrup submitted its technical proposal, Q6410-41, containing many recommendations to enhance the operation of the pH and pCO₂ brine sensors.

All of the recommendations in this proposal were addressed, and where proven beneficial and feasible, implemented.

The items of major import to the project include the following:

- (1) The gold interconnecting wires, internal to the sensor, were replaced with spring loaded pogo pins. This modification proved successful, surviving laboratory and field testing, and did not contribute any limitation to sensor life.
- (2) Bonding at the ISFET sensing chip and header interface and the header-to-support tube interface, previously accomplished with epoxy, was accomplished by anodic bonding after aluminum metallizing one surface of each interface. The exposed areas of metallizing were anodically treated and further protected by epoxy coating. In spite of the attention given to this area, it remained the weak point of the packaging and should be the primary development thrust in future work.
- (3) Membrane mounting improvements were incorporated in the pCO₂ sensor. These improvements involved both the membrane and getter system plus the physical mounting arrangement. This design proved rugged and reliable during the field trail having survived both feed and return brine exposure. The premature failure of the first membrane assembly was attributed to a poor gasket seal at

the base of the assembly and does not detract from the basic design. The second assembly, replaced in the field, maintained its integrity throughout the testing.

- (4) The porous silver H_2S getter system for the pCO_2 sensor was replaced by a sealed liquid system having a much greater capacity. The gettering capacity was not severely challenged in the field trial due to the low H_2S concentration of the Heber plant brine stream.
- (5) One of the proposed improvements that was not incorporated due to technical difficulties involved laser drilling the chip and header assembly to achieve backside contacting of the ISFET chip. Laser drilling of the previously bonded header chip sandwich would have allowed deposition in the resulting via. Due to the difficulty of obtaining a smooth transition in the via, the second alternative for back side contacting was employed. Results of the post field analysis indicated that this alternate method did not contribute, in any negative way, to the life expectancy.

Probes with these improvements were tested in the laboratory and in the field. ISFET performance was good but packaging failures limited sensor life to approximately 40 hours in hot brine.

7.2 RECOMMENDATIONS

As discussed in the preceding summary, the primary focus of future development should be the area of bonding. To achieve a package that will withstand the corrosive conditions of high temperature brine plus survive the high pressures involved, a different approach to the packaging is recommended. Further, to allow the maximum degree of freedom in design, it is also recommended that the pH sensor be divorced from the pCO_2 design, with its geometrical requirement for membrane mounting.

In particular, it is suggested that a design such as that indicated in Figure 7.1 would be suitable for pH sensing. The ISFET chip "A" is attached to the Pyrex header "B" by means of a Si-Pyrex anodic bond. The cutout "C" in the header permits access to the chip metallization so that it can be connected via wire bonding or beam leads to the header metallization "D". The wire bonds and header metallization are then protected by silicon cap "E", anodically bonded to the back side of the header. A trench "F" in the cap accommodates both the header metallization and wire bonds. All exposed Si edges would then be provided with a vapor deposited film of Ta or Ta₂O₅ to provide chemical protection.

In order to be compatible with the Bal seals used in existing probe design, it would be necessary to have a transition from the rectangular geometry illustrated in Figure 7.1 to one with circular cross section. It is felt that this could be accommodated by potting the proposed new header design into a cylindrical tube as illustrated in Figure 7.2.

This design approach only appears possible for the pH sensor, there being no provision for attachment of a membrane in this particular geometrical configuration.

