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IMPROVE THE LIFETIME OF THE HOLLOW FIBER SODIUM SULFUR CELL: FINAL REPORT

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IMPROVE THE LIFETIME OF THE HOLLOW FIBER SODIUM SULFUR CELL

Final Report

August 1987

by

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for

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SUMMARY

This report is a continuation of work directed towards identifying potentially superior glass compositions for use an electrolyte in the Dow sodium-sulfur cell. Prior work identified a glass candidate (T806) having superior resistance to metallic sodium and sodium polysulfides. However, lifetime testing of this glass was disappointing: mean lifetimes are only a few weeks for T806 cells versus ca. six months for cells employing the standard glass (D406).

Thermodynamic calculations showed possible reactivity between the above mentioned glasses and sulfur. Work was undertaken in this report to test the hypothesis that T806 cells were failing sooner because of a more rapid reaction with sulfur. Glass-sulfur reactivities were measured at 300°C and 400°C by means of a sensitive ion chromatography method for fifteen glass compositions also in the ternary system: sodium oxide/boron trioxide/silicon dioxide system. Detailed comparisons of sulfur reactivities for T806 and D406 glass compositions permit the rejection of the above hypothesis. In addition, no clearly superior glasses of acceptable sodium ion conductivity were identified with respect to sulfur corrosion.

Additional experiments are suggested that may shed light on the early failure of cells using T806 glass as the electrolyte. Attention is drawn to the possible involvement of the cathode foil, molybdenum coated aluminum foil. Specific experiments designed to test the influence of cathode foil are outlined.

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INTRODUCTION

The Dow sodium-sulfur, secondary cell uses glass capillaries that are sodium filled and are surrounded by sulfur and sodium polysulfides. The working portion of the cell is cylindrical and consists of a spiral wrap of alternating layers of glass capillaries and metallic foil; the capillaries lie parallel to the cell axis and the metallic foil serves as the cell cathode. Typical active capillary lengths are 18 cm and outside and inside diameters are 70 μm and 50 μm, respectively. The design is well suited for high power applications since designing for high power does not comprise energy density. Current research involves design and testing of high power and high energy density cells. A pulse power density of 220 W/Kg was demonstrated with a 20 amp. hr. cell. This particular cell was not optimized with respect to power density; power densities on the order of 500 W/Kg are thought possible.

Additional research is required to improve mean cell lifetime and provide for freeze-thaw capability. With the standard glass electrolyte (D406) in use since the 1970's, mean cell lifetime is approximately six months with champion cells lasting a year. Although research to date has not identified the exact failure mechanism, there are compelling reasons for developing an alternative glass electrolyte. Examination of electrolyte requirements is instructive. Ideally, the electrolyte should be inert to metallic sodium, sulfur, and sodium polysulfides and it should only conduct by sodium ion migration. The present glass electrolyte interacts with sodium at the cell operating temperature (300°C), causing significant loss of capillary tensile strength. This strength loss prevents the thermal cycle of cells aged at the operating temperature. In contrast, cells may be successfully thermal cycled if they are not heated above the 150°C filling temperature prior to cooling.

Another potential area for glass electrolyte improvement is resistance to sodium trisulfide. The lifetime of cells using D406 glass electrolyte is reduced to a few weeks if the catholyte composition is adjusted to sodium trisulfide and the cell is subsequently held in open circuit. Sodium trisulfide exposure of D406 glass results in surface attack and tensile strength reduction. In the operation of high power cells where it may be difficult to control catholyte composition at rapid rates of discharge, improved stability towards sodium trisulfide may also prove helpful.

In the early 1980's, several alternative glass compositions were formulated and screened with respect to resistance to metallic sodium and sodium trisulfide. One candidate, T806, showed superior resistance to the above reagents. Unfortunately, cell lifetimes were disappointing: mean lifetimes were only a few weeks for T806 cells versus six months for D406 cells.

The present study was undertaken to examine possible failure modes for cells constructed with T806 glass as the electrolyte. If this was successful, not only could it expedite development of glasses giving improved cell life while (hopefully) maintaining required corrosion resistance and mechanical integrity, but it also might lead to a clue as to the ultimate failure of cells using D406 capillaries.

This report tests the hypothesis that early failures of T806 cells are due to reaction of the glass electrolyte with sulfur. A sulfur stability problem had been encountered much earlier in the initial glass screening studies leading to the development of D406 glass. Glass tubes made from alkaline glasses (sodium disilicates) cracked upon sulfur exposure. With the above problems in mind, the relative sulfur reactivities of T806 and D406 glass compositions were determined. Unlike sodium silicates, these glasses contain boron trioxide, added to decrease glass alkalinity. Additional, neighboring glass compositions (from the ternary system:sodium oxide/silicon dioxide/boron trioxide) were also examined for sulfur reactivity. Factors limiting the ability to make thermodynamic predictions of reaction equilibria between glass and sulfur are discussed.

THERMODYNAMIC DATA FOR SULFUR REACTIONS WITH $Na_2O \bullet B_2 \bullet SiO_2$ GLASSES

Disproportionation reactions of sulfur by base (such as the "liver-of-sulfur" reaction between sulfur and potassium carbonate) have been known for over a century. A similar sulfur related failure mode was observed in the sodium-sulfur hollow glass fiber cells, when a very basic sodium disilicate glass was used as the electrolyte membrane. The problem was apparently alleviated by a change to the less basic sodium tetraborate region. Recent work on the interaction of glasses with sodium implicated some undesirable features associated with the very high boron region. The object of this work is to define a region thermodynamically resistant to sulfur disproportionation. This may also allow changes of the boron content in an effort to minimize interactions with metallic sodium.

The primary disproportionation expected are (reactions unbalanced)

$$S + \text{Glass} \longrightarrow \text{Glass*} + Na_2SO_4 + Na_2S_x$$

and

$$S + \text{Glass} \longrightarrow \text{Glass*} + Na_2SO_3 + Na_2S_x$$

Where Glass* denotes a glass composition partially depleted of Na_2O and Na_2S_x denotes the sodium polysulfide composition in two phase equilibrium with liquid sulfur.

The thermodynamic data of interest would by the combination of:

(I) ΔG of the reactions

$$Na_2O + \frac{(3x + 1)S}{4} \longrightarrow 1/4\ Na_2SO_4 + 3/4\ Na_2S_x$$

$$Na_2O + \frac{(2x + 1)S}{3} \longrightarrow 1/3\ Na_2SO_3 + 2/3\ Na_2S_x$$

(II) Partial molar free energy of Na_2O in the various glasses under consideration.

Discussion

The literature search for existing thermodynamic data was aimed on two fronts -- the interaction of sulfur and Na_2O, and the partial molar free energy of Na_2O in the various sodium borosilicate glasses. These are presented separately.

