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**THE DEVELOPMENT OF A HIGH TEMPERATURE pH ELECTRODE
FOR GEOTHERMAL FLUIDS**

FINAL REPORT - TASK 1

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April 1981

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DEVELOPMENT OF A HIGH TEMPERATURE pH ELECTRODE FOR GEOTHERMAL FLUIDS

L INTRODUCTION

The Department of Energy (DOE) through its Pacific Northwest Laboratory (PNL) operated for DOE by Battelle Memorial Institute desires to develop electrical and electrochemical probes that can measure various environmental characteristics of fluids under high temperature-high pressure conditions in geothermal wells and associated piping. An important probe of this type is one that measures pH.

As noted in the PNL RFP B-57829-A-E, there has been no serious application of pH measurements above 150°C. This stems from the fact that there have been no practical probes available that are capable of operation under the required conditions of temperature and pressure. Recently the General Electric Company has developed a new approach to such measurements in which an oxygen ion conducting ceramic membrane (e.g., stabilized zirconia) is being employed in a sensor somewhat analogous to the glass electrode⁽¹⁾. (Reference 1 is appended to this report.) The new sensor retains the specificity of the glass electrode, is equally insensitive to interference from redox active species, and possesses markedly superior resistance to attack by aqueous media at high temperatures.

Although work to date has established the feasibility of the concept, the new sensor has not been perfected in detail, nor has its behavior been demonstrated under a wide variety of conditions. In particular, work is required to demonstrate its capability under specific conditions of practical interest; e.g., its applicability to measurements on geothermal brines which is the focus of the present program. In this connection, there is only minimal concern that the sensor will suffer from exposure to the highly soluble components of such brines; rather, it is the scale-forming species that are more likely to cause problems by coating the electrode surface.

Also of concern, particularly for applications at pressures as high as 5000 psi, are the seals required for marrying the ceramic parts to the metallic pressure fittings. Even at lower temperatures the seals can be problematic. While difficulties have not been encountered during their initial use, leakage has sometimes been experienced during cycling between ambient conditions and 285°C at 1200 psi..

In addition, some improvement is required in the ceramic itself. At 285°C when the ceramic has relatively low electrical impedance, excellent response characteristics are

observed. At lower temperatures, particularly at 95° where considerable work has recently been done, very sluggish behavior is sometimes seen. While enough sensors have been operated at 95° to assure that the problem is not inherent to the oxide membranes, it is clear that work is required to improve the ceramic.

Finally, it is apparent that procedures and equipment will be required for periodic standardization and calibration of the measuring system consisting of the new sensor and a reference electrode. Even the long established glass electrode used for measurements at ambient temperature is not treated as an absolute instrument whose output potential can be equated theoretically with a specific pH. Careful workers invariably use calibration procedures to establish the response of such a sensor and its reference electrode on a routine basis. It is felt that a similar approach must be adopted with the new sensor and its reference electrode. In this connection, it has become clear that variations and drift in the output signal from the combined system are at least as likely to be associated with the reference electrode as with the new sensor.

It is the purpose of this report to summarize the status of the new sensor at the inception of the contract and to outline plans for the first year's investigation.

II. BACKGROUND

In this section we shall highlight the key findings of Reference 1 as they bear on the present application. In addition, we shall summarize previously unpublished information that sheds additional light on the new electrode and associated measuring equipment.

In principle, any oxygen ion conducting ceramic having suitable chemical stability and a transference number for the oxide ion very close to one should be suitable for the membrane. In practice, however, we have to date focused all of our attention on stabilized zirconias. This stems from the fact that suitable tubular forms are conveniently available as a result of previous applications in fuel cells and oxygen sensors.

Zirconias stabilized with yttria, calcia, and magnesia have been examined, but the performance of the yttria containing materials have been far superior to the others, possibly because of the former's generally higher specific conductivities. In the work discussed below, zirconias stabilized with 8.0 and 16.9 weight percent (w/o) yttria have been employed. Most of the tubes were obtained from Corning Glass Works, Ceramic Products Division, Solon, Ohio, the only commercial source presently known to us of tubes that are reasonably satisfactory for our purpose. More recently, we have started fabricating our own tubes in an effort to overcome some shortcomings in the Corning tubes, particularly for applications at temperatures below 285°C.

A. Initial Demonstration of Performance Characteristics

When work was first started on the new sensor, we employed saline solutions buffered to about pH 7.0 as the internal reference electrolyte in conjunction with a chlorided silver wire for the internal contact. This was done in emulation of normal practice with glass electrodes. By the proper choice of internal electrolyte in conjunction with the reference electrode, temperature effects tend to cancel nicely and give a fairly sharp isoelectric point over the limited temperature range normally encountered.

1. Response to pH. The first indication that the ceramic membranes could function as pH sensors was obtained from experiments performed at ambient temperature using zirconia tubes containing 0.1 m NaCl buffered to pH 7.0 with a phosphate buffer as the internal

electrolyte. An insulated, chlorided silver wire served as the internal electrode, and measurements were made against the reference arm of an Ingold combination electrode as the system was equilibrated with solutions of different pH including 0.1 m HCl, 0.1 m NaOH and phosphate buffers. From comparisons of the response to that of the Ingold glass electrode, it was found that the behavior of the zirconia membrane as a pH sensor was excellent. Because of its high impedance (10^{11} ohms at 25°C), however, the signals at ambient temperature were "noisy" and measurements had to be made with a high impedance electrometer (Keithly Model 602) in a faraday cage. Such noise was not a problem in later measurements at elevated temperatures because the membrane impedance falls rapidly as the temperature is raised⁽¹⁾.

For the measurements at 285°C (representative of nuclear reactor water), the structure shown in Figure 1 was employed. As at the lower temperature, a buffered saline inner electrolyte was used in conjunction with a chlorided silver wire. In this case, however, it was necessary to seal the open end of the zirconia tube to maintain the pressure. This was accomplished with a Teflon cap that was compressed within a Conax pressure fitting as shown in the figure. This unit was then mounted in the lid of a 1 liter 316 stainless steel or titanium autoclave that also held an insulated platinized-platinum wire and a reference electrode. The last consisted of a chlorided silver wire immersed in a 0.01 m KCl solution contained within an insulating tube; communication with the water in the autoclave was accomplished through a porous junction⁽²⁾.

The test system made provision for pumping water, acid, or base into the heated and pressurized autoclave. This permitted slow changes in pH by "titration" with dilute acid (0.0005 m H₂SO₄) or base (0.001 m NaOH) or rapid changes by the introduction of aliquots of more concentrated reagent.

Since a well-established comparison standard (like the commercial glass electrode used in the measurements at ambient temperature) is not available for 285°C, the response of the membrane was compared to that of an "oxygen electrode" formed by the platinized-platinum wire in contact with the reagents that were all saturated with air at ambient temperature before entering the autoclave. Under these conditions of constant oxygen concentration, the oxygen electrode can serve as a pH sensor because hydrogen ions are involved in the potential-determining reaction

Figure 1. Schematic diagram of sensor for use at elevated temperatures and pressures.

Although not rigorously established as a pH sensor, the response of the oxygen electrode to pH has been demonstrated at ambient temperature⁽³⁾, and it should behave more reversibly at the elevated temperature.

The data in Figure 2, obtained with a membrane stabilized with 16.9 w/o yttria, show excellent linear correlation between the membrane sensor and the oxygen electrode over a range of pH. Additional data illustrating the parallel responses of the membrane electrode and the oxygen electrode to relatively rapid changes of pH at 285° are shown in the inset to Figure 2. These transitions were accomplished by introducing aliquots of 0.1 m NaOH and 0.05 m H₂SO₄ into the feed stream to the autoclave. The rate of response in these experiments therefore reflects the transport rate of the added base or acid through the lines rather than the response time of the sensor itself.

The responses of membrane and oxygen electrodes were also compared with the theoretical value calculated for the transition between 0.0005 m H₂SO₄ and 0.001 m NaOH from available thermal data. Were sulfuric acid a typical "strong" acid at both temperatures, the pH of a 0.0005 m solution would be ~ 3.0 at both temperatures. Actually the second ionization constant falls from 1.2×10^{-2} at 25° to about 3.3×10^{-6} at 285°⁽⁴⁾. As a result, the second ionization is almost completely suppressed at elevated temperatures and the pH of a 0.0005 m solution at 285° is about 3.3. In the case of 0.001 m NaOH the pH at 285° is about 8.2 rather than 11 as at 25° because of the increased dissociation constant of water at the elevated temperature. From these calculated pH values and the theoretical RT/F slope of 110.8 mV/pH unit, a total response of 543 mv is expected for both the oxygen electrode and the membrane at 285°.

The comparisons were made for five different sensors in tests extending over a period of some six months. During this period, the same equipment was employed throughout, but the platinized-platinum and reference electrodes were replaced occasionally. A summary of data appear in Table I. In the first test employing relatively new equipment, the responses of the sensor and the oxygen electrode were 66.3 and 69.2 percent of theoretical, respectively. In successive tests, agreement with theory improved until leveling off at approximately 94.0 and 98.6 percent of theoretical for the sensor and oxygen electrode response. Throughout the period, the response of the membrane sensors was 95.3 percent of that of the oxygen electrode with a standard deviation of 3.8 percent, and no trend with time was evident.

Figure 2. Response of a sensor relative to that of the oxygen electrode at 285°C.

TABLE I

MEASURED POTENTIAL CHANGES FOR
 $0.0005 \text{ m H}_2\text{SO}_4 \rightleftharpoons 0.001 \text{ m NaOH}$
 AT 285°C

Oxygen Electrode Response			Membrane Response		
Run	ΔmV	% of Theor.	ΔmV	% of Theor.	% of Oxygen
ZR02-5	376	69.2	360	66.3	95.7
" -6	436	80.3	392	72.2	89.9
" -7	490	90.2	492	90.6	100.4
" -9	526	96.9	494	91.0	93.9
" -17	545	100.3	527	97.0	96.7
				Mean	95.3
				σ	3.8

It is believed that the initial large discrepancies from theory reflected a significant deviation in the actual pH changes from theory because of consumption of acid by corrosion of the walls of the relatively new equipment. During the course of several months of operation, the equipment passivated sufficiently that corrosion became minimal and excellent agreement between theory and experiment was finally obtained. The small residual differences at the end of the test period probably continue to reflect small losses of acid through corrosion, some shunting of the membrane path, and some variation in the junction potential of the reference electrode with the solution in the autoclave.