FIGURE 7.1. Proposed Chip-Header Assembly

FIGURE 7.2. Proposed Sensor Assembly

8.0 REFERENCES

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APPENDIX A - DETAILED LABORATORY FUNCTIONAL TEST DATA

SUMMARY OF ISFET PROBE # 693 TEST RESULTS 11/13/86 IN NBS KHP (185F) BUFFER

Vr, REFERENCE TO SOURCE ENF														ANALYSIS				
AC IN Vr, mV				SLOPE, mV/pH										FINAL VALUES				
TIME	TEMP	MEAN	σ	Id, pH	Vd, V	Vh, V	MEAN, Vr	σ , mV	MEAN	σ	Ik, nA	Ih, nA	2nd REF	TEMP	TIME	NBS pH	PH	ERROR
16:04:15	25.02	0.01	± 0.01	-93.937	-1.5000	0.0000	-1.6832	± 0.03	-0.53	± 0.02	-1	0	16.54			4.006	3.997	-0.009
16:13:28	25.03	0.05	± 0.01	-93.937	-1.5000	0.0000	-1.6832	± 0.03	-0.35	± 0.02	-1	0	16.54	25.02	16:21:08	4.006	3.997	-0.009
16:22:40	25.03	0.67	± 0.01	-93.937	-1.5000	-0.0000	-1.6832	± 0.02	-0.30	± 0.01	-1	0	16.57	25.02	16:30:20	4.006	3.997	-0.009
16:31:59	25.02	0.58	± 0.01	-93.937	-1.5000	0.0000	-1.6833	± 0.02	-0.43	± 0.01	-1	0	16.55	25.03	16:39:39	4.006	3.996	-0.010
17:29:06	0.05	0.96	± 0.01	-100.003	-1.5000	0.0000	-1.6350	± 0.00	0.05	± 0.00	0	0	18.51	0.04	17:36:46	4.006	4.049	0.043
17:38:19	0.04	0.94	± 0.01	-100.003	-1.5000	0.0000	-1.6350	± 0.00	-0.40	± 0.00	0	0	18.45	0.02	17:45:50	4.006	4.050	0.044
17:47:31	0.02	0.94	± 0.01	-100.002	-1.5000	0.0000	-1.6350	± 0.00	-0.15	± 0.00	0	0	18.40	0.01	17:55:11	4.006	4.051	0.045
17:56:44	0.01	0.95	± 0.01	-100.003	-1.5000	0.0000	-1.6350	± 0.01	0.42	± 0.00	0	0	18.31	0.01	18:04:24	4.006	4.051	0.045
18:37:39	9.96	0.00	± 0.02	-100.004	-1.5000	-0.0000	-1.6242	± 0.02	-0.45	± 0.00	0	0	16.53	9.96	18:45:19	3.999	4.005	0.006
18:47:03	9.96	0.00	± 0.01	-93.936	-1.5000	-0.0000	-1.6242	± 0.02	-0.50	± 0.00	0	0	16.44	9.99	18:54:43	3.999	4.005	0.006
18:56:33	9.99	0.69	± 0.02	-93.936	-1.5000	-0.0000	-1.6242	± 0.02	-0.07	± 0.01	0	0	16.37	10.00	19:04:13	3.999	4.004	0.005
19:05:45	10.00	0.98	± 0.01	-93.936	-1.5000	-0.0000	-1.6243	± 0.02	-0.31	± 0.01	0	0	16.33	10.00	19:13:25	3.999	4.004	0.005
19:46:50	19.90	0.04	± 0.01	-93.936	-1.5000	-0.0000	-1.6109	± 0.01	0.10	± 0.00	0	0	16.32	20.00	19:54:30	4.001	3.988	-0.013
19:56:14	20.00	0.04	± 0.01	-93.936	-1.5000	-0.0000	-1.6109	± 0.00	0.14	± 0.00	0	0	16.27	20.01	20:03:54	4.001	3.988	-0.013
20:05:27	20.01	0.06	± 0.01	-93.936	-1.5000	-0.0000	-1.6109	± 0.02	-0.52	± 0.01	0	0	16.24			4.001	3.988	-0.013
20:14:39	20.01	0.06	± 0.01	-93.937	-1.5000	-0.0000	-1.6109	± 0.02	0.29	± 0.01	0	0	16.22	20.01	20:22:19	4.001	3.988	-0.013
20:25:32	29.97	0.01	± 0.01	-93.937	-1.5000	-0.0000	-1.5962	± 0.03	0.16	± 0.02	-1	0	16.99	29.99	21:03:13	4.012	3.996	-0.016
21:04:45	30.00	0.01	± 0.01	-93.937	-1.5000	-0.0000	-1.5962	± 0.04	-0.46	± 0.02	-1	0	16.92	30.00	21:12:25	4.012	3.996	-0.016
21:13:58	30.00	0.68	± 0.01	-93.937	-1.5000	-0.0000	-1.5961	± 0.03	0.13	± 0.02	-1	0	16.92	30.00	21:21:20	4.012	3.996	-0.016
21:23:10	30.01	0.62	± 0.01	-93.937	-1.5000	-0.0000	-1.5961	± 0.02	0.25	± 0.01	-1	0	16.95	30.01	21:30:50	4.012	3.996	-0.016
22:03:57	40.01	0.77	± 0.02	-93.937	-1.5000	-0.0000	-1.5003	± 0.03	0.50	± 0.02	-1	0	17.73			4.031	4.021	-0.010