Interaction of Na_2O and S

Barin and Knacke's(1) compilation of thermodynamic data is used as a primary information source. From there the following G values (Kcal/mole) are adapted:

	S(1)	$Na_2O(S)$	Na(1)	$Na_2SO_3(S)$	$Na_2SO_4(S)$
500°K	-4.325	-109.866	-6.738	-279.492	-351.296
600°K	-5.679	-112.778	-8.573	-284.808	-357.402
700°K	-7.171	-116.030	-10.825	-290.657	-364.325

Unfortunately, the given values for the various sodium polysulfides have unacceptably high uncertainty limits. Barin and Knacke's cited source was that of Mills(2) where data in turn was derived from other primary sources$^{(3)}$ basing on a model of adding S to Na_2S. Inherent in these derivations is an uncertainty of some 3 Kcal/mole for the H term and 3-7 cal/°K-mole for the S term for the starting Na_2S. Thus, despite the careful measurement by various workers(3,5,6) on the vapor pressure of sulfur over polysulfide melts, this method of integration does not yield an adequate estimate for the free energy of formation of the various sodium polysulfides.

A different approach is adopted: We shall start with one mole of liquid sulfur at temperature T, (say 600°K) and N moles of liquid Na. The Na will now be discharged infinitely slowly through a cationic membrane by doing work against a very high impedance load.

$$\text{then Work done} = \int_0^N FEdn = \int_0^N F(E_o - iR_{internal})dn$$

$$= \int_0^N FE_o dn$$

where
F = Faraday's Constant
E = Closed circuit potential
E_o = open circuit potential

dn denotes the infinitesimal moles of Na transferred (z=1)

Since the process is done reversibly and at constant T and P

$$\Delta G = -\int_0^N FE_o dn + \int s dT + \int V dP$$

$$= -\int_0^N FE_o dn$$

for the reaction:

$$N \ Na(1) + S(1) \longrightarrow Na_NS$$

or $$G_{Na_NS} - NG_{Na(1)} - G_{S(1)} = \Delta G \quad -\int_0^N FE_o dn$$

or $$G_{Na_NS} = -\int_0^N FE_o dn + NG_{Na(1)} + G_{S(1)}$$

or $$G_{Na_2S_{2/N}} = 2/N(-\int_0^N FE_o dn + NG_{Na(1)} + G_{S(1)})$$

$$= -2/N \int_0^N FE_o dn + 2 \ G_{Na(1)} + 2/N \ G_{S(1)}$$

Now we take advantage of the fact that the solubility of Na_2S_x in sulfur is very low. Hence during the whole process, down to the "edge" of the two phase region,

$$E_o = \text{constant}$$

Hence $$G_{Na_2S_{2/N}} = -2/N(FE_oN) + 2 \ G_{Na(1)} + 2/N \ G_{S(1)}$$

or $$G_{Na_2S_{2/N}} = -2FE_o + 2 \ G_{Na(1)} + 2/N \ G_{S(1)}$$

For the reaction:

$$Na_2O + \frac{(3x + 1)}{4} S \longrightarrow 1/4 \ Na_2SO_4 + 3/4 \ Na_2S_x$$

$$\Delta G_1 = 1/4 \ G_{Na_2SO_4} + 3/4 \ G_{Na_2S_x} - G_{Na_2O} - \frac{(3x + 1)}{4} G_S$$

$$= 1/4 \ G_{Na_2SO_4} + 3/4(-2 \ FE_o + 2 \ G_{Na(1)} + xG_S) - G_{Na_2O} - \frac{(3x + 1)}{4} G_S$$

$$= 1/4 \ G_{Na_2SO_4} - 3/2 \ FE_o + 3/2 \ G_{Na(1)} - G_{Na_2O} - 1/4 \ G_s$$

Similarly, for the reaction

$$Na_2O + \frac{(2x+1)}{3} S \longrightarrow 1/3\ Na_2SO_3 + 2/3\ Na_2S_x$$

$$\Delta G_2 = 1/3\ G_{Na_2SO_3} - 4/3\ FE_o + 4/3\ G_{Na(l)} - G_{Na_2O} - 1/3\ G_S$$

Adopting values of E_o by Gupta & Tischer(7) at various temperatures, we obtain:

T	E_o	G_1	G_2
553°K	2.079V	-59.39	-55.17
573°K	2.078V	-59.57	-55.32
600°K	2.076V	-59.77	-55.48
650°K	2.072V	-60.23	-55.96
673°K	2.070V	-60.65	-56.18

It is of interest to note that the final form the ΔG takes is independent of the molar fraction of Na in the two phase region (i.e. the "x" or "N" drops out of the final expression). Also, note that the G values have only a very small temperature dependence, giving a good basis for designing accelerated tests at high temperatures.

Sodium Oxide Activity in Glasses

We were less successful coming up with reliable sodium oxide activity calculations in glasses from existing data. Not only are there no closely related measurements at the desirable temperature, but also the high temperature measurements had an inherent inconsistency. Thus the author shall only report that literature relative to basicity in glass systems and comment on their respective usefulness to the present study.

(1) Yokokawa et al(8,9) did an extensive amount of work by direct measurement of EMF differences between different glass melts, thereby calculating the difference of sodium oxide activity. While the experiments were well designed and data were vast, the interpretation of result is suspect. The conclusions drawn are inconsistent with known data and with intuition, for example:

(a) A poor estimate for $\Delta\bar{G}_{Na_2O}$ (borax) of -214 KJ/mole or -51.1 Kcal/mole at 1123°K(9)

Actually, from G of formation values from Barin & Knacke's, one could estimate $\Delta G_{B_2O_3}$ at $Na_2O \cdot 2B_2O_3$ as follows:

	High estimate	Low Estimate
	$Na_2O \cdot 2B_2O_3 \longrightarrow Na_2O \cdot B_2O_3 + B_2O_3$	$Na_2O \cdot 3B_2O_3 \longrightarrow Na_2O \cdot 2B_2O_3 + B_2O_3$
800°K	7.4 Kcal/mole	4.6 Kcal/mole
900°K	5.9 "	3.8 "
1000°K	4.2 "	2.9 "
1100°K	4.2 "	0.5 "
1200°K	3.6 "	

Hence we can estimate $\Delta\bar{G}_{B_2O_3}$ of $Na_2O \cdot 2B_2O_3$ @ 1123°K to be $\sim$-2.2 Kcal/mole, and from the formula used by Yokokawa,

$$\Delta\bar{G}_{Na_2O} \text{ (Borax)} = 3(-94.5 - 2/3(-2.2)(4.187)) = -261.5 \text{ KJ/mole}$$

$$= -63.3 \text{ Kcal/mole}$$

or, one can similarly estimate $\Delta\bar{G}_{Na_2O}$ directly; again with data from Barin and Knacke's:

	High estimate	Low Estimate
	$3(Na_2O \cdot 2B_2O_3) \longrightarrow Na_2O + 2(Na_2O \cdot 3B_2O_3)$	$2(Na_2O \cdot B_2O_3) \longrightarrow Na_2O + Na_2O \cdot 2B_2O$
500°K	63.55 Kcal/mole	56.51
600°K	64.11	57.21
700°K	64.39	57.95
800°K	64.53	58.73
900°K	63.79	59.57

A value somewhere in the vicinity of 62 Kcal/mole seems most likely.

(b) It indicates $Na_2O \cdot B_2O_3 \cdot SiO_2$ is MORE basic than $Na_2O \cdot 2SiO_2$ @ 1100°K. This is intuitively highly unlikely. This suggests the addition of one mole of B_2O_3 has <u>less</u> effect than one mole of SiO_2 into one mole of Na_2O SiO_2.