Additional data comparing the responses of sensors with that of the oxygen electrode at 285° are summarized in Table II. Included is information about the stabilizing agent and internal filling solution as well as the number of data points used in making the comparison and the period over which the data were taken. The overall average response was 94.7 percent of that of the oxygen electrode with a standard deviation of 4.4 percent. No significant difference is seen between the sensors stabilized with 8.0 w/o yttria and those with 16.9 w/o. The overall average of 94.7 is in good agreement with the value of 95.3 in Table I. The difference results from the fact that more data points were averaged for each run of Table II; only data obtained from the full transition between the acid and base were used for Table I.

2. Insensitivity to Redox Potential of the Environment. An additional aspect of the membrane electrode that has been examined is its stability in the presence of changes in the redox potential of the environment. This is one of the very real theoretical advantages of a membrane type pH sensor over sensors whose response involves electron transfer reactions. The effect is illustrated by the data in Figure 3. (Also included in this figure is the potential of the autoclave wall which was monitored against the reference electrode.)

It is seen that after changing from an air to a nitrogen purge of the incoming 0.0005 m H_2SO_4 , a slow downward drift in potential is evident for the platinum electrode and the wall of the autoclave. This is associated with simple dilution of the oxygen concentration in the water within the autoclave. After several hours, a more rapid drop occurred for both of these potentials. This is attributed to loss of the passive film on the autoclave with an associated increase in corrosion rate to liberate hydrogen. The platinum electrode and the autoclave wall then clearly show their sensitivity to this change in the redox environment. The zirconia membrane electrode, however, retained an essentially constant potential throughout the transients, i.e., it is insensitive to changes in the redox potential of the environment as expected from theory. The small transient in potential at the time of the depassivation is believed to be a response to a real change in pH.

TABLE IIRESPONSE OF YTTRIA STABILIZED ZIRCONIA MEMBRANES
RELATIVE TO THAT OF THE OXYGEN ELECTRODE AT 285°C

<u>Run No.</u>	<u>Sensor No.</u>	<u>Stabilizer Conc. Wt%</u>	<u>Internal Solution</u>	<u>Data Sets</u>	<u>Period of Time Days</u>	<u>Response % of O₂ Electrode</u>
ZRO2-5	Y-7	8.0	0.1m NaCl, pH 7.0	5	2.8	95.1
" -6	Y-9	8.0	" "	13	8.8	92.9
" -7	Y ₂ O ₃ -3	16.9	" "	12	5.7	96.4
" -9	Y ₂ O ₃ -4	16.9	0.01m NaCl, "	3	0.8	88.8
" -14	Y-15	8.0	" "	2	0.2	87.8
" -16	Y ₂ O ₃ -5	16.9	" "	8	4.0	96.2
" "	Y-15	8.0	" "	8	4.0	103.9
" -17	Y-17	8.0	" "	10	3.7	95.2
" -18	Y-18	8.0	0.001mHCl/0.009mKCl	2	1st Day	93.7
				3	2nd Day	93.3
				5	12th Day	98.2

Mean Response for 8.0% Stabilizer = 95.0; σ = 4.6

" " " 16.9% " = 93.8; σ = 4.3

Grand Mean = 94.7; σ = 4.4

Figure 3. Behavior of a sensor, the oxygen electrode, and the autoclave as the redox potential of the environment is changed at 285°C.

3. Other. A number of other properties of the sensors were investigated in the early tests. These included the resistivity of the ceramics, the feasibility of alternative internal junctions, and drift characteristics. All are discussed in Reference 1, but a fuller discussion of sensors with internal junctions other than buffered saline solutions will be found in the next section. New data on drift are also discussed below.

B. More Recent Work with Copper/Copper Oxide Internal Junctions

One additional aspect of the new sensor that was discussed briefly in the initial report⁽¹⁾ was the use of alternative, non-aqueous internal junctions consisting of metal/metal oxide mixes in contact with the inner wall of the ceramic and with a suitable lead wire to the terminal. Such junctions are not new, of course, and have been used successfully in the fabrication of the well-known stabilized zirconia high temperature oxygen sensors⁽⁵⁾. In addition to the use of metal/metal oxide couples, a mixture of two different oxides of a single metal can also be used in such direct junctions, for example, ferrous oxide-magnetite or magnetite-hematite combinations. In the case of the copper/copper oxide junction the reference potential is established by the following equilibrium:

In the original report⁽¹⁾ the performance of sensors containing copper/copper oxide and mercury/mercury oxide internal junctions were discussed. Data obtained at 95° with an Ingold glass electrode serving as the comparison standard are shown in Figure 4. Both internal junctions resulted in sensors having linear responses that were close to those of the glass electrode. At 285° sensors with the Cu/Cu₂O internal junction again gave linear responses against the oxygen electrode as standard.

These results indicate that either the aqueous or non-aqueous type of internal junction should be satisfactory on the basis of pH response. A final choice would therefore seem dependent upon such considerations as long term stability, temperature coefficient, and other parameters. Another factor of considerable importance is the fact that metal-oxide mixtures do not wet the ceramic. The working region of the sensor can therefore be well defined by the location of the internal fill and it can be confined to a region well removed from the seal to the pressure vessel where temperature gradients and zones of stagnation would be encountered. For these reasons it was felt that additional work should be undertaken with such internals.

Figure 4.

Response of sensors with Cu/Cu₂O and Hg/HgO internal junctions relative to that of a glass electrode at 95°C.

Because of the consistently excellent performance of the copper/copper oxide internal junction no other couples have been examined for application at high temperatures. (Indeed this also appears to be an excellent fill for lower temperature applications as well. However, for exploratory work at 95° or thereabouts, we have found the simple addition of mercury to be eminently useful; cf. next section. Because of its physiological activity, however, we do not feel there is any advantage to be gained from the use of mercury in practical sensors.) To date we have fabricated about 18 sensors with copper/copper oxide internal junctions. Most of these sensors were tested briefly and then diverted to other uses. Two, however, were employed in tests of long duration--about 40 days. During this period they retained their excellent response to pH changes and their rest potentials remained stable. This is shown by the data in Figure 5 where the rest potential of two oxygen electrodes vs. reference, two zirconia sensors vs. reference and the zirconia sensors vs. the oxygen electrodes are shown as a function of time.

These data for the sensing electrodes vs. the reference are more stable than those obtained earlier⁽¹⁾. This seems to reflect the use of a reference electrode that contained only silver chloride (i.e., no KCl). This approach was taken in view of the indications that many of the earlier drift problems were caused by loss of KCl from the reference electrodes⁽¹⁾. More will be said about this in a section that follows. In spite of the improved stability of the potentials vs. the modified reference electrodes, those between the zirconia and oxygen electrodes are even more stable. In view of these results we now feel that the copper/copper oxide internal junction is the junction of choice.

Additional data indicating the stability and capability of the zirconia sensor with an internal copper/copper oxide junction and the reference electrode containing only silver chloride are summarized in Table III. These data were obtained over a period of 37 days during which time the system was at 285° continuously. For most of the period pure water was flowed through the autoclave containing the electrodes, but periodically acid and basic transients (to 0.0005 m sulfuric acid and 0.001 m sodium hydroxide) were introduced.

In the table we have treated the data as though the transients were introduced as calibration points so that the pH of the water could be determined. Four different ways of using the "calibration points" were employed as explained in the footnotes to the table. As can be seen, quite reliable values for the pH of the water were thereby obtained. As is to be expected, the "two-point" calibration of Method I yielded the most reliable results.

Figure 5. Stability of various couples over a forty-day test period.

TABLE III

EFFECT OF CALIBRATION PROCEDURE ON THE MEASURED pH OF WATER AT 285°C

(From data of Run ZR02-19)

Day of Run	Potential vs. Ref		Slope (from data for acid and base)		Measured pH of water (Theoretical= 5.67)			
	medium	mv	mv/pH unit	% of theory	Method I	Method II	Method III	Method IV
5	water acid base	-504 -252 -761	103.9	93.8	5.74(.07)*	5.59(-.08)*	5.74(.07)*	5.59(-.08)*
8	water acid base	-500 -254 -761	103.5	93.4	5.70(.03)	5.54(-.13)	5.71(.04)	5.56(-.11)
12	water	-489	-	-	-	-	5.60(-.07)	5.46(-.21)
13	water acid base	-490 -241 -757	105.3	95.0	5.68(.01)	5.57(-.10)	5.61(-.06)	5.47(-.20)
16	water	-488	-	-	-	-	5.59(-.08)	5.45(-.22)
19	water acid base	-484 -235 -756	106.3	95.9	5.66(-.01)	5.57(-.10)	5.55(-.12)	5.41(-.26)
22	water	-480	-	-	-	-	5.51(-.16)	5.38(-.29)
28	water acid base	-480 -233 -758	107.1	96.7	5.63(-.04)	5.55(-.12)	5.51(-.16)	5.38(-.29)
37	water acid	-504 -232	-	-	-	5.77(.10)	5.75(.08)	5.59(-.08)
Avg. deviation from theoretical					0.012	-0.072	-0.051	-0.193
σ					0.041	.086	.093	.084

Method I: Acid point used to set scale and slope recalculated each day from data for acid and base.

Method II: Acid point used to set scale but slope assumed constant at 110.8 mv/pH unit (i.e., theoretical).

Method III: Data from first day's calibration used throughout to set scale and slope.

Method IV: Acid point from first day used throughout to set scale and slope assumed constant at 110.8 mv/pH.

* Data in parentheses indicate deviation from theoretical value.

C. Experience at 95°C

Because our original interest in the new sensor stemmed from our desire to measure the pH of water in nuclear reactor applications our attention has focused on performance at 285°C with a minimum amount of attention being given to other temperatures. Recently we have attempted comparisons with commercial glass electrodes in the temperature range of overlapping capability. For this purpose 95°C has been a convenient temperature because it permits operation at ambient pressure without interference from boiling even when dilute solutions are used.

In this work we have employed Ingold electrodes throughout. Included have been their General Purpose (GP) glass, their High Alkalinity (HA) glass and their high temperature silver/silver chloride reference electrodes. The test vessel has been a thermostated Teflon pot fitted with a reflux condenser and a magnetic stirrer. Provision has been made for accomplishing titrations with motor driven syringes, and direct additions of aliquots of acid and base can be made. A photograph of the test system appears in Figure 6. In most cases the transitions have been made between 0.1 m HCl and 0.1 m NaOH in the presence or absence of 1 m sodium chloride.