22:13:10	40.05	0.77	± 0.01	-93.937	-1.5000	-0.0000	-1.5003	± 0.02	0.27	± 0.01	-1	0	17.71	40.06	22:20:50	4.031	4.021	-0.010
22:23:14	40.04	0.78	± 0.01	-93.937	-1.5000	-0.0000	-1.5003	± 0.02	0.27	± 0.01	-1	0	17.72	40.05	22:30:54	4.031	4.021	-0.010
22:32:27	40.05	0.65	± 0.01	-93.937	-1.5000	-0.0000	-1.5002	± 0.02	-0.10	± 0.02	-1	0	17.76	40.05	22:40:06	4.031	4.021	-0.010
23:17:18	49.91	0.73	± 0.01	-93.937	-1.5000	-0.0000	-1.3641	± 0.01	0.05	± 0.01	-1	0	18.35	49.93	23:24:50	4.057	4.053	-0.004
23:26:31	49.93	0.63	± 0.02	-93.937	-1.5000	0.0000	-1.3641	± 0.00	0.10	± 0.00	-1	0	18.32	49.94	23:34:11	4.057	4.053	-0.004
23:35:44	49.94	0.73	± 0.01	-93.937	-1.5000	0.0000	-1.3641	± 0.02	-0.00	± 0.01	-1	0	18.36	49.94	23:43:23	4.057	4.053	-0.004
23:44:56	49.94	0.75	± 0.01	-93.937	-1.5000	-0.0000	-1.3641	± 0.00	-0.05	± 0.00	-1	0	18.99	49.94	23:52:36	4.057	4.053	-0.004
00:24:18	59.99	0.73	± 0.01	-93.936	-1.5000	0.0000	-1.3471	± 0.02	-0.02	± 0.02	-3	0	19.29	60.00	00:31:50	4.091	4.090	-0.001
00:33:49	60.00	0.71	± 0.01	-93.937	-1.5000	0.0000	-1.3471	± 0.03	0.04	± 0.02	-2	0	19.30	60.03	00:41:29	4.091	4.090	-0.001
00:43:26	60.03	0.71	± 0.02	-100.004	-1.5000	0.0000	-1.3472	± 0.03	-0.03	± 0.02	-2	0	19.32	60.03	00:51:06	4.091	4.088	-0.003
00:52:51	60.03	0.73	± 0.01	-93.937	-1.5000	0.0000	-1.3472	± 0.03	-0.29	± 0.02	-2	0	19.31	60.03	01:00:31	4.091	4.088	-0.003
01:30:03	70.04	0.71	± 0.01	-100.003	-1.5000	-0.0000	-1.3297	± 0.02	-0.09	± 0.02	-6	0	19.03	70.06	01:37:43	4.126	4.132	0.006
01:39:16	70.06	0.61	± 0.01	-100.003	-1.5000	0.0000	-1.3297	± 0.03	-0.36	± 0.02	-5	0	19.09	70.06	01:46:56	4.126	4.131	0.005
01:48:29	70.06	0.60	± 0.01	-100.004	-1.5000	0.0000	-1.3290	± 0.04	-0.66	± 0.02	-5	0	19.93			4.126	4.130	0.004
01:57:48	70.06	0.60	± 0.01	-100.003	-1.5000	0.0000	-1.3290	± 0.03	-0.60	± 0.02	-5	0	19.96	70.07	02:05:20	4.126	4.130	0.003
02:34:51	79.99	0.99	± 0.01	-100.002	-1.5000	-0.0000	-1.3119	± 0.00	-0.31	± 0.00	-11	0	20.35	80.01	02:42:31	4.164	4.179	0.015
02:44:04	80.01	0.60	± 0.01	-100.002	-1.5000	0.0000	-1.3120	± 0.02	-0.41	± 0.01	-10	0	20.39	80.02	02:51:44	4.164	4.178	0.014
02:53:16	80.04	0.60	± 0.01	-100.002	-1.5000	0.0000	-1.3120	± 0.00	-0.31	± 0.00	-10	0	20.32	80.04	03:00:56	4.164	4.177	0.013
03:02:29	80.04	0.60	± 0.01	-100.001	-1.5000	-0.0000	-1.3121	± 0.04	-0.74	± 0.02	-10	0	20.49	80.04	03:10:09	4.164	4.176	0.012
03:39:26	90.01	0.65	± 0.02	-100.001	-1.5000	0.0000	-1.4335	± 1.66	-2.60	± 1.06	-10	0	20.95			4.205	4.222	0.027
03:48:39	90.04	0.65	± 0.02	-100.002	-1.5000	-0.0000	-1.4337	± 0.04	-0.00	± 0.02	-17	0	21.02			4.205	4.229	0.024
03:59:36	90.06	0.64	± 0.01	-100.002	-1.5000	0.0000	-1.4339	± 0.04	-0.94	± 0.02	-16	0	21.07			4.205	4.226	0.020
04:08:48	90.04	0.65	± 0.01	-100.001	-1.5000	-0.0000	-1.4940	± 0.06	-1.44	± 0.02	-15	0	21.09	90.04	04:16:20	4.205	4.224	0.019
05:26:19	25.03	0.76	± 0.02	-100.002	-1.5000	0.0000	-1.6055	± 0.01	-0.54	± 0.00	0	0	20.36			4.006	3.999	-0.007
05:35:32	25.00	0.77	± 0.01	-100.002	-1.5000	0.0000	-1.6056	± 0.00	-0.19	± 0.00	0	0	19.00	25.00	05:43:12	4.006	3.998	-0.008
05:44:44	25.00	0.77	± 0.01	-100.002	-1.5000	0.0000	-1.6056	± 0.03	-0.72	± 0.02	0	0	19.39			4.006	3.997	-0.009