(c) According to Ref. 9, the difference between $\Delta\bar{G}_{Na_2O}$ of $Na_2O \cdot 1.5SiO_2$ & $Na_2O \cdot 2B_2O_3$ is 37.3 ± 0.6 KJ/mole. The existing data shows that for

$$2(Na_2O \cdot SiO_2) \longrightarrow Na_2O + Na_2O \cdot 2SiO_2$$

ΔG = 46 Kcal/mole, which is a good approximation for $\Delta\bar{G}_{Na2O}$ for $Na_2O \cdot 1.5SiO_2$. From this value, and the estimated $\Delta\bar{G}_{Na2O}$ of $Na_2O \cdot 2B_2O_3$ of 63 Kcal/mole, the difference should be (63-46) x 4.187 = 71 KJ/mole.

Most of the discrepancy could originate from an error in the fundamental assumption - that Na^+ is the only current carrying species. Under these high temperatures, and under the ambient air conditions, the relatively high H_2O level (in the glasses, see, e.g. Vissar, et al (10)) could introduce H^+ and OH^- as charge carriers, and any deviation from $t(Na^+) = \underline{1}$ would make a considerable error on relating the EMF measurement to $\Delta\bar{G}_{Na2O}$.

(2) From the known thermodynamic values for the crystalline phases of some sodium borates and silicates, one can "interpolate" a continuous curve, imposing boundary conditions. This, as well as assigning some reasonable ΔG of crystallization enable Hertz(11) to estimate $\Delta\bar{G}_{Na2O}$ along the Na_2O-B_2O_3 line (graph). The same could be done along the Na_2O-SiO_2 line. Those values are usable as guidelines, but the double burden of estimating both glass/crystal transition and borate/silicate mixing would yield less than reliable values for the ternary glass system.

(3) "Optical basicity" is not a measure of Na_2O activity. It rather is a function of the Lewis basicity of the glass network toward a given probe ion.

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EXPERIMENTAL DETERMINATION OF REACTION PRODUCTS OF SULFUR REACTIONS WITH $Na_2O \bullet B_2 \bullet SiO_2$ GLASSES

The Dow sodium-sulfur cell uses glass capillary tubes of a "sodium borate" glass as the electrolyte. This section summarizes determinations of the extent of the following reactions for selected compositions in the ternary system sodium oxide, silicon dioxide, and boron trioxide:

$$\text{N Glass} = \text{N Glass*} + Na_2O$$

$$Na_2O + (3n+1)/4\ S = .25\ Na_2SO_4 + .75\ Na_2S_n$$

Reaction I: $\text{N Glass} + (3n+1)/4\ S = \text{N Glass*} + .25\ Na_2SO_4 + .75\ Na_2S_n$

Where Glass* denotes a glass composition partially depleted of Na_2O.

Work during the last four years has shown that glass electrolyte D406 (Na_2O-$2B_2O_3$-$0.20SiO_2$-$0.16NaCl$) undergoes property changes with exposure to elemental sodium (1) and is apparently chemically reactive with sodium trisulfide (2). D406 glass composition has been used in Dow sodium sulfur cells since the 1970's. The mode of failure for these capillary tubes in cell environments is yet undetermined.

Preliminary data from ESCA (3) and from ion chromatography indicate that D406 may react with sulfur at 300°C for periods of five to thirty days resulting in a tensile strength loss of 200 MPa (29 Kpsi) (4). Work reported here will demonstrate that D406 is not inert towards sulfur over the temperature range of 300-400°C.

An improved glass composition demonstrating superior resistance to sodium metal (5) and to sodium trisulfide (5) was found in glass composition T806 (Na_2O-$1.1B_2O_3$-$1.3SiO_2$).

The results of cell lifetime data on glass composition T806 were disappointing: average lifetime being only about two weeks for cells normally cycled or cells left on open circuit. However, cells cycled only in the single phase region (Na_2S_x, x ~4) last significantly longer. Note, this is in sharp contrast to results obtained with D406 glass electrolyte. D406 cells cycled to or held at Na_2S_3 fail within two weeks (6). These data suggest a problem may exist between T806 glass composition and sulfur. Results from ESCA studies (3), from EDX-electron microscopy studies (7), and from ion chromatography studies showed that further investigation was warranted.

A rapid, cost effective method for following the extent of Reaction I is found in the application of ion chromatography analysis of aqueous extracts of powdered glass samples exposed to sulfur in sealed, evacuated Pyrex glass ampoules. The presence of extremely this surface films corresponding to a depletion of soda at the surface by Reaction I can be shown. A sensitivity of 0.3 μg/ml for sulfate ion allows the detection of sulfate ion which would be caused by a soda depletion layer as thin as 100 Å. Significantly enhanced sensitivities may be possible by applying sample preconcentration techniques that have demonstrated detection capabilities of 0.01 μg/ml for sulfate ion (8). The rapidity of the technique (about 1/2 hr per analysis) and the low cost, allows the construction of kinetic plots for each glass candidate screened. High vacuum techniques such as ESCA would make such an exercise very costly since over twenty glass compositions will be screened. ESCA and electron microscopy techniques will be employed to verify reaction products and surface morphology as needed.

EXPERIMENTAL PROCEDURE

Glass Preparation

Starting reagents for the four families of glasses examined in this work (the A, B, C, and D series) are as follows: sodium metasilicate, Na_2O-SiO_2 (Metso Anhydro 60, P.Q. Corporation), sodium disilicate, Na_2O-$2SiO_2$ (SS-C 200 Pwd., P.Q. Corporation), anhydrous Borax, Na_2O-$2B_2O_3$ (US Borax), and boric anhydride, B_2O_3 (J.T. Baker). Table I (Results Section) lists the compositions of glasses investigated. Glass batch size for each glass prepared is approximately 160 gm. Note that all glass making operations are conducted in a dry room with a relative humidity not exceeding 5%. The powders are mixed, and then fused for 1 to 1.5 hr at 1000°C in a platinum crucible. The melts are stirred at three separate intervals during the melting period. At the end of the fusing period, the molten glass is poured into an aluminum "V"-trough to yield sticks about 15 mm wide. The sticks are broken into 5 cm to 10 cm lengths. These are stored in tightly sealed jars.

Glass Grinding and Sieving

Prior to grinding, glass sticks are vacuum annealed with a holding time of 1 hr at temperatures ranging from 430°C to 460°C and cooled at a rate not exceeding 4°C/min. The annealed glass chunks are then crushed in an alumina mortar and pestle to a mesh size of about -6. Further grinding is performed in three passes through a Braun sample grinder using rotating alumina discs. Sieving is performed through a stack of four sieve trays (60, 80, 100, and 140 mesh size) on a L143 Ro-Tap siever. Sieved fractions are stored in tightly sealed glass vials.

In order to prevent contamination from members of a glass family with greater basicity, grinding and sieving are begun with the glass containing the lowest soda content. Batches of pyrex glass are run through the Braun sample grinder and the sieving trays between preparations of different glass families. Ion chromatographic analyses are performed on samples of these pyrex glasses to check for contamination at the start of grinding of a new glass family.