Data comparing the response of a zirconia sensor with that of a GP glass electrode in the presence of 1 m sodium chloride are shown in Figure 7. These were obtained by alternately adding aliquots of base and acid to a 1 m sodium chloride solution that originally contained 0.1 m hydrochloric acid. The influence of the well-known "sodium error" on the glass electrode is clearly indicated both by the slow drift following the initial introduction of the base and the subsequent variations in later responses. The behavior of the zirconia sensor, on the other hand, is very reproducible. Response times are also excellent following the rapid introduction of aliquots of the reagents. A similar favorable comparison results when the two types of electrode are compared on the basis of titration curves obtained with a motor driven syringe over a period of about 15 minutes as shown in Figure 8. (The two curves have been normalized in the acidic region because of the known influence of the alkaline error.)

A direct comparison of the voltage responses of a zirconia sensor and a glass electrode (this time the HA type) is shown in Figure 9. Here increments of 5 m sodium hydroxide were added at approximately five minute intervals to a solution that was initially about 0.06 m in hydrochloric acid. Upon reaching the alkaline side--approximately 0.06 m excess base--

Figure 6. System for testing sensors at 95°C.

Figure 7. Comparison of the responses of a zirconia sensor and a glass electrode at 95°C.

Figure 8. Titration curves obtained with a zirconia sensor and a glass electrode at 95°C.

Figure 9. Response of a sensor relative to that of a glass electrode at 95°C.

increments of acid were added to retrace the curve. It is seen that the correlation is excellent over the entire range of pH. This reflects the fact that the HA type glass electrode is less subject to the alkaline error than the GP type.

Further data indicating that long life can be obtained with a zirconia electrode at 95° are summarized in Table IV. These too were obtained by adding aliquots of base and acid but in increments of sufficient size to swing from acidic to basic pH and vice versa. Between increments the system was allowed to digest for several days in the presence of either acid or base. Conditions are indicated in the table. Although an HA type electrode was employed in this test it is seen that over a period of time, as sodium accumulated in the solution, a slight loss of response was observed in contrast to the behavior of the zirconia electrode. Upon replacing the solution with fresh, the full response of the glass electrode was again obtained. This is seen from the last set of data in the table. The transient responses of the glass electrode and the zirconia sensor on the first and thirtieth days are compared in Figure 10. Here it is seen that the time constant of the zirconia electrode, while quite adequate, for most applications is somewhat inferior to that of the HA glass electrode. It is not felt, however, that this is an inherent limitation of the electrode.

A word is in order concerning the pronounced drift in the rest potential of the sensor over the thirty day period of the test. This resulted from the fact that only mercury was added to the tube, a pronounced deviation from the procedure used with the copper/copper oxide. As a result the internal junction was very poorly poised. Nevertheless, the amount of drift that occurred during the time required to determine the response of the sensor to transients was negligible and caused no difficulty in evaluating this important behavior of the unit. A brief investigation of means of stabilizing the mercury internal junction indicated that this can be accomplished by anodically forming mercuric oxide at the mercury-zirconia interface, a time consuming procedure because of the very low currents that can be employed. Simple addition of mercuric oxide as well as mercury to the tube has been less effective.

While these data show quite clearly that the response of the zirconia type sensor can compare quite favorably with glass electrodes even at 95° , such excellent behavior was not universally obtained. This will be discussed further in a later section devoted to a discussion of the need for improved ceramics. Sensor SP-4 is representative of such an improved ceramic that was prepared in this laboratory.

TABLE IV

Comparison of Sensor SP-4 with a Glass Electrode (HA Type)
over a Thirty Day Period of Continuous Operation at 95°C

(Run AP-25)

Day	Standby Conditions		Test Cycles	Electrode	E vs. Reference (mV) on:					Response (mV) to pH Changes			
	Solution	Time			A*	B	A	B	A	A→B	B→A	A→B	B→A
1	0.05 <u>m</u> HCl	~1 hr	A→B→A	Glass SP-4	368 293	-310 -383	362 298			678 676	672 681		
2	"	over- night	A→B→A	Glass SP-4	368 415	-304 -265	365 418			672 680	669 683		
3	"	over- night	A→B→A	Glass SP-4	370 466	-300 -211	365 463			670 677	665 674		
7	"	4 days	A→B→A→B	Glass SP-4	372 473	-298 -201	367 469	-292 -203		670 674	665 670	659 672	
10	0.1 <u>m</u> NaOH	3 days	B→A→B→A	Glass SP-4		-264 -210	375 466	-275 -207	373 464		639 676	650 673	648 671
13	0.005 <u>m</u> HCl	3 days	A→B→A→B	Glass SP-4	385 490	-277 -181	387 488	-277 -181		662 671	664 669	664 669	
15	0.1 <u>m</u> NaOH	2 days	B→A→B→A	Glass SP-4		-249 -173	425 503	-245 -168	420 503		674 676	670 671	665 671
17	0.05 <u>m</u> HCl	2 days	A→B→A→B	Glass SP-4	390 522	-263 -150	392 521	-267 -149		653 672	655 671	659 670	
22	0.1 <u>m</u> NaOH	5 days	B→A→B→A	Glass SP-4		-234 -136	441 540	-231 -132	438 541		675 676	672 672	669 673
30	0.05 <u>m</u> HCl	8 days	A→B→A	Glass SP-4	407 616	-220 -56	408 611			627 672	628 667		
At this point system was rinsed and solution was replaced with fresh 0.05 <u>m</u> HCl; measurements were continued after temperature equilibrium had been re-established.													
30	0.05 <u>m</u> HCl	~3 hr	A B A	Glass SP-4	393 611	-290 -70	393 607			683 681	683 677		

*A = acid
B = base

Figure 10. Comparison of responses of a zirconia sensor and a glass electrode to rapid changes in pH at 95°C.

D. Drift

A word is in order about drift. In the work to date it has arisen from two principal sources: (1) changes in the electrolyte concentration within the reference electrodes, and (2) changes in the internal junction within the sensor especially when poorly buffered aqueous electrolytes such as 0.001 m HCl-0.009 m KCl are used.

That a significant drift has been associated with the reference electrodes was illustrated by the data in Figure 10 of Reference 1. At the time it was indicated that much of this drift resulted from loss of KCl from the reference electrode (an Indig type reference electrode⁽²⁾ was employed). This prompted the use of water containing only an excess of silver chloride as the reference in runs ZR02-19 and 20. This resulted in a marked improvement in stability of potentials for periods of operation as long as forty days.

Even under these conditions, however, the potential of the zirconia sensor with a copper/copper oxide internal junction vs. the oxygen electrode at a fixed pH was more stable than the potential of either of these electrodes vs. the references, cf. Figure 5. Because of their stability, it is useful to employ either the zirconia electrode or the oxygen electrode at a fixed pH and dissolved oxygen concentration as a "reference electrode" in comparing the various reference electrodes among themselves. This is done in Figure 11 where the oxygen electrode has been employed as the common reference.

Under these conditions it is quite clear that loss of KCl from the 0.01 and 0.1 m KCl Indig electrodes causes their potentials to drift towards that of the reference initially filled with only water and silver chloride as a limit. For operation at 285° the latter might therefore be considered as a fairly useful reference. It is likely, however, that because of the large temperature coefficient for the solubility of silver chloride that a similar large temperature coefficient would reflect in the reference potential. Also, at lower temperatures such a reference would probably have an excessively high resistance because of the low solubility of silver chloride.

Also shown in Figure 11 is one example of drift that we experienced with our version of the Danielson electrode⁽⁶⁾. While lesser in magnitude than that of most of our Indig electrodes, it is still appreciable when used in pure water and relatively dilute acids and bases.

Figure 11. Drift of reference electrodes of various types and with various filling solutions.

It is possible that the drift of both types of reference electrode could be reduced by careful control of the porosity of the plug used to form the junction. This is a parameter that we shall heed in future work. In any event, however, it seems clear that extreme care will be called for to avoid difficulties from this drift phenomenon, and the need for calibration procedures is underscored.

E. The Need for Improved Ceramics

In Reference 1 it has been indicated that ceramics with higher specific conductivities than those presently available would be desirable particularly for sensors that were to be employed at temperatures lower than 95° . More recently we have discovered another shortcoming of presently available ceramics; many of those employed to date have shown a tendency to develop long time constants for their response to pH changes at low temperatures. Most of the data bearing on this phenomenon have been obtained at 95° .

The first hint of this behavior was obtained from Sensor Y-14 (made with a Corning tube) used to obtain the data in Figures 7 and 8. After several days of use at 95° the sensor no longer developed the full potential response in the time required to obtain a titration curve such as that shown in Figure 8. However, if at the end of the titration sufficient time were allowed the full potential shift would eventually develop. This is illustrated in Figure 12. Also shown in this figure are titration curves and subsequent potential changes for three other sensors. All of them were much worse than Y-14. Unfortunately it has since been found that they rather than Y-14 seem to be more representative of typical Corning ceramics.

After examination of a number of the tubes involved it has been concluded that this behavior is caused by the presence of a concentration of open pores in the outer surface of the ceramic. It is believed that many of these pores consist of small openings communicating with relatively large voids so that they provide a long time-constant network for diffusion of acid and base into and out of the voids.

Thus the pH of the outer solution can change rapidly to cause a partial voltage response, but the electrolyte within such pores changes pH much more slowly, mostly by diffusion. Since the resistance of the ceramic is very high at 95° , the aqueous phase in the pores shunts the ceramic and the pores can dominate the overall behavior. At higher temperatures, when the resistance of the ceramic is much lower, the pore factor becomes much less significant.

Figure 12. Titration curves for several zirconia sensors showing sluggish response at 95°C .

On the basis of this hypothesis we have been directing attention to methods of developing denser ceramics having more nearly perfect outer surfaces. Progress is being made in this direction as witnessed by the excellent behavior of Sensor SP-4 discussed in an earlier section.

This development work is continuing in our laboratory and we are also searching for new commercial sources of the required ceramic.

III. SENSOR DESIGN

In considering the design of a satisfactory sensor, attention must be focused on several key items:

- o Selection of ceramic/surface finish
- o Selection of internal junction
- o Design of mount to system
- o Design of seals

These items will be discussed individually as they bear on the structure selected for the present application. To facilitate discussion, Figure 13 shows the structural details of the preferred design which differs somewhat from that of the sensor shown in Figure 1.