SUMMARY OF ISFET PROBE # 682 TEST RESULTS 10/23/86
IN NBS KHP (1857) BUFFER

V _r , DC REFERENCE TO SOURCE ENV														ANALYSIS					
		AC IN V _r , mV		SLOPE, mV/mV										FINAL VALUES					
TIME	TEMP	MEAN	σ	I _d , pA	V ₀ , V	V ₀ , V	MEAN, V _r	σ, mV	MEAN	σ	I _h , nA	I _b , nA	2nd REF	TEMP	TIME	NBS pH	LINEAR pH	ERROR	
20:04:13	25.05	0.75	± 0.02	-100.001	-1.5000	0.0000	-3.0243	± 0.00	0.29	± 0.00	-4	0	7.11	25.05	20:11:53	4.006	3.991	-0.015	
20:13:26	25.05	0.77	± 0.02	-100.001	-1.5000	0.0000	-3.0243	± 0.00	-0.44	± 0.00	-7	0	7.19	25.05	20:21:06	4.006	3.990	-0.016	
20:22:39	25.05	0.76	± 0.02	-100.001	-1.5000	0.0000	-3.0243	± 0.02	-0.42	± 0.01	-3	0	7.14	25.05	20:30:19	4.006	3.990	-0.016	
20:31:52	25.05	0.78	± 0.02	-100.000	-1.5000	0.0000	-3.0243	± 0.00	-0.50	± 0.00	-3	0	7.02	25.05	20:39:32	4.006	3.990	-0.016	
21:32:49	0.12	0.67	± 0.01	-100.001	-1.5000	0.0000	-3.0777	± 0.03	0.29	± 0.02	-17	0	10.29	0.09	21:40:29	4.006	4.076	0.070	
21:42:02	0.06	0.66	± 0.02	-100.001	-1.5000	0.0000	-3.0776	± 0.07	-0.20	± 0.04	-18	0	10.19	0.07	21:49:42	4.006	4.078	0.072	
21:51:15	0.07	0.67	± 0.01	-100.001	-1.5000	0.0000	-3.0777	± 0.00	-0.31	± 0.00	-12	0	10.15	0.08	21:50:55	4.006	4.077	0.071	
22:00:27	0.08	0.67	± 0.01	-100.001	-1.5000	0.0000	-3.0777	± 0.06	-0.20	± 0.04	-10	0	10.06	0.07	22:00:08	4.006	4.076	0.070	
22:45:19	9.99	0.67	± 0.02	-100.001	-1.5000	0.0000	-3.0581	± 0.00	0.26	± 0.00	-7	0	7.00	10.02	22:52:59	3.999	4.012	0.013	
22:54:39	10.03	0.83	± 0.02	-100.000	-1.5000	0.0000	-3.0580	± 0.05	0.96	± 0.02	-6	0	7.61			3.999	4.012	0.013	
23:03:52	10.02	0.82	± 0.02	-100.001	-1.5000	0.0000	-3.0580	± 0.00	0.00	± 0.00	-5	0	7.64	10.00	23:11:32	3.999	4.012	0.013	
23:13:05	10.00	0.82	± 0.02	-100.002	-1.5000	0.0000	-3.0581	± 0.00	-0.15	± 0.00	-5	0	7.63	10.00	23:20:45	3.999	4.012	0.013	
23:50:00	19.97	0.79	± 0.02	-100.000	-1.5000	0.0000	-3.0363	± 0.00	0.23	± 0.00	-7	0	6.76	20.01	00:07:14	4.001	3.907	-0.014	
00:00:47	20.01	0.79	± 0.01	-100.000	-1.5000	0.0000	-3.0362	± 0.02	0.53	± 0.00	-7	0	6.60			4.001	3.907	-0.014	
00:18:00	20.02	0.80	± 0.02	-100.000	-1.5000	0.0000	-3.0362	± 0.04	-0.15	± 0.03	-7	0	6.95	20.02	00:25:40	4.001	3.906	-0.015	
00:27:12	20.03	0.80	± 0.02	-100.000	-1.5000	0.0000	-3.0362	± 0.00	0.34	± 0.00	-6	0	6.93	20.03	00:34:53	4.001	3.906	-0.015	
01:12:03	29.90	0.65	± 0.02	-100.000	-1.5000	0.0000	-3.0131	± 0.02	0.20	± 0.01	-5	0	6.75	30.00	01:19:43	4.012	3.906	-0.026	
01:21:16	30.01	0.75	± 0.01	-100.000	-1.5000	0.0000	-3.0130	± 0.00	0.00	± 0.00	-4	0	6.82	30.01	01:28:56	4.012	3.906	-0.026	
01:30:29	30.01	0.76	± 0.03	-100.000	-1.5000	0.0000	-3.0130	± 0.00	0.15	± 0.00	-5	0	6.68	30.02	01:38:09	4.012	3.907	-0.025	
01:39:42	30.02	0.64	± 0.01	-100.000	-1.5000	0.0000	-3.0130	± 0.03	-0.09	± 0.02	-5	0	6.80	30.02	01:47:22	4.012	3.906	-0.026	
02:24:32	39.93	0.74	± 0.02	-100.000	-1.5000	0.0000	-2.9087	± 0.00	0.43	± 0.00	-6	0	6.91	39.96	02:32:12	4.031	4.006	-0.024	
02:33:45	39.97	0.73	± 0.01	-100.000	-1.5000	0.0000	-2.9086	± 0.00	-0.16	± 0.00	-5	0	6.05	39.97	02:41:25	4.031	4.007	-0.024	
02:42:58	39.97	0.73	± 0.02	-100.001	-1.5000	0.0000	-2.9084	± 0.54	-4.32	± 0.33	-5	0	6.00			4.031	4.010	-0.021	
02:52:11	39.96	0.75	± 0.02	-100.000	-1.5000	0.0000	-2.9086	± 0.24	0.10	± 0.15	-4	0	6.72	39.96	02:59:52	4.031	4.006	-0.025	
03:37:06	49.83	0.62	± 0.04	-100.000	-1.5000	0.0000	-2.9636	± 0.04	0.20	± 0.02	-5	0	7.32	49.87	03:44:46	4.057	4.030	-0.010	
03:46:19	49.87	0.71	± 0.03	-100.000	-1.5000	0.0000	-2.9636	± 0.04	-0.05	± 0.03	-5	0	7.26	49.89	03:53:59	4.057	4.037	-0.020	
03:55:32	49.88	0.71	± 0.02	-100.000	-1.5000	0.0000	-2.9636	± 0.03	0.69	± 0.01	-4	0	7.24			4.057	4.036	-0.020	
04:04:45	49.89	0.60	± 0.01	-100.001	-1.5000	0.0000	-2.9636	± 0.00	-4.32	± 0.00	-4	0	7.26	49.88	04:12:25	4.057	4.036	-0.021	
04:14:39	60.03	0.71	± 0.01	-100.000	-1.5000	0.0000	-2.9369	± 0.00	0.06	± 0.00	-10	0	7.04	60.06	04:49:20	4.091	4.001	-0.010	
04:52:36	60.05	0.70	± 0.01	-100.001	-1.5000	0.0000	-2.9370	± 0.00	-0.36	± 0.00	-9	0	7.96	60.06	05:00:17	4.091	4.079	-0.012	
05:03:33	60.06	0.60	± 0.02	-99.997	-1.5000	0.0000	-2.9370	± 0.05	-1.16	± 0.01	-11	0	7.01			4.091	4.078	-0.013	
05:13:38	60.03	0.69	± 0.01	-99.997	-1.5000	0.0000	-2.9372	± 0.06	-0.94	± 0.03	-10	0	8.03	60.00	05:21:10	4.091	4.077	-0.014	
05:50:34	69.06	0.66	± 0.02	-99.996	-1.5000	0.0000	-2.9103	± 0.00	0.26	± 0.05	-11	0	8.32	69.90	05:50:15	4.126	4.134	0.008	
06:00:00	69.90	0.57	± 0.02	-99.997	-1.5000	0.0000	-2.9103	± 0.03	-0.71	± 0.01	-11	0	8.36			4.126	4.133	0.007	
06:09:13	69.90	0.65	± 0.02	-99.996	-1.5000	0.0000	-2.9104	± 0.05	-0.34	± 0.03	-10	0	8.25	69.90	06:16:54	4.126	4.122	0.006	
06:19:36	69.90	0.64	± 0.03	-100.004	-1.5000	0.0000	-2.9105	± 0.06	0.45	± 0.04	-10	0	8.25	69.90	06:27:16	4.126	4.131	0.005	
06:56:50	79.06	0.61	± 0.01	-100.002	-1.5000	0.0000	-2.8821	± 0.06	-0.32	± 0.04	-10	0	8.44	79.00	07:04:31	4.164	4.200	0.037	
07:06:56	79.90	0.60	± 0.02	-100.001	-1.5000	0.0000	-2.8821	± 0.26	3.21	± 0.15	-16	0	8.44			4.164	4.199	0.036	
07:17:01	79.91	0.61	± 0.02	-100.001	-1.5000	0.0000	-2.8822	± 0.06	-0.63	± 0.04	-17	0	8.53			4.164	4.190	0.034	
07:26:14	79.09	0.62	± 0.03	-100.001	-1.5000	0.0000	-2.8822	± 0.07	-0.12	± 0.05	-16	0	8.32	79.00	07:33:54	4.164	4.199	0.035	
08:03:10	89.90	0.57	± 0.02	-100.002	-1.5000	0.0000	-2.8524	± 0.00	-0.35	± 0.05	-20	0	8.46			4.205	4.204	0.079	
08:13:16	89.93	0.54	± 0.01	-100.002	-1.5000	0.0000	-2.8525	± 0.12	-1.27	± 0.07	-25	0	8.51			4.205	4.201	0.076	
08:23:23	89.93	0.55	± 0.01	-100.002	-1.5000	0.0000	-2.8526	± 0.09	-0.93	± 0.05	-23	0	8.65			4.205	4.200	0.075	
08:32:36	89.93	0.50	± 0.02	-100.002	-1.5000	0.0000	-2.8527	± 0.05	-0.77	± 0.02	-22	0	8.64	89.93	08:40:17	4.205	4.270	0.074	
09:54:14	24.93	0.66	± 0.01	-100.002	-1.5000	0.0000	-3.0250	± 0.00	-1.15	± 0.00	-2	0	10.15			4.006	3.973	-0.033	
10:03:20	24.89	0.66	± 0.01	-100.003	-1.5000	0.0000	-3.0250	± 0.00	0.00	± 0.00	-1	0	9.05	24.00	10:11:00	4.006	3.972	-0.034	
10:12:41	24.88	0.56	± 0.02	-100.002	-1.5000	0.0000	-3.0250	± 0.03	-0.49	± 0.02	0	0	9.99	24.07	10:20:21	4.006	3.972	-0.034	