Sample Preparation

Thirty centimeter lengths of 7 mm Pyrex tubing having both ends open were thoroughly rinsed with deionized water. The center section was then heated in a flame and drawn apart to give two 15 cm lengths having one end flame sealed. These tubes were oven dried for 2 hr at 300°C before cooling to room temperature in dry room atmosphere (ca. 5% RH). Identification marks were then scribed onto the tubes prior loading with glass powder (200 mg) and sulfur (200 mg, 99.9999% from AESAR). Unless otherwise specified, the mesh size of the glass powder is +100-80. The loaded sample tubes are evacuated to give a pressure of not more than 0.050 mm Hg (typically .001 - .005 mm Hg) before flame sealing under vacuum. Note, the vacuum system was trapped with liquid nitrogen to prevent contamination of the samples with pump oil. Sealed sample tubes containing glass powder and sulfur are transferred to heater blocks that maintain the temperature at either 300°C or 400°C until removal for sample analysis. Note, samples are heated in a vertical position to allow maximum contact of glass powder with liquid sulfur.

Sample Workup

Sealed tubes are maintained in a vertical position upon removal for cooling. Sulfur is removed from the glass powder by in situ distillation. A heater block is prewarmed to 300°C prior to the horizontal insertion of the tube end containing the solidified sulfur-glass mixture. Distillation is generally complete within 1/2 hour. Reaction products are extracted from the glass powder surface by either deionized water (pH 7) or by one of three ion chromatograph eluants: (1) 4 mM potassium phthalate-0.4 mM phthalic (pH 3.85), (2) 4 mM potassium hydrogen phthalate (pH 4.5), and (3) 20 mM phthalic acid (pH 2.3). Extraction times are generally limited to 20 sec in order to prevent the extraction solution from becoming too basic by glass dissolution. Where eluant extracts are performed, sufficient eluant is used to prevent the pH from dropping below about 5. Extract pH control is important because it determines solution chemistry occurring after sulfur exposure. Details of this chemistry are presented in section 7 of Appendix A.

Experience has shown that 4 mM potassium hydrogen phthalate is the preferred chromatographic eluant system when acidic workups are performed. The column disturbance peak accompanying sample injections, the "system peak", occurs after sulfate and thiosulfate ions. Integration problems were sometimes encountered with eluant system no. 1 above where the "system peak" elutes a few minutes prior to sulfate. The latter eluant system generally requires pH adjustment with the hydrogen form of Dowex cation exchange resin in order to obtain a flat baseline prior to sulfate elution. Upward sloping baselines invariably caused integration errors on the sulfate peak. This subject is discussed further in section 2 of Appendix A.

Ion Chromatography

Ion chromatography is run on a Wescan 266 Ion Chromatography Module incorporating a high sensitivity conductivity detector, thermally insulated column compartment, and sample injector valve fitted with a 250 μl loop. Ion separation is achieved on a Wescan standard anion column (269-001) equipped with an anion guard cartridge (Wescan 269-003). Flow rates used (see Table I) were delivered by a Waters Associates, Inc., chromatography pump (model M 6000A). The conductivity detector is operated at a full scale sensitivity of 1 μmho. The detector output is plotted and integrated on a Shimadzu C-R1B Chromatopac. Parameter settings for the integrator can be found in Appendix B. Elution times and flow rates are shown in Table I.

TABLE I

RETENTION TIMES AND FLOW RATES USED IN CHROMATOGRAPHIC SEPARATIONS

		Elution Times		
Eluant System	Flow Rate	SO_4^{2-}	$S_2O_3^{2-}$	"System Peak"
4 mM KHP-0.4 mM PA	3.0 ml/min	16.8 min	21.2 min	ca. 7-12 min
4 mM KHP	2.0	11.7	17.0	17-18 min
20 mM PA	2.0	7.5	----	2-3 min

Note: KHP = potassium hydrogen phthalate and PA = phthalic acid.

Linear detector responses were obtained for sulfate and thiosulfate ions in the solution concentrations used in this work. Appendix C shows sample calibration plots for the 4 mM KHP-0.4 mM PA eluant system. Response factors do change with eluant system, lower pH systems giving more sensitivity.

RESULTS

Sulfur Exposure of Selected Glasses

The composition of glasses screened against sulfur are listed in Table II. Glass densities were measured for each of the four glass series. Densities are reported in Table XXXIII of Appendix J.

TABLE II

GLASS COMPOSITIONS STUDIED

	"Cation Percentages"		
Code Name	Na_2O	"Si_2O_4"	B_2O_3
LBA-45	0.45	0.275	0.275
LBA-40	0.40	0.300	0.300
LBA-35	0.35	0.325	0.325
LBA-33.3	0.333	0.333	0.333
T806	0.364	0.236	0.400
LBB-40	0.40	0.200	0.400
LBB-35	0.35	0.217	0.433
LBB-30	0.30	0.233	0.467
LBB-25	0.25	0.250	0.500
LBC-40	0.40	0.150	0.450
LBC-35	0.35	0.1625	0.4875
LBC-30	0.30	0.175	0.525
LBC-27.2	0.272	0.182	0.546
LBD-39	0.39	0.061	0.549
LBD-35	0.35	0.065	0.588
LBD-31	0.31	0.069	0.621
[D406	0.307	0.031	0.614 +(0.049)] (NaCl)

Specific numeric data are tabulated in Appendix D for various exposure times to sulfur both at 400°C and at 300°C. Figures 1-4 show kinetic plots of the reaction pair shown below normalized to the calculated loss sodium oxide (soda) per square centimeter of glass surface in $\mu g\ cm^{-2}$. The measured quantity is total sulfate ion produced.

$$\text{Glass} = \text{Glass}^* + Na_2O$$

$$Na_2O + (3n+1)\ S = .25\ Na_2SO_4 + .75\ Na_2Sn$$

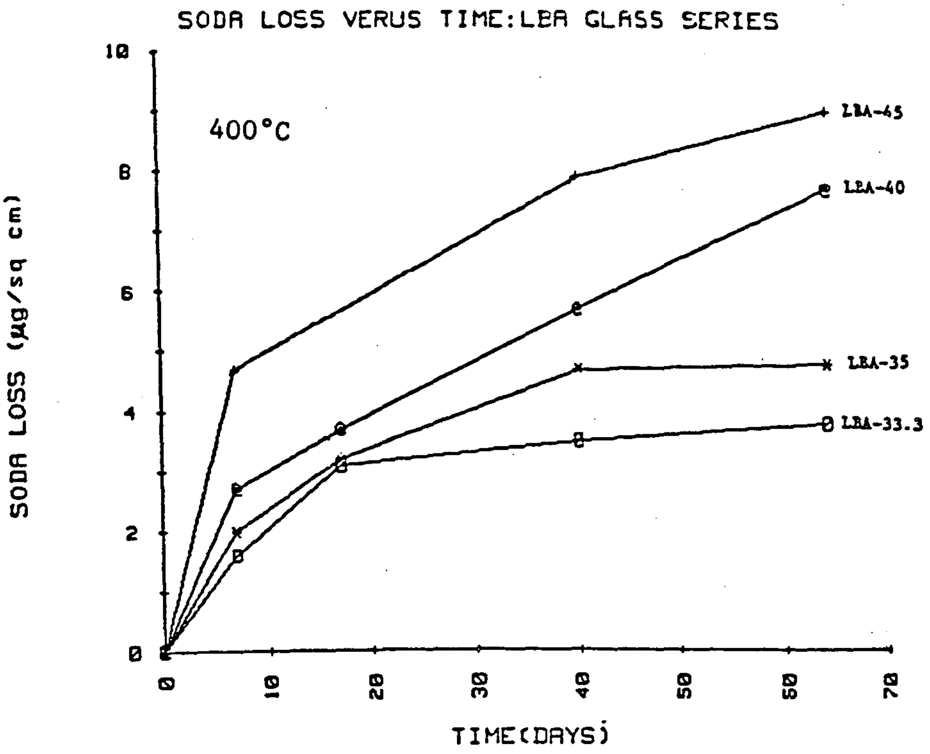
$$\text{Net:} \quad \text{Glass} + (3n+1)\ S = \text{Glass}^* + .25\ Na_2SO_4 + .75\ Na_2S_n$$