A. Ceramic

As noted in Section II, the Corning ceramic has been eminently suitable for measurements in the vicinity of 285°C but has been less satisfactory at lower temperatures because of long response times. The ultimate need for an improved ceramic is therefore quite evident, but we feel that the Corning material will be satisfactory for the first year's program aimed at the general demonstration of the applicability of the new sensor to measurements on geothermal brines. Because no other routine sources of satisfactory ceramic are presently known, the Corning material must be considered the ceramic of choice at the inception of the program.

The desired ceramic is obtained from the Corning Glass Works, Ceramic Products Division, Solon, Ohio. It is identified as Stabilized Composition 1372, 1/4" OD x 6" long x 1/32" wall, impervious, slip cast zirconia tube closed at one end (rounded closure); yttria stabilized (8.0 per cent). All tubes are helium leak tested by Corning. While variations in OD and wall thickness have been observed, they have caused no problems other than that the plastic components of seals require individual fitting.

More detailed specifications on the ceramics have not yet been developed, but evidence to date indicates that specifications will eventually be required with regard to acceptable density, surface roughness, deviation from roundness, freedom from surface defects (especially open

Figure 13. Schematic diagram of preferred sensor for use with geothermal brines.

pores) and microstructure. It has been observed, for example, that ceramics showing long life at 285° fracture transgranularly. Those that fracture intergranularly tend to be attacked at grain boundaries during use and have a short life.

B. Internal Reference Junction

On the basis of our work to date we have selected the dry copper/cuprous oxide mixture as our preferred internal junction for several reasons: 1) we have found it to be readily prepared by simple mixing of the powders and packing into the tube; 2) when prepared in this fashion it has been found to be extremely stable and reproducible; 3) in contrast to aqueous internals it permits ready designation of the active region of the sensor because it does not wet the wall with a conducting film; and 4) in the absence of an internal aqueous phase seal fabrication is simplified.

For the junction we shall employ a 1:1 (by weight) mixture of finely divided copper and cuprous oxide (Fisher Copper Metal-Electrolytic Dust, purified; Baker Cuprous Oxide Powder, Analyzed Reagent) to a depth of two inches. A 30 mil copper wire will be employed as the contact and lead from the sensor.

C. Mounting and Sealing

All of the demonstration units will be assembled upon the basic Conax Type EG-125 Gland. These glands terminate in a 1/4" male NPT for mounting in a flange or wall. For sensors to be operated for extended periods of time in the test equipment at 285° and pressures of 1200 psig or higher, titanium glands will be employed. For the field exposures standard stainless steel (Type 316) or titanium glands will be used depending upon the conditions anticipated at the test site.

In mounting the ceramic in the glands it has been necessary to modify the standard Conax seals. In our early work a simple Teflon cap was used over the ceramic tube as shown in Figure 1. Although satisfactory for initial demonstration work, this seal was not suitable for sensors that were to be cycled between high and low temperatures. A modified seal was therefore designed.

The seal of choice at present is shown in Figure 13. In addition to the gland material, four materials are employed in fabricating this seal: Teflon, Vespel, silver and alumina. (Vespel, a polyimide supplied by duPont, is thermally stable well above 285° and has proven very satisfactory for sensors with the dry type internal junction. The polymer is readily hydrolyzed and rapidly decomposes when employed with an aqueous internal junction.)

Compression of the Teflon actually makes the seal while the other elements serve to transmit the pressure and prevent the Teflon from creeping into voids and gaps when under pressure. Vespel serves this purpose well as long as it is not exposed to moisture; hence the silver ring at the interface with the test fluid. (Gold or another moderately malleable metal would also serve.) The alumina insert serves as the final backup to the plastic parts. In use the seal is normally tightened with a torque wrench to about 50 in lbs at the start. After cooling from the first cycle to 285° retorquing is required to maintain the pressure since some compaction of the Teflon occurs at the elevated temperature. It is anticipated that alternative sealants and improved seal design will eliminate this need for retightening.

A slightly modified seal has been employed in a few cases. This is shown in Figure 14. In this design a portion of the Vespel cap of Figure 13 has been replaced with stainless steel. This was done to preserve the integrity of the seal in the event that the sensor tube ruptured and allowed test fluid to reach the cap on the ceramic tube. This arrangement has been developed for installation in relatively inaccessible locations.

As noted earlier, the seal of Figure 13 has proven satisfactory in our work to date although some difficulties with breakage have been experienced just beyond the seal itself. This is presumably caused by a concentration of stresses in the region. Although not considered a major problem for sensors to be operated at pressures up to 1200 psig, it is anticipated that additional problems will be encountered when operation at 5000 psig is attempted. For this pressure range the seal will probably require major redesign.

D. Summary

On the basis of the above the components of the sensor at the inception of the program are summarized in Table V. While most of the parts are available commercially, because of irregularities in the ceramic and metal parts some of the items involved in the seals require individual fabrication for proper fit. These are marked with an asterisk in the table.

Figure 14. Alternative seal design.

TABLE V

Components of pH Sensor

Ceramic Element:	Corning Type 1372 Stabilized Zirconia Yttria stabilized (8.0 wt. %) 1/4" OD x 6" long x 1/32" wall Rounded closure at one end (Corning Glass Works, Ceramic Products Division, Solon, Ohio)
Metallic Gland & Cap:	Conax Type EG-125 Gland Titanium or Type 316 S.S. (Conax Corp., 2300 Walden Ave., Buffalo, New York 14225)
Internal Junction and Lead Wire:	Fisher Copper Metal-Electrolytic Dust, Purified (Fisher Chemical Co.) Baker Cuprous Oxide Powder, Analyzed Reagent (Baker Chemical Co.) Copper Wire, 30 mil Glass wool packing
Seal:	Silver ring, 30 mil wire* Teflon ring* Vespel cap* Teflon disk* Vespel disk* Alumina insulator (Conax Corp.) Stainless steel ring (Conax Corp.)

* These parts must be machined for fit. Both the Teflon and the Vespel (Type SP-1) are available from duPont in the form of 3/4" diameter rod.

IV. TEST EQUIPMENT

A. Reference Electrode

In order to make electrical measurements a reference electrode is required as a partner for the sensor. A Danielson type reference⁽⁶⁾ will be employed for this purpose. As noted above we have already had experience with this type of reference in connection with some of our other work. As with the Indig type reference⁽²⁾, we have not found it drift-free when used with high purity water and dilute acids and bases, but we have been generally satisfied with its performance. Our structure is essentially that described by Danielson, but we have eliminated his zirconia wick without suffering difficulties at high pressures. Bubbles do form, however, during depressurization and cooling.

While we have no specific plans for modifying this electrode, we do anticipate evolutionary changes as we learn more about it. In particular, we shall monitor the effect of the porosity of the ceramic diffusion junction on drift.

Initially we plan to use 0.1 m KCl as the filling solution, but we shall probably also employ alternative fillings as well. Normally we plan to employ two of the reference electrodes in each test--probably in many cases each with a different filling solution.

B. Test System

A diagram of the test system is shown in Figure 15. In general it parallels that used in Reference 1. Provision will be made for pumping water, acid, base and simulated brines containing carbonate buffers and sulfides into the heated and pressurized titanium autoclave which has a capacity of 1 liter. It will also be possible to introduce aliquots of more concentrated acid or base to bring about more rapid changes in pH. The pump will be a Lapp Pulsafeeder Model LS-20 with a titanium head. All fittings and other parts of the pressurized section will also be made of titanium.

All entering streams will be purged with nitrogen to reduce the oxygen concentrations to low levels. To control the pH of the brine solutions before they enter the autoclave they will be contacted with carbon dioxide-nitrogen mixtures in a packed column following a procedure described by D. Macdonald⁽⁷⁾. The pH and redox potential of the solution emerging from the

Figure 15. System for evaluating sensors with simulated geothermal brines.

column will be monitored with a commercial glass electrode and a platinized platinum flag, both referred to a common reference electrode. Similar measurements will be made at ambient temperature on the stream emerging from the autoclave. In this way irreversible chemical changes occurring during passage through the autoclave should be detectable. Such changes may be greater than desired because of corrosion; in the absence of dissolved oxygen the autoclave will probably depassivate. Provision will also be made for sampling the streams and for checking the flowrate.

Rather than incorporate low concentrations of sulfide in the master feed solutions with concurrent danger of loss during purging, we plan to inject a more concentrated solution of sodium sulfide at a slow rate into the feed stream just prior to entry into the pump.

C. Instrumentation

Temperature of the autoclave will be controlled with a Leeds and Northrup Electromax III proportional controller. High temperature pH and potential measurements will be made with a Keithly Type 616 electrometer multiplexed with an Orion 855 Electronic Switch. The pH sensor, a platinized platinum redox probe, the autoclave, and a second reference electrode will be measured against the primary reference electrode. In addition the pH sensor will be measured against the platinum redox probe. The lower temperature measurements, pH and redox potential of the inlet and outlet streams to the autoclave, will be made with an Orion Model 801 Digital pH meter, again multiplexed with an Orion Model 855 Electronic Switch. Ingold glass combination electrodes will be used. All potentials and the temperature will be recorded on a Linear Instruments Corp. three channel recorder.

V. PROTOCOLS

A. Testing of Lead Units

All sensors will be tested at 285° after assembly. This will serve the dual purpose of thermally setting the Teflon seals and confirming the functionality of the sensors.

The test itself will consist of measuring the response to a change from one millimolal acid to one millimolal base and a determination of the resistance of the sensor at 285°. This information will provide a basis for comparison with a similar set of measurements following field exposure or exposure in the laboratory to brines.

B. Testing of Sensors on Synthetic Brines--1200 PSIG

These tests are designed to determine the stability of the sensors under a variety of conditions. It is planned that each test will extend over a period of about ten days and will involve the steps indicated in Table VI.

In each case a reference performance will be obtained during the first two days by determining the response to a change from 1 millimolal HCl to 1 millimolal NaOH. Then the sensor will be aged for about a week in a selected saline solution covering the range of conditions indicated in Table VII; detailed compositions of the solutions to be employed are given in Table VIII. During this period potentials will be monitored to check for drift or degradation. On the ninth day the carbon dioxide level of the solution will be changed to induce a pH change and the response of the sensor will be monitored and compared with the best estimate that can be made theoretically for the high ionic strength solutions involved. Finally, after an overnight flush of the system with water, the response of the sensor to a transition from one millimolal acid to one millimolal base will be redetermined and compared with the starting value. Barring excessive attack on the system--particularly the autoclave which will probably depassivate in the absence of oxygen in the water--the response to the change from dilute acid to base should be readily calculable.