SUMMARY OF ISFET PROBE # 685 TEST RESULTS 10/25/86
IN NBS KHP (185F) BUFFER

W ₁ DC REFERENCE TO SOURCE EMF														ANALYSIS				
AC IN W ₁ , mV				SLOPE, mV/pH										FINAL VALUES				
TIME	TEMP	MEAN	S	I ₀ , pA	V ₀ , V	V ₀ , V	MEAN, W ₁	S, mV	MEAN	S	I ₀ , nA	I ₀ , nA	2nd REF	TEMP	TIME	NBS pH	LINEAR pH	ERROR
12:44:13	24.99	0.76	± 0.03	-100.002	-1.5000	0.0000	-2.3256	± 0.00	-0.00	± 0.00	-1	0	6.67	24.99	12:51:53	4.006	4.002	-0.004
12:53:26	24.99	0.74	± 0.01	-100.001	-1.5000	0.0000	-2.3257	± 0.02	0.27	± 0.01	-1	0	6.70	24.99	13:01:07	4.006	4.001	-0.005
13:02:39	24.99	0.75	± 0.02	-100.001	-1.5000	0.0000	-2.3257	± 0.02	-0.13	± 0.01	-1	0	6.72	24.99	13:10:19	4.006	4.001	-0.005
13:11:52	24.99	0.68	± 0.02	-100.001	-1.5000	0.0000	-2.3257	± 0.01	-0.24	± 0.01	-1	0	6.71	24.99	13:19:32	4.006	4.000	-0.006
14:00:48	-0.05	0.04	± 0.01	-100.002	-1.5000	0.0000	-2.3669	± 0.00	0.07	± 0.00	-1	0	9.41	-0.10	14:16:28	4.006	4.039	0.033
14:18:00	-0.10	0.05	± 0.01	-100.002	-1.5000	0.0000	-2.3669	± 0.00	0.12	± 0.00	-1	0	9.51	-0.11	14:25:41	4.006	4.039	0.033
14:27:16	-0.11	0.05	± 0.02	-100.001	-1.5000	0.0000	-2.3669	± 0.00	0.17	± 0.00	-1	0	9.54	-0.11	14:34:57	4.006	4.040	0.034
14:36:29	-0.11	0.05	± 0.02	-100.002	-1.5000	0.0000	-2.3669	± 0.00	-0.00	± 0.00	-1	0	9.60	-0.12	14:44:09	4.006	4.040	0.034
15:17:17	9.90	0.00	± 0.02	-100.001	-1.5000	0.0000	-2.3515	± 0.00	0.07	± 0.00	-1	0	7.72	9.95	15:24:58	3.999	4.005	0.006
15:26:31	9.95	0.63	± 0.02	-100.001	-1.5000	0.0000	-2.3514	± 0.00	0.19	± 0.00	-1	0	7.66	9.96	15:34:11	3.999	4.005	0.005
15:35:43	9.96	0.00	± 0.02	-100.002	-1.5000	0.0000	-2.3515	± 0.02	-0.54	± 0.01	-1	0	7.63			3.999	4.004	0.005
15:44:57	9.96	0.79	± 0.02	-100.002	-1.5000	0.0000	-2.3515	± 0.00	-0.31	± 0.00	-1	0	7.63	9.96	15:52:37	3.999	4.003	0.004
16:25:48	19.91	0.75	± 0.01	-100.001	-1.5000	0.0000	-2.3348	± 0.05	0.44	± 0.03	-1	0	7.02	19.95	16:33:29	4.001	3.995	-0.006
16:35:01	19.95	0.73	± 0.01	-100.001	-1.5000	0.0000	-2.3348	± 0.05	-0.11	± 0.03	-1	0	6.94	19.95	16:42:42	4.001	3.994	-0.007
16:44:15	19.95	0.75	± 0.02	-100.000	-1.5000	0.0000	-2.3348	± 0.05	-0.19	± 0.03	-1	0	6.91	19.96	16:51:55	4.001	3.994	-0.007
16:53:29	19.96	0.76	± 0.01	-100.000	-1.5000	0.0000	-2.3347	± 0.01	-0.37	± 0.00	-1	0	6.89	19.96	17:01:09	4.001	3.994	-0.007
17:34:18	29.09	0.72	± 0.02	-100.000	-1.5000	0.0000	-2.3172	± 0.02	0.27	± 0.01	-2	0	7.34	29.93	17:41:59	4.012	4.001	-0.011
17:43:31	29.93	0.50	± 0.02	-100.001	-1.5000	0.0000	-2.3172	± 0.02	-0.29	± 0.01	-2	0	7.33	29.93	17:51:12	4.012	4.000	-0.012
17:52:44	29.94	0.72	± 0.01	-100.002	-1.5000	0.0000	-2.3172	± 0.05	-0.24	± 0.03	-2	0	7.35	29.94	18:00:25	4.012	4.000	-0.012
18:01:57	29.94	0.62	± 0.12	-100.001	-1.5000	0.0000	-2.3165	± 1.71	-15.14	± 1.05	-1	0	7.31	29.95	18:19:33	4.012	4.011	-0.001
18:52:42	39.04	0.73	± 0.02	-100.002	-1.5000	0.0000	-2.2985	± 0.00	-0.25	± 0.00	-1	0	7.07			4.031	4.026	-0.005
19:10:22	39.90	0.73	± 0.03	-100.002	-1.5000	0.0000	-2.2986	± 2.97	-76.51	± 0.05	-1	0	7.06			4.031	3.987	-0.044
19:19:36	39.90	0.69	± 0.02	-100.002	-1.5000	0.0000	-2.2989	± 0.00	-0.63	± 0.00	-2	0	7.09			4.031	4.017	-0.013
19:34:01	39.00	0.99	± 0.03	-100.003	-1.5000	0.0000	-2.2990	± 0.02	-0.91	± 0.00	-1	0	7.90	39.09	19:41:41	4.031	4.016	-0.015
20:18:48	49.06	0.62	± 0.01	-100.003	-1.5000	0.0000	-2.2801	± 0.23	0.17	± 0.15	-1	0	8.39	49.90	20:34:36	4.057	4.042	-0.015
20:36:20	49.91	0.69	± 0.01	-99.998	-1.5000	-0.0000	-2.2801	± 0.00	-0.63	± 0.00	-1	0	8.24	49.91	20:44:01	4.057	4.041	-0.016
20:45:34	49.91	0.72	± 0.03	-99.998	-1.5000	0.0000	-2.2802	± 0.03	-0.06	± 0.02	-1	0	8.28	49.92	20:53:14	4.057	4.040	-0.017
20:54:47	49.91	0.62	± 0.04	-99.998	-1.5000	0.0000	-2.2802	± 0.04	-0.53	± 0.02	-1	0	8.24	49.91	21:02:27	4.057	4.039	-0.018
21:31:42	59.99	0.71	± 0.01	-99.997	-1.5000	0.0000	-2.2589	± 0.99	19.47	± 0.47	-3	0	8.60			4.091	4.097	0.006
21:49:09	60.06	0.60	± 0.01	-99.997	-1.5000	-0.0000	-2.2596	± 0.06	-1.92	± 0.02	-3	0	8.95			4.091	4.084	-0.007
21:58:23	60.06	0.70	± 0.02	-99.997	-1.5000	-0.0000	-2.2598	± 0.01	-0.49	± 0.00	-3	0	8.96	60.06	22:06:03	4.091	4.082	-0.009
22:07:26	60.06	0.70	± 0.01	-99.998	-1.5000	0.0000	-2.2598	± 0.03	-0.22	± 0.02	-2	0	8.99	60.06	22:15:16	4.091	4.081	-0.010
22:40:28	70.02	0.66	± 0.01	-99.997	-1.5000	-0.0000	-2.2388	± 0.06	0.19	± 3.12	-5	0	9.01	70.00	22:48:00	4.126	4.135	0.008
22:50:45	70.11	0.67	± 0.01	-99.997	-1.5000	0.0000	-2.2392	± 0.04	-0.54	± 0.02	-5	0	8.99			4.126	4.127	0.001
23:00:17	70.11	0.68	± 0.02	-99.997	-1.5000	0.0000	-2.2393	± 0.03	-0.42	± 0.02	-5	0	9.06	70.11	23:07:57	4.126	4.126	-0.001
23:09:30	70.11	0.60	± 0.02	-99.997	-1.5000	0.0000	-2.2393	± 0.14	0.83	± 0.09	-5	0	9.01	70.11	23:17:11	4.126	4.126	-0.001
23:42:24	80.09	0.66	± 0.03	-99.998	-1.5000	0.0000	-2.2178	± 0.03	0.16	± 0.02	-10	0	9.19	80.15	23:50:04	4.164	4.162	0.018
23:51:49	80.15	0.67	± 0.02	-99.997	-1.5000	0.0000	-2.2178	± 0.03	-0.03	± 0.02	-9	0	9.29	80.17	23:59:29	4.165	4.161	0.016
00:01:54	80.16	0.99	± 0.02	-99.997	-1.5000	0.0000	-2.2179	± 0.04	-0.04	± 0.01	-9	0	9.22			4.165	4.160	0.015
00:11:07	80.17	0.67	± 0.01	-99.998	-1.5000	0.0000	-2.2179	± 0.01	-0.49	± 0.00	-6	0	9.40	80.17	00:18:47	4.165	4.179	0.014
00:48:14	90.16	0.60	± 0.02	-99.997	-1.5000	-0.0000	-2.1954	± 0.74	-0.35	± 0.47	-19	0	9.33			4.206	4.247	0.041
00:57:28	90.20	0.50	± 0.02	-99.998	-1.5000	0.0000	-2.1957	± 0.06	-1.53	± 0.02	-18	0	9.46			4.206	4.243	0.037
01:06:42	90.20	0.65	± 0.03	-99.997	-1.5000	-0.0000	-2.1958	± 0.05	-1.06	± 0.02	-17	0	9.64			4.206	4.241	0.035
01:15:55	90.20	0.66	± 0.02	-99.997	-1.5000	-0.0000	-2.1950	± 0.04	-1.02	± 0.01	-16	0	9.68	90.20	01:23:35	4.206	4.239	0.033
02:33:22	25.06	0.74	± 0.01	-99.997	-1.5000	0.0000	-2.3282	± 0.05	-1.20	± 0.02	0	0	11.22			4.006	3.957	-0.049
02:42:35	25.01	0.75	± 0.02	-99.998	-1.5000	0.0000	-2.3283	± 0.03	-0.51	± 0.02	0	0	10.76			4.006	3.956	-0.050
02:51:49	25.00	0.77	± 0.02	-99.998	-1.5000	0.0000	-2.3284	± 0.02	-0.05	± 0.00	0	0	10.39			4.006	3.954	-0.052