Where Glass* is a glass partially depleted in sodium oxide.

Figures 5 and 6 schematically show the extent of reaction on the ternary system Na_2O-B_2O_3-"Si_2O_4" after 28 days at 400°C and 300°C, respectively. It was hoped that much larger breaks in reactivity would be observed when some threshold of sodium oxide content was exceeded. A reactivity break probably exists in the $Na_2O \cdot B_2O_3 \cdot SiO_2$ system examined at some lower sodium oxide content. For example, sulfur corrosion is not detected when Pyrex glass is sulfur exposed at 400°C. Pyrex [80.5% SiO_2, 12.9% B_2O_3, 3.8% Na_2O, 0.4% K_2O and 2.2% Al_2O_3] contains 6.6 "cation %" sodium oxide and is shown in Figure 5 where K_2O and Al_2O_3 are omitted.

Figure 1

Calculated Sodium Oxide (Soda) Loss From LBA Glass Series Versus Time



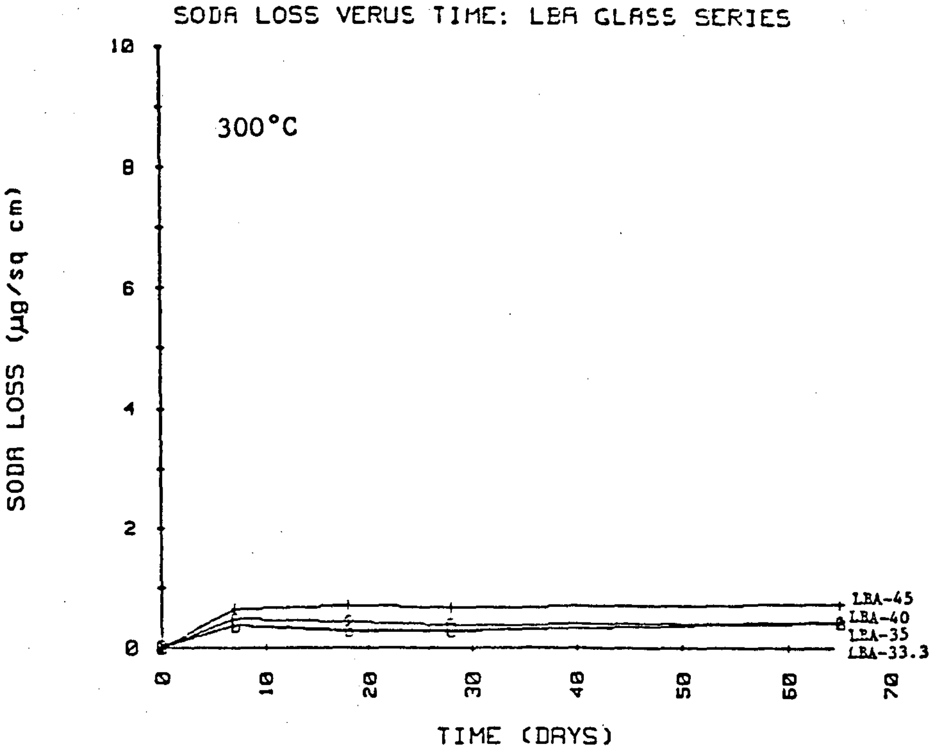


Figure 2

Calculated Sodium Oxide Loss From T806 and LBB Glass Series Versus Time