If the sensor has clearly withstood its exposure to the initial test conditions, the same unit will immediately be tested under the next set of conditions. Otherwise a new sensor will be substituted.

TABLE VI

A TYPICAL TEST

Day	1	Start up on water
	2	Water $\rightarrow$ 0.001 <u>m</u> HCl $\rightarrow$ 0.001 <u>m</u> NaOH $\rightarrow$ carbonate/saline/(H ₂ S)
	3	Carbonate/saline/(H ₂ S)
	4	"
	5	"
	6	"
	7	"
	8	"
	9	" $\rightarrow$ change CO ₂ level $\rightarrow$ water
	10	Water $\rightarrow$ 0.001 <u>m</u> HCl $\rightarrow$ 0.001 <u>m</u> NaOH; off

TABLE VII

Range of Conditions to be Used in Aging Tests
(Tests to be run in numbered sequence)

		Hi Saline			Lo Saline			
		No H ₂ S	With H ₂ S		With H ₂ S			
		Hi pH ^(a)	Lo pH ^(b)	Hi pH ^(c)	Int pH ^(d)	Lo pH ^(e)	Hi pH ^(f)	Lo pH ^(g)
150 ^o C				3				
225 ^o				4				
285 ^o	1	2	5	7*	6		8	9

- a) ~ 0.1 m total carbonate/low CO₂; Solution E of Table VIII
- b) ~ 0.034 m " " /high CO₂; " C " " "
- c) ~ 0.1 m " " /low CO₂; " F " " "
- d) ~ 0.1 m " " /high CO₂; " B " " "
- e) ~ 0.034 m " " /high CO₂; " D " " "
- f) ~ 0.1 m " " /low CO₂; " I " " "
- g) ~ 0.034 m " " /high CO₂; " J " " "

*Only if thought necessary at the time of testing.

TABLE VIII

Compositions of Synthetic Brines to be Used in Tests

	NaCl conc.		NaHCO ₃ conc.		CO ₂ conc.		H ₂ S conc. (total)		Approx. pH at 25°C
	molar	ppm	molar	ppm (as CO ₂)	molar	ppm	molar	ppm	
A	3.9	200,000	0.1	3800	0.034	1300	0	0	6.8
B	3.9	200,000	0.1	3800	0.034	1300	2.9×10^{-4}	10	6.8
C	3.9	200,000	.001	38	0.034	1300	0	0	5.0
D	3.9	200,000	.001	38	0.034	1300	2.9×10^{-4}	10	5.0
E	3.9	200,000	0.1	3800	0.00034	13	0	0	9.0
F	3.9	200,000	0.1	3800	0.00034	13	2.9×10^{-4}	10	9.0
G	3.9	200,000	.001	38	0.00034	13	0	0	7.0
H	3.9	200,000	.001	38	0.00034	13	2.9×10^{-4}	10	7.0
I	0.35	2,000	0.1	4300	0.00034	15	2.9×10^{-4}	10	9.0
J	0.35	2,000	.001	43	0.034	1500	2.9×10^{-4}	10	5.0
K	0.35	2,000	0.1	4300	0.034	1500	2.9×10^{-4}	10	6.8
L	0.35	2,000	.001	43	0.00034	15	2.9×10^{-4}	10	7.0

C. Field Exposure of Sensors

In performing field exposures, arrangements will be made by Battelle for tests at two (or at most three) field sites selected for their known tendency to deposit scale. The Contractor will provide sensors for field exposures (not involving electrochemical field tests) from among the lead units. The sensors will be inserted by field-site personnel under Battelle direction into unflushed fluid in the bore-hole and into flashed fluid in the steam separator or the return line in locations chosen in collaboration with the Contractor Principal Investigator. Initial exposures will be for one or two weeks. Depending on initial results, a second set of tests will be carried out for longer or shorter periods of time in order to obtain an estimate of sensor life. The sensors will be returned to the Contractor who will determine the electrochemical performance after exposure. Surface scales and deposits will also be identified and weight changes determined. If necessary, descaling and reactivation procedures will be conducted by the Contractor.

D. Demonstration of Sensors at 5000 PSIG

Tests under these conditions will be performed using an apparatus being loaned to us by Battelle Northwest. The major goal of the work at this pressure will be to demonstrate that the sensors are capable of operation at such extreme pressures. This will be accomplished by simple response tests for changes from acidic to alkaline pH. It is anticipated that the major hurdle will be the design of a seal capable of operation at elevated temperatures at these pressures. The ceramic itself has already been found capable of withstanding pressures of 10,000 psig compression at ambient temperature.

E. Determination of Operating Parameters of Sensors

In this phase of the work more detailed examination of the response of the sensors will be undertaken than under Section VB. Such response data will be obtained over smaller increments of pH change using hydrochloric acid and sodium hydroxide in the presence and absence of large excesses of sodium chloride. Interpretation of such data will entail a review of the calculation of pH at the high ionic strengths involved. We shall also attempt correlations within the carbonate buffer system, and we shall obtain data pertaining to temperature effects on response and response rate. This work will again employ the test system of Figure 15.

F. Calibration System

As noted above, the need for a simple calibration system for the sensors is self-evident. Although it will complicate their use, reliable data are unattainable without it. For the most precise measurements calibration should be done with at least two standards. For less precision, one will do.

In either case a straightforward method of introducing samples and standards to the sensor is required. A schematic of our planned approach for a prototype unit is shown in Figure 16. It is visualized that the volume of the chamber will be small so that a minimum of time will be required to reach a steady state. The unit will be attached to the main test line with suitable valving to permit the passage of the test fluid or the standard. For the data to be meaningful the temperature of the unit will be maintained at that of the main stream. This will be controlled by a differential temperature measuring technique.

Two heat exchangers are shown to condition the incoming streams to the sensor. One, connected directly to the sensor housing, would aid in temperature stabilization during normal operation. The other, used only with the calibrating solution, would precondition the cold solution before it reached the measuring system.

The usefulness of sulfate, phosphate and borate buffers as standards will be examined. The pH values for such solutions have already been established in the literature^(4,8,9). It will remain to be shown that liquid junctions and other spurious effects do not prevent the obtainment of reasonable estimates for the pH of synthetic brine solutions containing strong acids and bases as well as carbonate buffers. Clearly, within the confines of the present contract we can demonstrate only the principle of such procedures. More detailed studies beyond the present program will be required for rigorous demonstrations.

Figure 16. Sampling/calibration system.

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VII. APPENDIX

TECHNICAL INFORMATION SERIES

AUTHOR Niedrach LW	SUBJECT pH sensors	NO. 79CRD265
		DATE February 1980
TITLE A New Membrane-Type pH Sensor for Use in High-Temperature/High-Pressure Water		GE CLASS 1
		NO. PAGES 10
ORIGINATING COMPONENT	CORPORATE RESEARCH AND DEVELOPMENT SCHENECTADY, N.Y.	
SUMMARY <p>The new sensor represents a significant step forward in recognizing the need for the direct measurement of pH of geothermal brines, of water in nuclear reactors, and in high-temperature thermodynamic studies. The heart of the unit is an oxygen-ion-conducting ceramic that serves as the membrane. Yttria-stabilized zirconias have been employed in this role in the present work. Using structures somewhat akin to the structure of the conventional glass electrode, test units have been run continuously without failure for periods as long as 13 days at temperatures of 285 °C and at pressures of 1200 psi. Under these conditions the response over the pH range 3 to 8 (at 285 °C) has been essentially linear with a slope up to 97% of theoretical. Unlike sensors involving electron transfer couples (e.g., the hydrogen electrode, the palladium hydride electrode, and metal-metal oxide couples), the membrane is insensitive to changes in the redox environment. In turn, the relatively inert membrane exerts no influence on the environment; this behavior contrasts markedly with that of the hydrogen electrode and many other candidates for use at high temperatures.</p>		
KEY WORDS <p>pH, hydrogen ion concentration, oxygen-ion-conducting ceramics, stabilized zirconia, yttria-stabilized zirconia, oxygen electrode</p>		

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A NEW MEMBRANE-TYPE pH SENSOR FOR USE IN HIGH-TEMPERATURE/HIGH-PRESSURE WATER

Leonard W. Niedrach

INTRODUCTION

Work leading to the concept of the new sensor was inspired by the recognized need for devices for the direct measurement of the pH at elevated temperatures of geothermal brines, of water in nuclear reactors, and in other high-temperature applications including basic thermodynamic studies of aqueous systems. For such applications, it was felt that membrane-type sensors would be superior to ones based on electron transfer couples (e.g., the hydrogen electrode, the palladium hydride electrode, and metal-metal oxide couples) because, unlike the latter, membrane electrodes are normally insensitive to changes in the redox environment and are resistant to poisoning by impurities such as sulfides. In turn, membrane materials can often be found that exert no significant influence on the environment. These considerations are paramount, of course, in accounting for the universal acceptance of the glass electrode for pH measurements at ambient temperature. In view of the difficulties that have been encountered in attempts to modify the classical glass electrode for high-temperature/high-pressure applications,⁽¹⁻³⁾ alternative membranes were sought for the purpose.

In this connection the well-known lanthanum fluoride electrode for the determination of fluoride ion concentrations was selected as a useful model to establish criteria for the desired membrane material. This electrode functions because fluoride ions in the crystal and in the solution serve as the potential determining species at the interface. At equilibrium the electrochemical potential of the fluoride ion, as defined in general form by

$$\bar{\mu}_{X^{-n}} = \mu_{X^{-n}}^{\circ} + RT \ln a_{X^{-n}} + nF\phi \quad (1)$$

where $\bar{\mu}_{X^{-n}}$ is the electrochemical potential, $\mu_{X^{-n}}^{\circ}$ is the standard chemical potential, $a_{X^{-n}}$ is the activity of the fluoride ion, ϕ is the inner or galvanic potential, n is the charge on the ion of interest, and the other terms have their usual meanings, is equal in both phases. The potential drop at the interface is therefore given by

$$\Delta\phi = \phi_m - \phi_s = \frac{1}{nF} (\mu_{X^{-n}}^{\circ} - \mu_{X^{-n}}^{\circ} - RT \ln a_{X^{-n}} + RT \ln a_{X^{-n}}) \quad (2)$$

where the subscripts a and m identify the aqueous and membrane phases, respectively. Since the fluoride ion is the sole anion in the crystal, its activity in the solid phase remains constant, and the only variable term involved in establishing the total potential drop across the interface is the fluoride ion activity in the aqueous phase.