SUMMARY OF ISFET PROBE # 686 TEST RESULTS 10/27/86
IN NBS KHP (185F) BUFFER

W, DC REFERENCE TO SOURCE EMF													ANALYSIS					
Δ IN V _r , mV				SLOPE, mV/pH										FINAL VALUES				
TIME	TEMP	MEAN	σ	I _d , μA	V _d , V	V _o , V	MEAN, W	σ, mV	MEAN	σ	I _h , nA	I _b , nA	2nd REF	TEMP	TIME	NBS pH	LINEAR pH	ERROR
16:04:13	25.00	0.57 ± 0.03		-100.003	-1.5000	0.0000	-2.7876 ± 0.05	-0.27 ± 0.04	-1	0			0.15	25.01	16:11:33	4.006	3.988	-0.018
16:13:26	25.01	0.60 ± 0.03		-100.003	-1.5000	0.0000	-2.7876 ± 0.05	-0.14 ± 0.04	-1	0			0.14	25.01	16:21:07	4.006	3.988	-0.018
16:22:51	25.01	0.60 ± 0.02		-99.996	-1.5000	0.0000	-2.7876 ± 0.05	0.02 ± 0.04	-1	0			0.15	25.00	16:30:31	4.006	3.988	-0.018
16:32:22	25.00	0.60 ± 0.03		-100.002	-1.5000	0.0000	-2.7877 ± 0.05	0.21 ± 0.03	-1	0			0.17	25.01	16:40:02	4.006	3.988	-0.018
17:33:17	0.05	0.62 ± 0.04		-100.003	-1.5000	0.0000	-2.8295 ± 0.00	0.01 ± 0.00	-1	0			18.53	0.02	17:40:57	4.006	4.056	0.050
17:42:30	0.02	0.63 ± 0.03		-100.003	-1.5000	0.0000	-2.8296 ± 0.07	-0.27 ± 0.05	-1	0			18.56	0.01	17:50:11	4.006	4.057	0.051
17:51:43	0.01	0.60 ± 0.02		-100.002	-1.5000	0.0000	-2.8296 ± 0.04	-0.19 ± 0.02	-1	0			18.60	0.00	17:59:24	4.006	4.057	0.051
18:00:56	0.01	0.63 ± 0.02		-100.002	-1.5000	0.0000	-2.8296 ± 0.00	0.07 ± 0.05	-1	0			18.59	0.00	18:00:36	4.006	4.057	0.051
18:41:46	9.92	0.62 ± 0.03		-100.003	-1.5000	0.0000	-2.8142 ± 0.00	0.34 ± 0.00	-1	0			9.00	9.97	18:49:26	3.999	4.005	0.006
18:50:59	9.97	0.61 ± 0.02		-100.002	-1.5000	0.0000	-2.8142 ± 0.06	-0.12 ± 0.04	-1	0			0.95	9.97	18:50:39	3.999	4.005	0.006
19:00:12	9.97	0.61 ± 0.03		-100.004	-1.5000	0.0000	-2.8142 ± 0.03	-0.21 ± 0.02	-2	0			0.90	9.98	19:07:52	3.999	4.004	0.005
19:09:37	9.98	0.61 ± 0.03		-99.997	-1.5000	0.0000	-2.8142 ± 0.07	-0.20 ± 0.04	-3	0			0.06	9.99	19:17:17	3.999	4.004	0.005
19:50:30	19.93	0.61 ± 0.02		-99.997	-1.5000	0.0000	-2.7978 ± 0.00	0.00 ± 0.00	-4	0			0.45			4.001	3.986	-0.015
19:59:43	19.96	0.60 ± 0.02		-99.997	-1.5000	0.0000	-2.7978 ± 0.00	0.03 ± 0.00	-4	0			0.40	19.98	20:07:24	4.001	3.986	-0.015
20:06:56	19.98	0.64 ± 0.04		-99.998	-1.5000	0.0000	-2.7978 ± 0.00	-0.33 ± 0.00	-4	0			0.36	19.98	20:16:37	4.001	3.986	-0.015
20:18:15	19.98	0.61 ± 0.02		-99.998	-1.5000	0.0000	-2.7978 ± 0.00	0.09 ± 0.00	-4	0			0.33	19.99	20:25:56	4.001	3.986	-0.015
20:59:23	30.03	0.58 ± 0.02		-99.997	-1.5000	-0.0000	-2.7785 ± 0.05	0.07 ± 0.02	-2	0			0.78			4.012	3.988	-0.024
21:06:36	30.08	0.61 ± 0.09		-99.999	-1.5000	0.0000	-2.7785 ± 0.04	-0.00 ± 0.02	-2	0			0.00	30.08	21:16:16	4.012	3.987	-0.025
21:17:49	30.08	0.60 ± 0.04		-99.998	-1.5000	-0.0000	-2.7778 ± 1.50	3.99 ± 0.96	-1	0			0.70			4.012	3.987	-0.025
21:27:00	30.09	0.58 ± 0.02		-99.998	-1.5000	0.0000	-2.7784 ± 0.03	0.02 ± 0.02	-1	0			0.71	30.09	21:34:49	4.012	3.987	-0.025
22:08:10	40.00	0.58 ± 0.02		-99.997	-1.5000	-0.0000	-2.7589 ± 0.78	9.61 ± 0.45	-2	0			0.34			4.031	4.011	-0.020
22:17:23	40.04	0.56 ± 0.02		-99.998	-1.5000	-0.0000	-2.7591 ± 0.00	0.29 ± 0.00	-3	0			0.30	40.05	22:25:03	4.031	4.005	-0.026