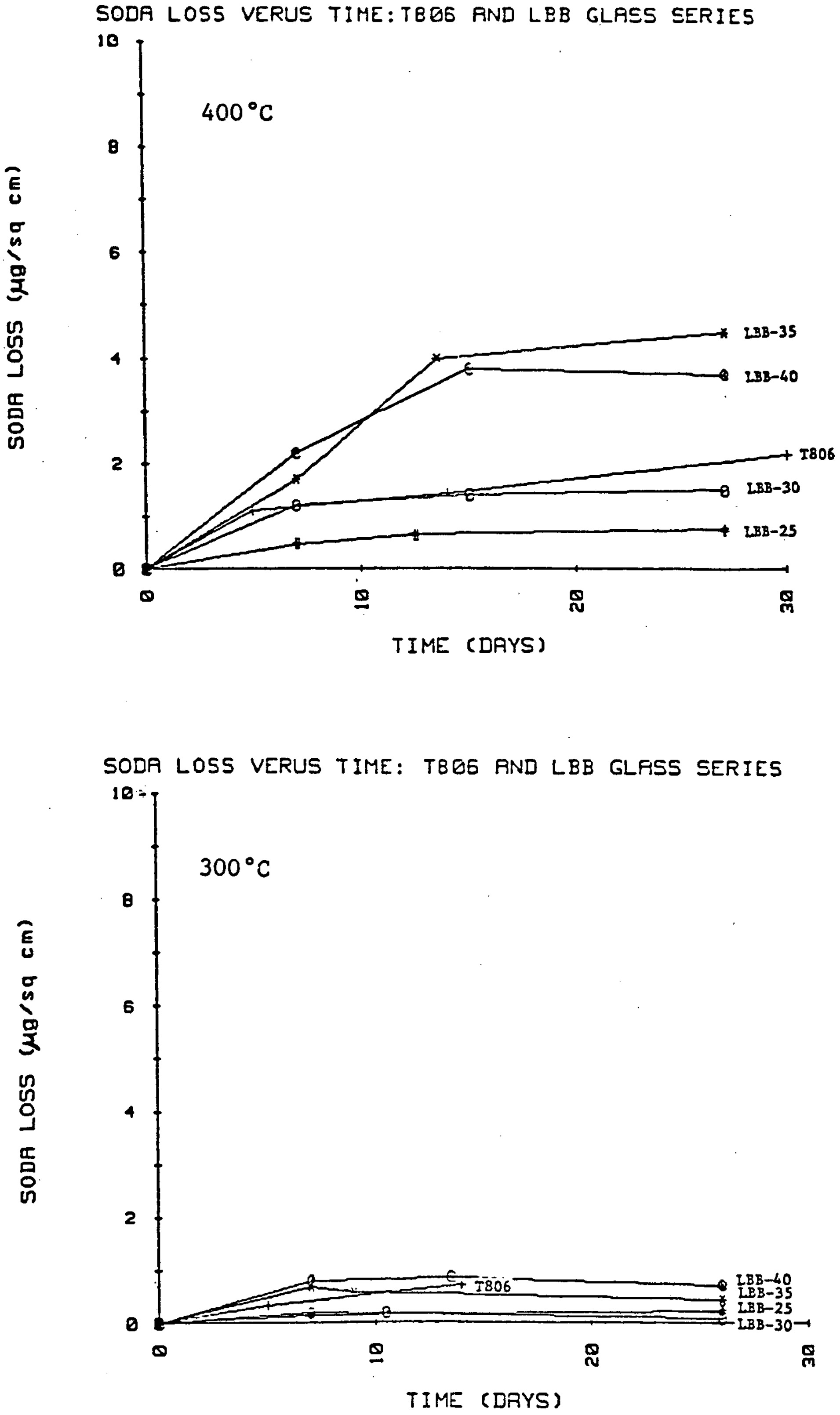


Figure 3

Calculated Sodium Oxide (Soda) Loss From LBC Glass Series Versus Time

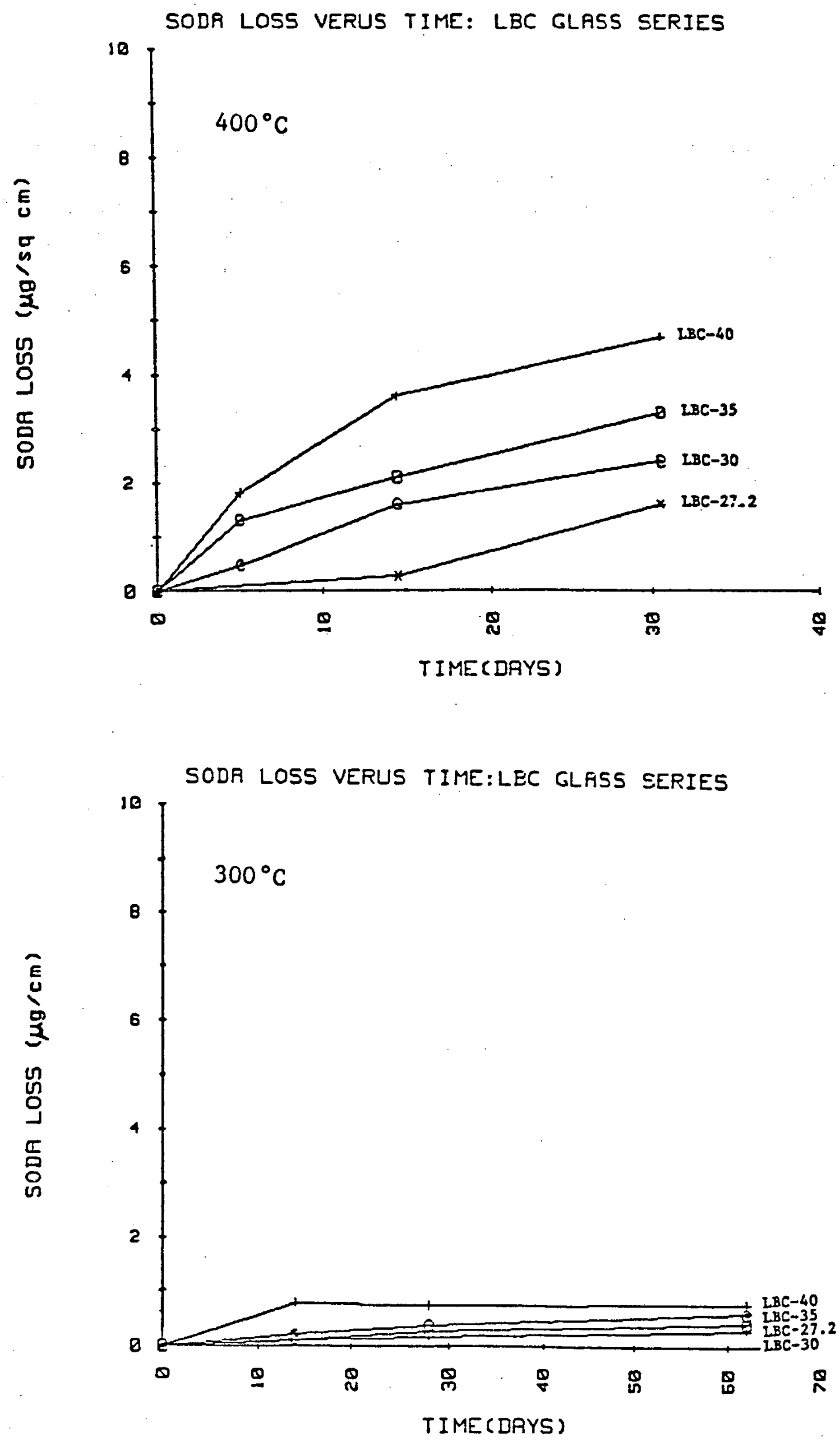


Figure 4

Calculated Sodium Oxide Loss From D406 and LBD Glass Series Versus Time

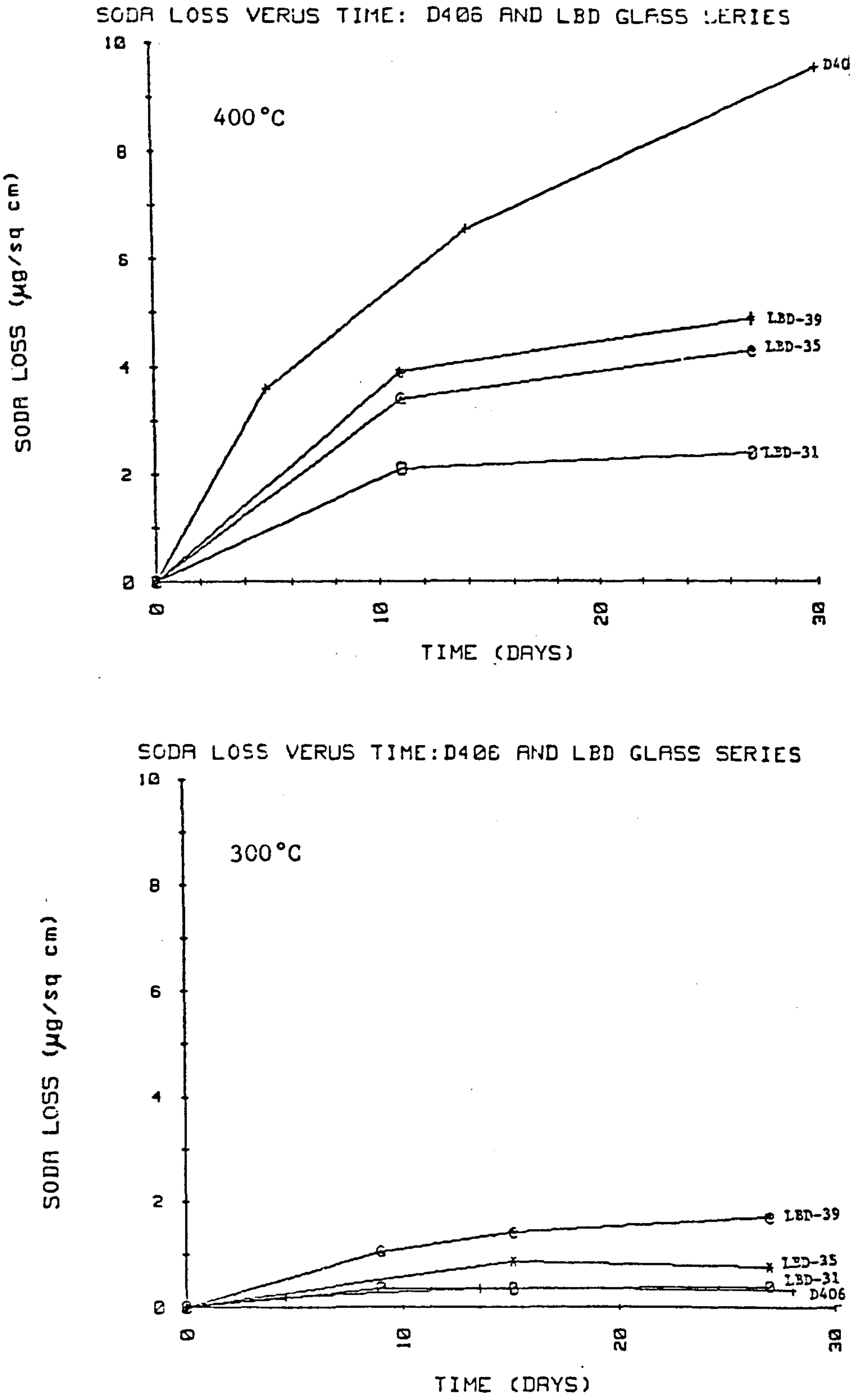
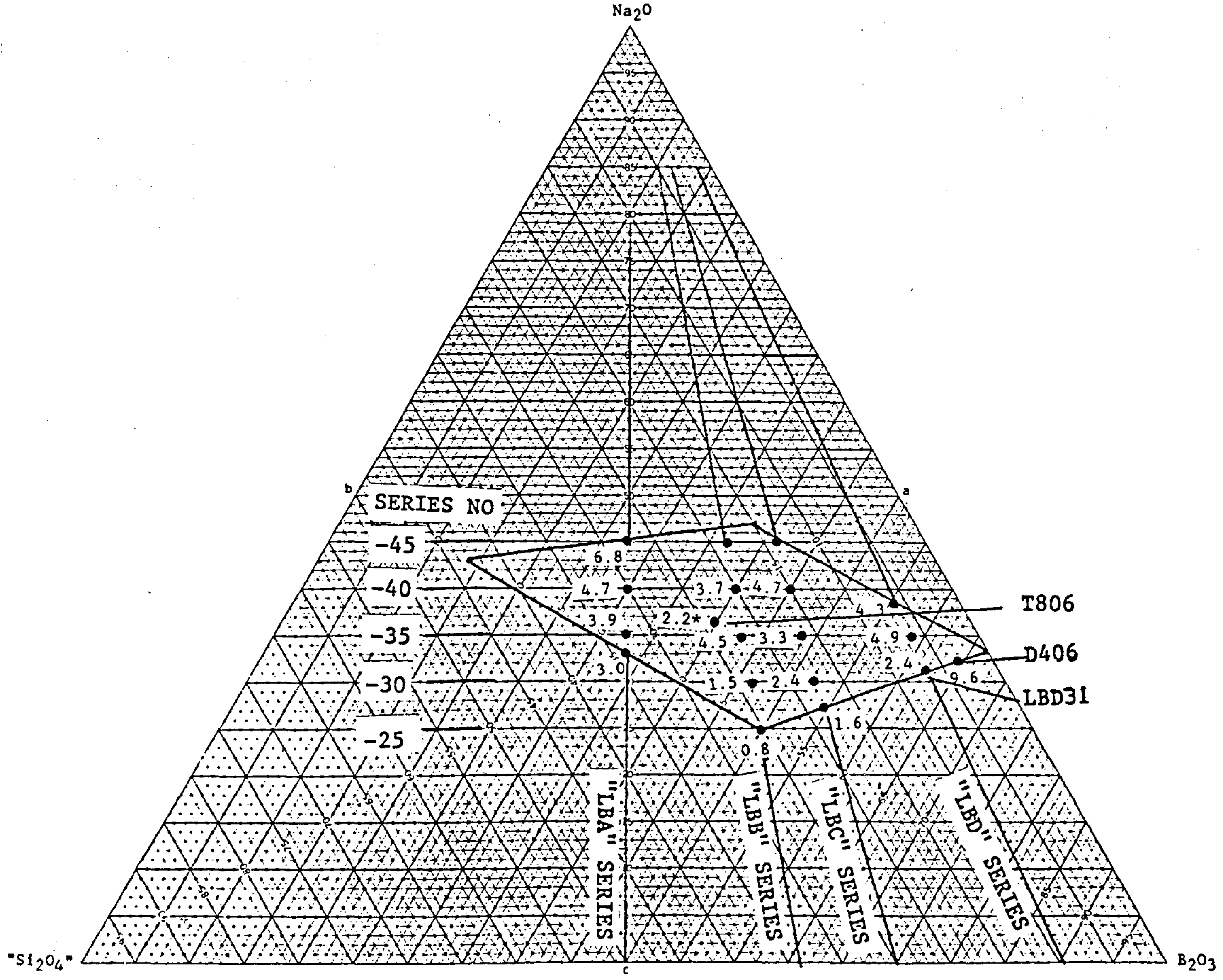


Figure 5

Calculated Sodium Oxide Extracted From Glass Via Reaction I
400°C Exposure for 28 Days