It was reasoned that a parallel relation might exist between an oxygen-ion-conducting ceramic and the oxygen ion concentration (and hence indirectly the pH) in an adjacent aqueous phase. If so, an oxygen-ion-conducting ceramic should function as a membrane-type pH sensor. This report addresses itself to the experimental verification that this implied sensitivity to pH can indeed be realized in practice.

Stabilized zirconia tubes of the type employed in high-temperature fuel cells and oxygen sensors were chosen as representative oxygen-ion-conducting membranes for initial tests. Zirconia has the virtue *vis a vis* glass of being markedly less soluble in water at elevated temperatures. In addition, much work has been done to characterize a wide variety of these ceramics and to develop fabrication techniques in connection with their earlier applications. Materials stabilized with yttria, calcia, and magnesia have been examined in the work to date, but the performance of the yttria-containing materials has been far superior to the others, possibly because of their generally higher specific conductivities.⁽⁴⁾ The work to be reported will therefore be limited to yttria-stabilized zirconia at two levels, 8.0 and 16.9 weight percent (w/o).

It is anticipated that a wide variety of alternative oxygen ion conductors will also be applicable as long as the transference number for the oxygen ion is close to 1.0 and that for electron and/or hole conduction is at least an order of magnitude, and preferably several orders of magnitude, less. In considering alternative materials an important criterion will be the specific conductivity. While that of the yttria-stabilized zirconia is adequate for practical applications at temperatures above 95 °C, it would be desirable to be able to cover the full temperature range from ambient upward. Among the zirconias those stabilized with scandia have the highest reported conductivities,^(4,5) and they may be adequate. Certain doped cerias also look promising from this point of view.⁽⁵⁻⁷⁾

It has been the purpose of this work to demonstrate the performance of the new sensor in a preliminary way, establish some of its important operating characteristics, and obtain some indication of stability. Before it

can become a practical device, an adequate system including reference electrode and calibration procedures must be developed, but little attention has been devoted to these aspects so far. It will become clear, however, that the reference electrode may prove less stable and reproducible than the membrane sensor itself.

Although most of the data have been obtained at 285 °C, they have been supplemented by enough at lower temperatures to indicate that with lower resistance ceramics the full range from ambient temperature to 285 °C or higher can be encompassed with a practical device.

EXPERIMENTAL

Structure of the Sensors

Most of the sensors used in this work were somewhat akin to the conventional glass electrode in that a buffered saline solution in contact with a chlorided silver wire served as the internal element within the membrane sheath. For work in the temperature range 25 to 95 °C stabilized zirconia tubes closed at one end were employed. Initially a 0.1 m NaCl or KCl solution containing one pH 7 pHydrion* buffer tablet per 100 ml was employed as the inner electrolyte, and contact was made by a chlorided silver wire immersed in this solution. In some cases the solution (including the buffer) was diluted by a factor of 10. For longer term experiments, particularly at 95 °C, the open end of the tube was covered with a Teflon** fluorocarbon resin cap.

A few sensors for use at 25 to 95 °C were also prepared with "direct junction" internals. One such type was prepared by inserting a 30-mil, coiled copper lead wire into the tube and packing it in place with a 50:50 mixture by weight of finely divided copper and cuprous oxide (Fisher copper metal—electrolytic dust, purified; Baker cuprous oxide powder, analyzed reagent) to a depth of 3 in. This type of junction has been used in the past in the fabrication of the well-known stabilized zirconia high-temperature oxygen sensors,⁽⁸⁻¹⁰⁾ and alternative metal-metal oxide or mixed oxide couples could also be used. A second direct junction contact was prepared by filling the tube with mercury to a depth of 3 in. and inserting a platinum lead wire. It was presumed that enough mercuric oxide was present as a contaminant that this too served as a metal-metal oxide-type contact. Sensors of this type were also closed with Teflon caps.

To extend the work to higher temperatures, the sealed structure shown in Figures 1 and 2 was employed. An important element is the compressible Teflon seal in the Conax pressure fitting. This seal maintains the pressure that builds up within the tube—the order of 1000 psi at 285 °C—and serves to insulate the lead wire from

*Trademark of Micro Essential Laboratory

**Trademark of Du Pont de Nemour & Company, Inc.

Figure 1. Schematic diagram of sensor for use at elevated temperatures and pressures.

Figure 2. Photograph of an assembled sensor.

the metallic parts of the fitting. The same internal electrolytes were employed as those at lower temperatures, and in one case a solution containing 0.001 m HCl and 0.009 m KCl was used. Because of the thermal expansion of such solutions, care was taken to allow sufficient

free volume within the tube; normally they were filled to only 70% of capacity.

Some work was also done at the elevated temperature with the copper/cuprous oxide direct-junction structure. This was sealed into the Conax fitting as above.

Test System and Protocols

Initial tests at ambient temperature were performed by immersing the sensor into appropriate solutions in an open beaker. An Ingold* combination electrode was used as a comparison standard, and its reference electrode also served the zirconia sensor. Because of the very high impedance of the ceramics at ambient temperature ($\sim 10^{11} \Omega$), it was necessary to make measurements in a faraday cage and to use a high-input impedance electrometer (Keithley Model 602).

All other measurements were made with the test system shown schematically in Figure 3. Here provision was made for pumping water, acid, or base into the heated and pressurized (if necessary) autoclave, which had a capacity of 1 l. In this way the solution in the autoclave could be slowly "titrated" with acid or base, or aliquots of more concentrated reagent could be introduced to cause more rapid changes in pH. Both 316 stainless steel and titanium autoclaves have been used.

The Conax fitting on the sensor permits direct mounting in the lid of the autoclave. Frequently two were tested concurrently. Also mounted to the lid through Conax fittings were an insulated platinized platinum wire and a reference electrode, which consisted of a chlorided silver rod immersed in a 0.01 m KCl solution contained within an insulating tube⁽¹¹⁾; the latter communicated with the water in the autoclave

Figure 3. System for evaluating sensors.

*Trademark of Ingold Electrodes, Inc.

through a porous asbestos or zirconia junction. For some of the measurements at 95 °C an Ingold Series 514 high-temperature combination pH electrode was mounted through the lid in place of the special reference electrode. In such cases the system was not pressurized, but otherwise procedures were standard.

During a run the potentials of all electrodes as well as the autoclave were monitored against the reference. In addition the ambient temperature pH could be measured downstream of the pressure control with an Ingold combination pH electrode. Keithley electrometers (initially Model 602 and later Model 616) were used for all the potential measurements. Automatic switching among the electrodes was accomplished with an Orion Model 855 automatic electrode switch. Output was recorded continuously on a Hewlett Packard Model 7100B strip chart recorder.

The reagents were normally pumped through the system at a constant rate of 3 mL/min with a Lapp Pulsafeeder Pump Model LS-20 while the pressure was maintained at 1200 psi, a pressure of about 200 psi over the vapor pressure of water when the system is at the highest operating temperature of 285 °C. When more rapid transients were under study, water was pumped at the same rate through the system, and suitable aliquots of 0.1 m NaOH or 0.05 m H₂SO₄ were introduced into the stream. Thermal convection produced essentially ideal mixing within the autoclave, particularly at the higher temperatures.

Temperatures were controlled with a Leeds and Northrup Electromax III controller. They were monitored continuously with a chromel-alumel thermocouple.

Resistance Measurements

Occasionally resistance measurements on the sensors were desired. These were accomplished with the electrometer by connecting the built-in shunts across the inputs from the sensor and the reference electrode. Under these conditions the resistance is given by

$$R = R_{sh} (E_{oc} - E_{sh}) / E_{sh} \quad (3)$$

where R is the series resistance of the membrane, the solution in the autoclave, and the reference electrode; R_{sh} is the resistance of the shunt; E_{oc} is the voltage measured without the shunt; and E_{sh} is that with the shunt. At the lower temperatures, R approximates that of the membrane itself. At higher temperatures a correction was derived by measuring the resistance between the platinum electrode and the reference.

Comparison Standards for pH Sensors

Ideally one would like to establish the performance of a new sensor on the basis of comparisons of experi-

mental observations with values predicted from accepted thermodynamic data. Unfortunately, at the outset of this work it was not clear that the experimental system was clearly enough defined for this purpose. Thus uncertain liquid junction potentials were anticipated at the reference electrode-solution interface, some consumption of acid through corrosion of the autoclave and connecting tubing as well as some ceramic parts could occur, and rigorous steps were not taken to exclude carbon dioxide from the basic solutions.

It was therefore elected to judge the performance of the sensors on the basis of comparisons with other reference standards. For measurements at ambient temperature and 95 °C, no problem occurred because commercially available glass electrodes could be used unambiguously for the purpose. At higher temperatures, however, this is not the case, and an alternative comparison was sought. Although a hydrogen electrode would seem a natural choice, our system and experience has been geared for work with aerated solutions. We therefore elected to use the "oxygen electrode" formed at the platinized platinum wire in the autoclave as the comparison standard at 285 °C. This electrode, in contact with the aqueous solutions (all of which were equilibrated with air at ambient temperature before entering the autoclave) can, in principle, serve as a pH sensor because of the hydrogen ions involved in the potential determining reaction

Although the oxygen electrode has not been rigorously established as a pH sensor, its response to pH has been demonstrated at ambient temperature,⁽¹²⁾ and during the course of the present work additional support was generated, particularly from direct comparisons with the glass electrode at 95 °C. Comparison of its behavior at 285 °C with thermal data also proved reassuring, particularly during later experiments after the equipment had had time to age and passivate (cf. below).