22:26:42	40.05	0.57 ± 0.03		-99.998	-1.5000	-0.0000	-2.7586 ± 0.64	16.12 ± 0.20	-3	0			0.22			4.031	4.013	-0.018
22:36:00	40.06	0.57 ± 0.02		-99.998	-1.5000	-0.0000	-2.7575 ± 0.38	-10.23 ± 0.09	-3	0			0.27	40.05	22:43:40	4.031	4.031	-0.000
23:21:00	49.09	0.58 ± 0.02		-99.998	-1.5000	-0.0000	-2.7385 ± 0.10	-2.74 ± 0.02	-7	0			0.09			4.057	4.046	-0.011
23:30:13	49.92	0.57 ± 0.02		-99.998	-1.5000	-0.0000	-2.7387 ± 0.06	-0.82 ± 0.03	-6	0			10.04			4.057	4.042	-0.015
23:39:26	49.94	0.58 ± 0.03		-99.998	-1.5000	0.0000	-2.7389 ± 0.05	-1.48 ± 0.00	-3	0			0.06			4.057	4.038	-0.019
23:48:39	49.94	0.59 ± 0.04		-99.998	-1.5000	-0.0000	-2.7398 ± 0.04	-0.05 ± 0.01	-6	0			0.92	49.93	23:56:20	4.057	4.037	-0.020
00:12:10	60.00	0.56 ± 0.02		-99.997	-1.5000	0.0000	-2.7179 ± 0.02	0.02 ± 0.01	-6	0			10.55	60.05	00:31:50	4.091	4.075	-0.016
00:34:23	60.06	0.57 ± 0.03		-99.997	-1.5000	-0.0000	-2.7180 ± 0.00	-0.16 ± 0.00	-6	0			10.52	60.06	00:42:03	4.091	4.074	-0.018
00:43:36	60.06	0.56 ± 0.02		-99.998	-1.5000	0.0000	-2.7178 ± 0.00	-0.30 ± 0.20	-6	0			10.53			4.091	4.076	-0.016
00:52:49	60.08	0.55 ± 0.02		-99.998	-1.5000	0.0000	-2.7177 ± 0.06	-1.37 ± 0.02	-10	0			10.44	60.08	01:00:30	4.091	4.077	-0.014
01:37:53	69.99	0.57 ± 0.03		-99.997	-1.5000	-0.0000	-2.6961 ± 0.03	-0.09 ± 0.02	-17	0			10.72	70.03	01:45:34	4.126	4.124	-0.002
01:47:59	70.04	0.55 ± 0.01		-99.997	-1.5000	-0.0000	-2.6962 ± 0.02	-0.54 ± 0.00	-19	0			10.69			4.126	4.123	-0.003
01:57:12	70.03	0.57 ± 0.04		-99.998	-1.5000	-0.0000	-2.6962 ± 0.00	-0.41 ± 0.00	-18	0			10.72	70.03	02:04:53	4.126	4.122	-0.004
02:06:26	70.03	0.55 ± 0.02		-99.997	-1.5000	0.0000	-2.6963 ± 0.00	-0.48 ± 0.00	-19	0			10.79	70.03	02:14:06	4.126	4.121	-0.005
02:39:10	80.01	0.56 ± 0.01		-99.997	-1.5000	0.0000	-2.6734 ± 0.41	0.53 ± 0.27	-30	0			10.89			4.164	4.165	0.001
02:48:32	80.04	0.55 ± 0.04		-99.998	-1.5000	0.0000	-2.6734 ± 0.00	-0.35 ± 0.00	-35	0			10.91			4.164	4.163	0.001
02:57:45	80.07	0.55 ± 0.03		-99.997	-1.5000	0.0000	-2.6735 ± 0.03	-0.71 ± 0.01	-33	0			11.02			4.164	4.161	0.003
03:06:50	80.07	0.53 ± 0.02		-99.997	-1.5000	-0.0000	-2.6735 ± 0.03	-0.48 ± 0.02	-33	0			11.06	80.07	03:14:38	4.164	4.161	0.003
03:43:57	90.06	0.54 ± 0.02		-99.997	-1.5000	-0.0000	-2.6497 ± 0.00	-0.25 ± 0.05	-40	0			10.96	90.09	03:51:30	4.205	4.222	0.017
03:53:11	90.07	0.53 ± 0.02		-99.997	-1.5000	0.0000	-2.6498 ± 0.00	-0.62 ± 0.00	-50	0			11.10			4.205	4.251	0.046
04:02:30	90.09	0.54 ± 0.02		-99.997	-1.5000	0.0000	-2.6495 ± 0.45	-0.68 ± 0.21	-61	0			11.21			4.205	4.255	0.049
04:13:27	90.09	0.53 ± 0.03		-99.996	-1.5000	0.0000	-2.6499 ± 0.00	-0.99 ± 0.00	-60	0			11.33	90.09	04:21:00	4.205	4.258	0.054
05:11:16	25.05	0.58 ± 0.04		-100.003	-1.5000	0.0000	-2.7890 ± 0.00	-0.67 ± 0.00	-3	0			12.77			4.006	3.958	-0.056
05:40:47	25.01	0.58 ± 0.02		-100.003	-1.5000	0.0000	-2.7899 ± 0.00	-0.67 ± 0.00	-2	0			12.27			4.006	3.958	-0.056
05:50:00	25.00	0.58 ± 0.03		-100.004	-1.5000	0.0000	-2.7900 ± 0.01	-0.77 ± 0.00	-2	0			11.93			4.006	3.949	-0.057

SUMMARY OF ISFET PROBE # 697 TEST RESULTS 11/18/86
IN NBS KHP (185f) BUFFER

W, DC REFERENCE TO SOURCE GND																		
ANALYSIS																		
AC IN W, mV																		
SLOPE, mV/pH																		
FINAL VALUES																		
LINEAR																		
TIME	TEMP	MEAN	σ	I_d , μA	V_d , V	V_{ds} , V	MEAN, W	σ , mV	MEAN	σ	I_{ds} , nA	I_b , nA	2nd REF	TEMP	TIME	NBS pH	LINEAR pH	ERROR
12:04:14	25.03	0.02	± 0.01	-93.937	-1.3000	0.0000	-1.3662	± 0.02	0.31	± 0.01	0	0	18.32	25.03	12:11:54	4.006	3.968	-0.038
12:13:26	25.03	0.03	± 0.01	-93.937	-1.3000	0.0000	-1.3662	± 0.03	-0.13	± 0.02	0	0	18.34	25.03	12:21:06	4.006	3.963	-0.037
12:22:38	25.03	0.03	± 0.01	-93.938	-1.3000	0.0000	-1.3661	± 0.03	-0.09	± 0.02	0	0	18.34	25.03	12:30:18	4.006	3.970	-0.037
12:32:02	25.03	0.04	± 0.01	-93.937	-1.3000	0.0000	-1.3661	± 0.03	-0.16	± 0.02	0	0	18.35	25.02	12:39:42	4.006	3.970	-0.036
13:32:57	0.06	0.04	± 0.02	-93.938	-1.3000	0.0000	-1.3629	± 0.04	0.70	± 0.02	0	0	18.34			4.006	4.129	0.123
13:42:09	0.05	0.05	± 0.03	-93.937	-1.3000	0.0000	-1.3627	± 0.03	0.67	± 0.01	0	0	18.09			4.006	4.132	0.126
13:51:22	0.03	0.03	± 0.06	-93.937	-1.3000	0.0000	-1.3625	± 0.03	0.60	± 0.01	0	0	18.05			4.006	4.134	0.128
14:00:47	0.03	0.03	± 0.01	-93.937	-1.3000	0.0000	-1.3625	± 0.04	0.83	± 0.01	0	0	18.02	0.02	14:06:27	4.006	4.137	0.131
14:42:04	9.96	0.03	± 0.01	-100.003	-1.3000	0.0000	-1.3778	± 0.03	0.48	± 0.01	0	0	17.97	9.99	14:49:44	3.999	4.049	0.050
14:51:16	10.00	0.03	± 0.02	-100.003	-1.3000	0.0000	-1.3770	± 0.02	-0.11	± 0.01	0	0	17.93	10.00	14:58:56	3.999	4.048	0.049
15:00:29	10.00	0.04	± 0.01	-100.003	-1.3000	0.0000	-1.3771	± 0.03	-0.36	± 0.02	0	0	17.90			3.999	4.047	0.048
15:09:41	10.01	0.02	± 0.01	-100.003	-1.3000	0.0000	-1.3771	± 0.02	0.14	± 0.02	0	0	17.88	10.01	15:17:21	3.999	4.047	0.048
15:38:32	19.98	0.00	± 0.01	-100.002	-1.3000	0.0000	-1.3700	± 0.02	-0.50	± 0.01	0	0	18.24			4.001	3.991	-0.010
15:59:45	20.01	0.01	± 0.01	-100.002	-1.3000	0.0000	-1.3701	± 0.03	-0.69	± 0.02	0	0	18.22			4.001	3.989	-0.012
16:08:57	20.01	0.01	± 0.01	-100.002	-1.3000	0.0000	-1.3701	± 0.03	-0.57	± 0.01	0	0	18.19			4.001	3.989	-0.012
16:18:10	20.01	0.01	± 0.01	-100.003	-1.3000	0.0000	-1.3701	± 0.03	-0.23	± 0.02	0	0	18.18	20.01	16:25:49	4.001	3.989	-0.012
16:58:59	29.96	0.99	± 0.01	-100.002	-1.3000	0.0000	-1.3612	± 0.04	0.45	± 0.02	0	0	19.01	29.97	17:06:39	4.012	3.968	-0.044
17:08:12	29.98	0.00	± 0.02	-100.002	-1.3000	0.0000	-1.3611	± 0.04	0.50	± 0.02	0	0	19.02			4.012	3.969	-0.043
17:17:24	29.99	0.99	± 0.01	-100.003	-1.3000	0.0000	-1.3610	± 0.03	0.49	± 0.02	0	0	19.01	29.99	17:25:04	4.012	3.970	-0.042
17:26:36	29.99	0.99	± 0.01	-100.003	-1.3000	0.0000	-1.3610	± 0.03	0.00	± 0.02	0	0	18.99	29.99	17:34:16	4.012	3.971	-0.041
18:07:23	40.01	0.99	± 0.01	-100.003	-1.3000	0.0000	-1.3525	± 0.04	5.70	± 1.95	-1	0	19.91			4.031	3.944	-0.087
18:18:14	40.03	0.61	± 0.01	-100.003	-1.3000	0.0000	-1.3495	± 0.04	0.62	± 0.02	0	0	19.92			4.031	3.991	-0.040
18:27:27	40.04	0.62	± 0.02	-100.002	-1.3000	0.0000	-1.3512	± 0.26	-0.37	± 0.08	0	0	19.91			4.031	3.964	-0.068
18:36:39	40.04	5.05	±13.19	-100.002	-1.3000	0.0000	-1.3492	± 0.04	0.65	± 0.02	0	0	19.90	40.04	18:54:00	4.031	3.995	-0.036
19:35:26	49.91	0.99	± 0.02	-100.001	-1.3000	0.0000	-1.3372	± 0.05	1.83	± 0.02	-1	0	20.06			4.057	4.025	-0.031
19:44:39	49.89	0.99	± 0.01	-100.002	-1.3000	0.0000	-1.3371	± 0.06	1.32	± 0.02	-1	0	20.04			4.057	4.028	-0.029
19:53:52	49.90	0.56	± 0.01	-100.002	-1.3000	0.0000	-1.3369	± 0.05	0.91	± 0.02	-1	0	20.03			4.057	4.030	-0.027
20:03:04	49.90	0.99	± 0.01	-100.002	-1.3000	0.0000	-1.3368	± 0.04	0.35	± 0.02	-1	0	20.02	49.90	20:10:44	4.057	4.032	-0.025
20:39:56	59.91	0.98	± 0.02	-100.002	-1.3000	0.0000	-1.3238	± 0.06	1.49	± 0.02	-1	0	21.70			4.091	4.074	-0.017
20:49:09	59.95	0.71	± 0.06	-100.002	-1.3000	0.0000	-1.3237	± 0.62	0.23	± 0.37	-1	0	21.69			4.091	4.074	-0.017
21:00:05	59.96	0.57	± 0.02	-100.002	-1.3000	0.0000	-1.3235	± 0.03	0.49	± 0.02	-1	0	21.73	59.95	21:07:45	4.091	4.077	-0.013
21:09:18	59.98	0.56	± 0.01	-100.002	-1.3000	0.0000	-1.3234	± 0.03	0.31	± 0.02	-1	0	21.75	59.96	21:16:50	4.091	4.078	-0.013
21:42:09	69.93	0.54	± 0.02	-100.002	-1.3000	0.0000	-1.3099	± 0.05	1.83	± 0.02	-2	0	22.90			4.126	4.125	-0.001
21:51:22	70.00	0.56	± 0.01	-100.002	-1.3000	0.0000	-1.3098	± 0.04	0.16	± 0.02	-2	0	22.57	69.96	21:59:02	4.126	4.126	-0.000
22:01:25	70.00	0.55	± 0.01	-100.002	-1.3000	0.0000	-1.3097	± 0.03	0.31	± 0.02	-2	0	22.56	70.00	22:09:06	4.126	4.127	0.001
22:10:37	70.00	0.57	± 0.01	-100.002	-1.3000	0.0000	-1.3096	± 0.04	0.62	± 0.02	-2	0	22.35	70.00	22:18:19	4.126	4.127	0.001
22:47:34	79.98	0.55	± 0.02	-100.002	-1.3000	0.0000	-1.2959	± 0.04	-0.27	± 0.02	-4	0	23.10	79.94	23:03:21	4.164	4.176	0.012
23:04:54	79.96	0.55	± 0.01	-100.002	-1.3000	0.0000	-1.2958	± 0.04	0.44	± 0.02	-4	0	23.10	79.96	23:12:34	4.164	4.176	0.013
23:14:06	79.99	0.53	± 0.01	-100.002	-1.3000	0.0000	-1.2957	± 0.03	0.36	± 0.02	-4	0	23.23	80.00	23:21:46	4.164	4.177	0.013
23:25:54	80.02	0.56	± 0.02	-100.002	-1.3000	0.0000	-1.2957	± 0.04	-0.15	± 0.03	-4	0	23.20	80.02	23:33:34	4.164	4.177	0.013
23:58:40	89.99	0.55	± 0.01	-100.002	-1.3000	0.0000	-1.2814	± 0.03	0.11	± 0.02	-14	0	23.57	90.03	00:07:14	4.205	4.228	0.023
00:10:31	90.01	0.54	± 0.01	-100.003	-1.3000	0.0000	-1.2818	± 0.07	1.67	± 0.03	-10	0	23.61			4.205	4.223	0.018
00:19:43	90.04	0.54	± 0.02	-100.002	-1.3000	0.0000	-1.2817	± 0.04	-0.32	± 0.02	-9	0	23.71	90.04	00:27:23	4.205	4.223	0.018
00:29:48	90.04	0.54	± 0.01	-100.002	-1.3000	0.0000	-1.2818	± 0.05	-0.33	± 0.02	-8	0	23.69	90.04	00:37:27	4.205	4.222	0.017
01:46:59	25.03	0.61	± 0.01	-100.003	-1.3000	0.0000	-1.3641	± 0.04	-0.75	± 0.02	0	0	22.69			4.006	4.004	-0.002
01:56:30	25.01	0.59	± 0.01	-100.003	-1.3000	0.0000	-1.3641	± 0.03	-0.47	± 0.02	0	0	22.13	25.00	02:04:10	4.006	4.004	-0.002
02:05:43	25.00	0.60	± 0.01	-100.003	-1.3000	0.0000	-1.3642	± 0.03	-0.43	± 0.02	0	0	21.72	24.99	02:13:23	4.006	4.003	-0.003

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