RESULTS AND DISCUSSION

pH Response

Performance at 25 °C—Performance was first demonstrated in brief experiments at ambient temperature with yttria-stabilized tubes. Data comparing the response of two membranes stabilized with 16.9 w/o yttria at 25 °C with that of a commercial glass electrode upon immersion in 0.1 m sodium hydroxide, 2 m hydrochloric acid, and a phosphate buffer (pHydriion at pH 7.0) are shown in Figure 4. As can be seen, the slopes of the two curves are very close to the ideal value of 1.000. At the moment these results are academic rather than practical. While they establish the response to pH, the high impedance of the present ceramic tubes at ambient temperature ($\sim 10^{11} \Omega$) makes them unacceptable for general application at this temperature. It is

Figure 4. Response of two sensors relative to that of a glass electrode at 25 °C.

likely, however, that suitable membranes can be fabricated from alternative oxygen-ion-conducting ceramics — e.g., doped cerias—that will have lower resistivities and thereby permit practical measurements at ambient temperature. Alternatives that are capable of operating at ambient temperatures are desirable, not in order to replace the glass electrode but in the interest of having a single sensor responsive to pH from ambient temperature to higher levels so that pH can be followed continuously over an entire heating or cooling transient. Low-temperature capability would also permit ready calibration and testing with the minimal complications associated with ambient conditions.

Performance at 95 °C—Data comparing the response of a membrane stabilized with 8.0 w/o yttria with that of the high-temperature Ingold electrode at 95 °C are shown in Figure 5. Also included in the figure are corresponding data for the oxygen electrode formed at the platinized platinum wire. Although the response of this membrane electrode is only 92% of the glass, it is still in an acceptable range. The response of the oxygen electrode at this temperature is 88% of the glass. By using the ratio of the two, it is found that in this case the membrane response is 104% of that of the platinum electrode. In two other runs the same membrane electrode (with fresh internal solution) was tested at 95 °C without the glass electrode in the system. In these cases comparison only with the oxygen electrode was possible and values of 106 and 107% were obtained for the sensor, in reasonable agreement with the above value.

Figure 5. Responses of a sensor and the oxygen electrode relative to the response of a glass electrode at 95 °C.

(As will be discussed below, two additional sensors with direct junction internals were also examined at 95 °C and gave linear responses that were 101 and 103% of that of the Ingold glass electrode.) It is thus clear that quite reasonable, and close to theoretical, responses can be obtained from the new electrodes at 95 °C.

Behavior at 285 °C—Because primary interest in the new sensors is in their application at higher temperatures, most of the emphasis has been placed on tests at 285 °C. Data in Figure 6 show that there is again an excellent linear correlation between the response of the membrane sensor and that of the oxygen electrode over a range of pH established at the extremes by 0.0005 m H_2SO_4 and 0.001 m NaOH . In this case 16.9 w/o yttria served as the stabilizer, and the data in the figure were accumulated over a period of 5.7 days. The response is 96% of that of the oxygen electrode, which at this temperature probably performs close to theoretical (cf. below). For comparison purposes, similar data for eight independent sensors tested at 285 °C are summarized in Table 1. Included is information about the stabilizing agent and internal filling solution as well as the number of data points used in making the comparison and the period over which the data were taken. The overall average response was 94.7% of that of the oxygen electrode with a standard deviation of 4.4%. No significant difference is seen between the sensors stabilized with 8.0 w/o yttria and those with 16.9 w/o.

Figure 6. Response of a sensor relative to that of the oxygen electrode at 285 °C.

Table 1
RESPONSE OF YTTRIA-STABILIZED ZIRCONIA MEMBRANES RELATIVE TO THAT OF THE OXYGEN ELECTRODE AT 285 °C

Run No.	Sensor No.	Stabilizer Concentration Wt%	Internal Solution	Data Sets	Period of Time Days	Response % of O_2 Electrode
ZR02-5	Y-7	8.0	0.1 m NaCl, pH 7.0	5	2.8	95.1
ZR02-6	Y-9	8.0	0.1 m NaCl, pH 7.0	13	8.8	92.9
ZR02-7	Y_2O_3 -3	16.9	0.1 m NaCl, pH 7.0	12	5.7	96.4
ZR02-9	Y_2O_3 -4	16.9	0.01 m NaCl, pH 7.0	3	0.8	88.8
ZR02-14	Y-15	8.0	0.01 m NaCl, pH 7.0	2	0.2	87.8
ZR02-16	Y_2O_3 -5	16.9	0.01 m NaCl, pH 7.0	8	4.0	96.2
ZR02-16	Y-15	8.0	0.01 m NaCl, pH 7.0	8	4.0	103.9
ZR02-17	Y-17	8.0	0.01 m NaCl, pH 7.0	10	3.7	95.2
ZR02-18	Y-18	8.0	0.001m HCl/0.009 m KCl	2	1st Day	93.7
-	-	-	-	3	2nd Day	93.3
-	-	-	-	5	12th Day	98.2

Mean Response for 8.0% Stabilizer = 93.0; $\sigma = 4.6$

Mean Response for 16.9% Stabilizer = 93.8; $\sigma = 4.3$

Grand Mean = 94.7; $\sigma = 4.4$

Additional data showing the parallel dynamic responses of the new membrane-type sensor and the oxygen electrode to pH changes are shown in Figure 7. The first transition was accomplished by introducing a 15 mL aliquot of 0.1 m NaOH when the solution in the autoclave was 0.0005 m H_2SO_4 . The second transition was brought about by back-titrating the base with 0.0005 m H_2SO_4 .

Figure 7. Response of a sensor and the oxygen electrode to rapid and slow changes in pH at 285 °C.

As further support for the performance of the new sensors, an attempt was made to compare their responses with those predicted from available thermodynamic data. For this purpose, the data of Marshall and Jones⁽¹³⁾ for the second dissociation constant of sulfuric acid at elevated temperatures were employed along with those of Sweeton, Mesmer, and Baes⁽¹⁴⁾ for the dissociation constant of water. Activity coefficients for the dilute solutions were estimated from the theoretical predictions of Helgeson and Kirkham.⁽¹⁵⁾

Calculated values for the pH of the 0.0005 m H₂SO₄ and 0.001 m NaOH solutions at 285 °C as well as the theoretical response from interchanging the two are summarized in Table 2. It is to be noted that the relatively high pH for the acid (relative to 3.02 at 25 °C) results from the marked decrease in the second ionization constant of sulfuric acid with increasing temperature — 3.3×10^{-6} at 285 °C vs. 1.2×10^{-2} at 25 °C. For the 0.001 m NaOH the pH is lower at 285 °C than at 25 °C because of the increased dissociation constant of water at the elevated temperature. Compared with these two effects, the influence of activity coefficient corrections on the calculated pH values of these dilute solutions is minor — of the order of 0.03 to 0.05 units.

Response data for a number of sensors and the oxygen electrode, based on the full transition from acid to base or reverse only, are summarized in Table 3, where they are also intercompared and compared with theory. A definite trend is evident among the data in that the agreement with theory improves in the successive tests, which are arranged in chronological order. This trend with time suggests, in part at least, that the discrepancies in the earlier runs reflect real variations in the pH of the solutions as a result of corrosion of the test system, most likely by the acidic solutions. During successive runs it would appear that a protective film developed on the walls and the rate of corrosion diminished, thereby introducing smaller discrepancies, which by the time of Run ZR02-17 were insignificant. The value for the oxygen electrode in Run ZR02-17 strongly supports the original assumption that the oxygen electrode at elevated temperatures functions well as a pH sensor and was a valid choice as a comparison standard. In comparing the sensors with the oxygen electrode in these tests, a mean value of 95.3% was obtained, in good

Table 2
THEORETICAL POTENTIAL CHANGES FOR
0.0005 m H₂SO₄ $\rightleftharpoons$ 0.001 m NaOH
AT 285 °C

pH of 0.0005 m H ₂ SO ₄	3.32
pH of 0.001 m NaOH	8.22
Δ pH	4.90
mv/pH unit	110.8
Δ mv	543.0

Table 3
MEASURED POTENTIAL CHANGES FOR
0.0005 m H₂SO₄ $\rightleftharpoons$ 0.001 m NaOH
AT 285 °C

Oxygen Electrode Response			Membrane Response		
Run	Δ mv	% of Theoretical	Δ mv	% of Theoretical	% of Oxygen
ZR02-5	376	69.2	360	66.3	95.7
ZR02-6	436	80.3	392	72.2	89.9
ZR02-7	490	90.2	492	90.6	100.4
ZR02-9	526	96.9	494	91.0	93.9
ZR02-17	545	100.3	527	97.0	96.7
					Mean 95.3
					σ 3.8

agreement with the data in Table 1. The individual differences result from the fact that more data points were averaged for each run of Table 1; only data obtained from the full transition between the acid and base were used for Table 3.

Sensitivity to Redox Potential of the Environment

Because membrane-type sensors normally have the desirable feature of being insensitive to the redox potential of the solution being monitored, the behavior of the stabilized zirconia sensors was examined as the redox potential of the solution in the autoclave was changed. This was accomplished by changing from an air to a nitrogen purge of the 0.0005 m H₂SO₄ solution being fed to the autoclave. The effect is illustrated by the data in Figure 8, which includes plots of the potentials of the sensor, the oxygen electrode, and the autoclave against the reference electrode.

It is seen that, after changing from an air to a nitrogen purge of the incoming 0.0005 m H₂SO₄, a slow downward drift in potential was evident for the platinum electrode and the autoclave. After several hours a more rapid drop occurred for both of these potentials. This drop is attributed to loss of the passive film on the autoclave with an associated increase in corrosion rate and liberation of hydrogen. The platinum electrode then clearly showed its sensitivity to this change in the redox environment. The oxygen-ion-conducting ceramic membrane, however, retained an essentially constant potential throughout the transients. The small

Figure 8. Behavior of a sensor, the oxygen electrode, and the autoclave as the redox potential of the environment is changed at 285 °C.

increase in potential at the time of the depassivation is believed to have been a response to a real change in pH.

It is useful to consider whether this behavior is consistent with the known properties of stabilized zirconia and whether it is likely to be a universal property of oxygen-ion-conducting ceramic membranes. A key factor to consider in this connection is the domain over which the ceramic functions "solely" as an oxygen ion conductor — i.e., $t_{O^2-} \geq 0.99$, where t_{O^2-} is the transference number for the oxygen ion. If electronic or positive hole conduction becomes significant, deleterious shunting can occur and the full signal cannot be developed across the membrane.

Since the same principle applies in the older applications of these ceramics in fuel cells and oxygen sensors, attention has been addressed to the influence of environmental redox conditions on the oxygen ion conductance, particularly by Patterson,^(16,17) whose data for calcia-stabilized zirconia (CSZ) and yttria-doped thoria (YDT) have been adapted to Figure 9. In this figure the shaded areas to the right of the boundaries identify the oxygen-ion-conducting domains for the two ceramics as defined by $t_{O^2-} \geq 0.99$. At any given temperature, environments having oxygen partial pressures (or equivalent redox potentials) in excess of that of the upper boundary cause excessive positive hole conductivity, while partial pressures below the lower boundary result in excessive electronic conductivity. Although less data are available for yttria-stabilized zirconia, there is some indication⁽¹⁸⁾ that the oxygen-ion-conducting domain is somewhat wider than that for CSZ.

Also shown on the figure is the domain of oxygen partial pressures and temperatures that is encompassed by the equilibrium established in an aqueous system in the presence of from 1 atm of oxygen to 1 atm of hydrogen. This domain was calculated from available thermal data.⁽¹⁹⁾ It is evident that over this entire range of conditions CSZ is a satisfactory oxygen ion conductor. The data for YDT serve as an example of what can occur in other cases. Here it is seen that at oxygen levels greater than 10^{-6} atm the positive hole conductivity exceeds 1%, and less satisfactory performance than for CSZ is to be expected under such conditions. On the other hand, in reducing environments the YDT has a considerably larger margin of safety than the CSZ for

Figure 9. Domains for oxygen ion conductivity in calcia-stabilized zirconia and yttria-doped thoria.

the operating range postulated. (It has been reported, however, that under some situations YDT suffers further complications in that hydrogen can enter the lattice and introduce proton conduction,⁽²⁰⁾ which would also influence performance.) Limited data for doped cerias⁽⁷⁾ suggest that at 1 atm of hydrogen, their oxygen ion conductivity might be somewhat compromised but that they should function satisfactorily at higher oxygen partial pressures.

The behavior of the cerias is of particular interest in that the oxygen ion conductivity is considerably higher than the oxygen ion conductivities of the zirconia or thoria systems, and they should be attractive for use at temperatures closer to ambient. This factor has promoted interest in their use in fuel cells,^(6,7) and recently their virtue in oxygen sensors operational at lower-than-usual temperatures has been demonstrated.⁽²¹⁾

Drift

A word is in order about drift. In the work to date drift has arisen from two principal sources: (1) changes in the electrolyte concentration within the reference electrodes, and (2) changes in the internal electrolyte in the sensor, especially when the poorly buffered 0.001 m HCl — 0.009 m KCl electrolyte was used.

That a significant drift has been associated with the reference electrodes is illustrated by the data, all obtained with 0.0005 m H₂SO₄ in the autoclave, in Figure 10 from Runs ZR02-5, 7, and 18. The data from

Figure 10. Drift in the potential of sensors and the oxygen electrode relative to 0.01 m KCl/AgCl/Ag reference electrode at 285 °C.

Runs ZR02-5 and 7 show the drifts of the oxygen electrode and the sensor to be essentially parallel. In both cases the more concentrated buffered electrolytes, which should have good stability, were used as the internals of the sensors. It is therefore felt that in these cases the drift was largely associated with the reference electrode. In Run ZR02-18 mixed results were obtained. The drift of the oxygen electrode over the first few days was similar to that from the other two runs, and it eventually plateaued. The drift is again believed to be associated with the reference electrode. The much larger drift of the sensor is clearly a result of changes in the very poorly buffered internal electrolyte, 0.001 m HCl -0.009 m KCl, most probably as a result of reaction of the small amount of acid with the zirconia or, more likely, with impurities in the zirconia. If so, pretreatments of the ceramic with acid or the use of a more concentrated acid as the filling solution (e.g., 0.01 m HCl) should reduce the problem.

The drift in the reference electrode is larger than anticipated from previous experience.⁽²²⁾ It may reflect differences in operating procedures. For example, we have normally been operating with solutions equilibrated with air (dissolved oxygen concentration about 8 ppm), while in earlier applications in simulated and actual nuclear reactor water (BWR type) the oxygen levels ran about 0.2 ppm. At the higher oxygen levels diffusion through the Teflon walls of the reference or through the diffusion junction itself could be higher and thereby promote chloride ion consumption from the solutions via the reaction

As chloride is removed from solution via such a mechanism, the potential of the reference couple would increase, thereby causing a decline in the potential of other electrodes measured against it. This type of behavior has been observed with neutral saline solutions in

contact with silver/silver chloride electrodes in confined spaces.⁽²³⁾ The fact that the potential eventually leveled off in Run ZR02-18 is not inconsistent with such behavior. At 285 °C the solubility of silver chloride is much higher than at room temperature⁽²⁴⁾ and could be instrumental in establishing the plateau at a potential not too far removed from the initial value. It is likely too that some KCl is lost from the reference electrode by diffusion through the porous asbestos or zirconia plug. Detailed analysis of the solutions after use should be helpful in diagnosing the problem, but this has not yet been done.

This type of drift has not interfered with the work to date because responses to pH can be determined over relatively short periods of time when the influence from drift can be minimized. It is clear, however, that for the successful exploitation of the new pH sensors a clearer understanding of the problem will be required.

Conductivity of Membranes

In order to establish more firmly that the sensors are indeed functioning as true membranes, it was felt necessary to demonstrate that their conductivities are comparable with those normally associated with such ceramics from earlier measurements at high temperatures. This is necessary because under certain limited conditions porous media can give responses resembling those from an intact membrane. (Lev has discussed this type of behavior as encountered with "incompletely sealed" cation-sensitive glass microelectrodes⁽²⁵⁾). With relatively large pores the behavior is like a liquid junction, and only a diffusion potential is established. However, with pores of dimensions small with respect to the thickness of a double layer, exclusion of cations or anions can occur and the theoretical response of a membrane can be achieved. Under such conditions, transport of current through the pores is by ionic migration in an aqueous medium, and relatively low activation energies, of the order of 5 kcal/mole, should be encountered.

Measurements of cell resistance were made at various temperatures with both 8.0 and 16.9 w/o yttria-stabilized tubes by using the electrometer and the parallel shunt method outlined above. Such measurements were made with the sensor immersed in acidic and basic solutions, with no difference in results. Parallel measurements were made between the oxygen electrode and the reference, and between the autoclave and the reference to obtain corrections for the resistance of the porous plug in the reference. Finally, the resistance measurements were converted to specific conductivity on the basis of the physical dimensions of the tubes. In the calculations allowance was made for the expansion of the water within the tubes with increasing temperature. Plots of the data in terms of the logarithm of the specific conductivity vs. reciprocal temperature are shown in Figure 11. From a least-squares fit of the data, the activation energies and conductivities at 1000 °C were calculated. These calculations are listed in Table 4 with

Figure 11. Conductivities of yttria-stabilized zirconias.

Table 4
IONIC CONDUCTIVITIES AND ACTIVATION ENERGIES FOR ZIRCONIA STABILIZED WITH 16.9 W/O YTTRIA*

Conductivity at 1000 °C ($\Omega^{-1}\text{cm}^{-1} \times 10^3$)	Activation Energy (kcal/mole)	Source
3.2	24.1	This work
1.5**	20.2**	This work
7.7	19.8	As reported in Ref. 4
4.8	—	"
10.0	20.0	"
12.0	20.0	"
5.8	—	"
10.0	—	"
8.7	—	"
12.0	—	"

*This is equivalent to 10 mole percent.

**8.0 w/o yttria, which is equivalent to 4.5 mole percent.

data from the literature for zirconia stabilized with 10 mole percent (16.9 w/o) yttria obtained at higher temperatures in connection with the application of these ceramics in fuel cells and oxygen sensors. (Less data are available for comparison with the 8.0 w/o material, but the activation energy has been observed to decrease slightly with decreasing yttria content^(26,27)). It is seen that our results are quite comparable with the earlier data, and, in addition, the activation energies are

high for conductivities in an aqueous phase. Both observations give assurance that the sensors are indeed functioning as true membranes. Helium leak tests also indicated that the sensors were impervious both before and after exposure in the autoclave, but it is difficult to translate this type of observation into behavior upon immersion in aqueous solution.

One additional comment should be made about the behavior of porous media as sensors. It is improbable that porous media would show the pronounced *specificity* for hydrogen ion over the wide range actually observed. While it is possible that cation *selectivity* would prevail over the full range from 0.1 m NaOH to 2 m HCl at ambient temperature, it is extremely likely that the response would shift from the hydrogen ion to the sodium ion as the solution became strongly basic. This shift would manifest itself by an inversion of the slope in the basic media when the sensor response is plotted against that of the glass electrode.

Alternative Internal Junctions

One additional aspect of the sensor that was examined briefly was the performance with the alternative, nonaqueous internal junctions consisting of Cu/Cu₂O and Hg/HgO. The former was employed in several sensors that were operated at both 95 and 285 °C, while the single sensor prepared with the mercury couple was run only at 95 °C.

Data obtained at 95 °C with the Ingold glass electrode serving as the comparison standard are shown in Figure 12. Both internals resulted in sensors having

Figure 12. Response of sensors with Cu/Cu₂O and Hg/HgO internal junctions relative to that of a glass electrode at 95 °C.

linear responses that were close to those of the glass electrode. An equivalent sensor prepared with an aqueous internal and tested in the same group was somewhat lower in response (cf. Figure 5).

At 285 °C sensors with the Cu/Cu₂O internal again gave linear responses against the oxygen electrode as standard. In the two cases tested the responses were 89.8 and 96.1% of that of the oxygen electrode.

These results indicate that either the aqueous or nonaqueous type of internal should be satisfactory on the basis of pH response. A final choice may be dependent upon long-term stability and/or the temperature coefficients of the two types of sensors.

SUMMARY AND CONCLUSIONS

Oxygen-ion-conducting ceramic membranes have been shown to function as pH sensors over the temperature range from 25 to 285 °C. Indeed it is likely that their operating range will extend to the critical temperature. The conductivities of the yttria-stabilized membranes used in the experimental work were found to be comparable in magnitude and activation energy with literature values for related materials measured at elevated temperatures in connection with their application in high-temperature fuel cells and oxygen sensors.

The yttria-stabilized zirconia sensors were also found to be stable for periods of operation at 285 °C as long as 13 days, and they are insensitive to changes in the redox potential of the system being measured. This stability to changes in the redox potential of the system is consistent with known properties of the ceramic.

The internal junction used with the sensor can be varied from aqueous to nonaqueous types employing inorganic redox couples such as mixed metal-metal oxides. Which type is ultimately preferred will be decided on the basis of criteria that have not yet been evaluated, such as long-term stability and temperature coefficient.

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