Reaction I: N Glass + (3n+1) S = N Glass* + Na_2SO_4 + 3 Na_2S_n

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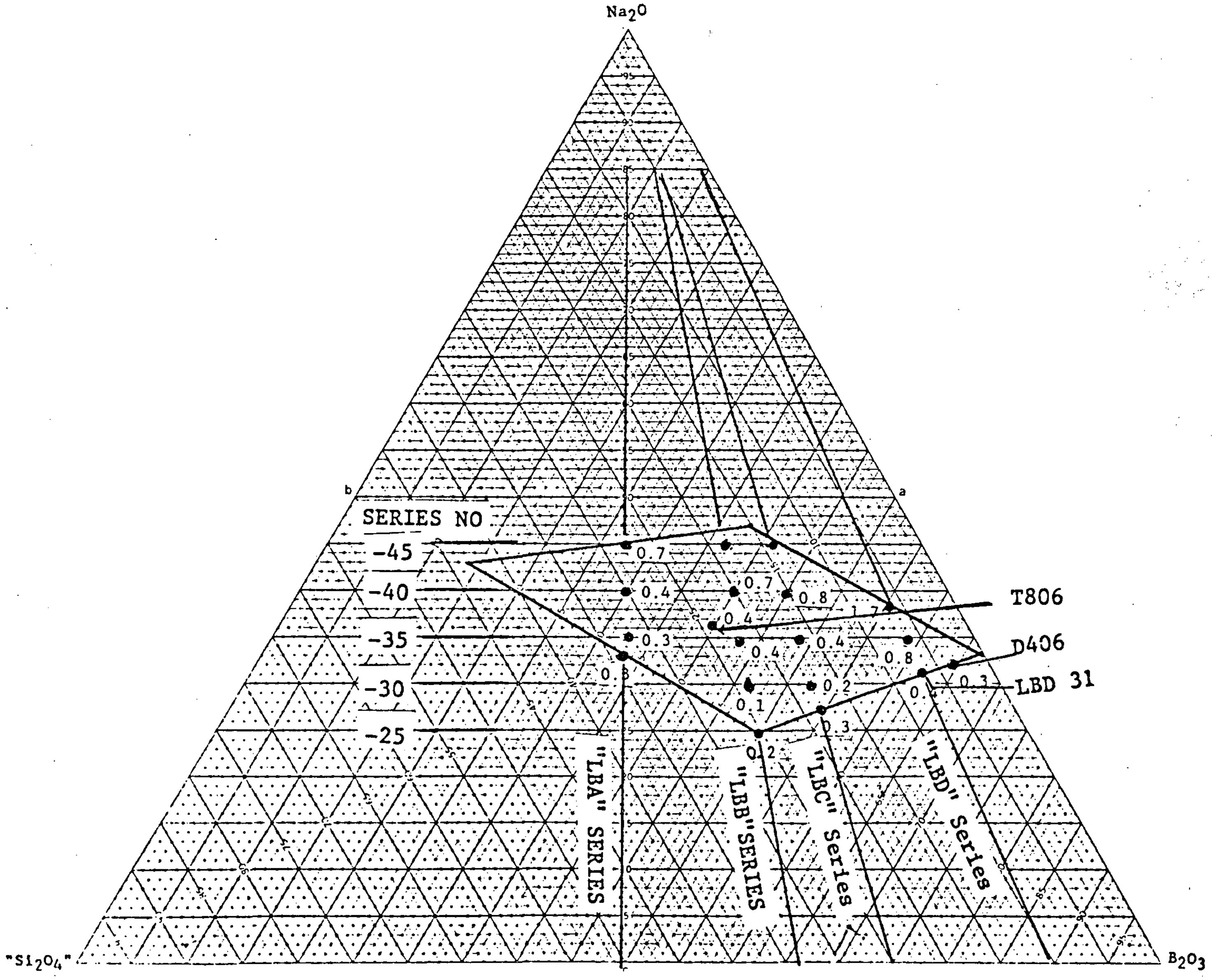
Note: Sodium oxide losses are reported in units of $\mu g\ cm^{-2}$ of glass surface.

Figure 6

Calculated Sodium Oxide Extracted From Glass Via Reaction I
300°C Exposure for 28 Days



<u>Reaction</u> <u>I:</u> N Glass + (3n+1) S = N Glass* + Na_2SO_4 + 3 Na_2S_n

---

Note: Sodium oxide losses are reported in units of $\mu g\ cm^{-2}$ of glass surface.

In addition to low reactivity, a glass must have sufficiently low resistivity for use as a solid electrolyte; the resistivity of D406 is $2.4 \times 10^4\ \Omega$cm. The resistivity for the lowest soda members of the four glass families studied is estimated at $\sim 10^5\ \Omega$cm. The latter value is already larger than what is desirable; even lower soda contents (chosen to eliminate sulfur reactivity) would probably make the glasses unusable as solid electrolytes.

Since no such breaks in sulfur reactivity were observed in the range of compositions examined, we decided to pursue detailed comparisons of glass compositions D406 and T806. The goal being to test the premise that the preceding reaction is responsible for early cell failures of sodium-sulfur cells using T806 as the electrolyte.

<u>Comparisons of Sulfur Corrosion For D406 and T806 Glass Powders</u>

Prior to intermediate temperature testing to be described shortly, the best available data for sulfur corrosion of glass compositions D406 (Na_2O-$2B_2O_3$-$0.2SiO_2$-$0.16NaCl$) and T806 (Na_2O-$1.1B_2O_3$-$1.3SiO_2$) via Reaction I at 400°C and 300°C are listed in Table III.

Reaction I: $4\ Na_2O$ (from glass) $+ (3n+1)\ S = Na_2SO_4 + 3\ Na_2S_n$

TABLE III

EXTENT OF SULFUR CORROSION FOR GLASSES D406 AND T806

Temperature	Exposure Time	Sodium oxide loss ($\mu g\ cm^{-2}$) ± Std. Dev. Glass D406	Glass T806
400°C	5 days	3.6 ± 0.2 (No. = 6)	1.11 ± 0.16 (No. = 5)
300°C	5 days	<u>ca.</u> 0.2	0.32 ± 0.06 (No. = 8)
300°C	21 days	0.33 ± 0.12 (No. = 4)	-----------
300°C	74 days	0.57 ± 0.17 (No. = 5)	-----------

At 400°C, D406 corrodes significantly faster than T806. Meaningful comparisons of 300°C corrosion rates are difficult because of the small amounts of reaction product (sulfate ion) and low level contamination of the starting glasses with sulfate ion, the detectable corrosion product. Sulfate levels resulting from the workup of glass powders never exposed to sulfur were used to calculate "equivalent" corrosion values via Reaction I. Their contribution, 0.05-0.1 ug Na_2O/cm^2, accounts for 20-50% of the 300°C corrosion rates.

In an attempt to extrapolate to 300°C corrosion values as well as to obtain some physical insight into the sulfur corrosion mechanism of each glass, corrosion measurements were determined with exposure times of 14 and 30 days at the following temperatures: 325°C, 350°C, and 400°C. The test results are summarized in Table IV.

TABLE IV

SULFUR CORROSION VIA REACTION I AS A FUNCTION OF TEMPERATURE

Glass	Temp. (°C)	Sodium oxide lost per cm^2 (μg/cm^2) After 14 days (Avg. of 3)	After 30 days (Avg. of 2)
D406	400	6.55 ± 0.26	9.59 ± 0.34
D406	350	1.13 ± 0.03	1.71 ± 0.12
D406	325	0.47 ± 0.11	0.74 ± 0.26
D406	[300]	[0.16] extrapolated	[0.26]
T806	400	1.44 ± 0.04	2.18 ± 0.2
T806	350	0.61 ± 0.13	0.43 ± 0.07
T806	325	0.42 ± 0.02	0.43 ± 0.01
T806	[300]	[0.25] extrapolated	

Respective measurements after sulfur exposure of T806 and D406 for 14 days are shown in Figure 7 where the natural logarithm of total corrosion is plotted against the reciprocal of absolute temperature (Arrhenius activation plot). Excellent linear fits are obtained for each glass. Note the differing slopes for glasses T806 and D406. This gives rise to large differences in calculated activation energies for sulfur corrosion; the value for D406 is 56.3 Kcal/mole versus 26.7 Kcal/mole for T806. An Arrhenius plot of D406 after sulfur corrosion for 30 days at the above temperatures gives an excellent fit for the data with a calculated activation energy of 54.8 Kcal/mole. The Arrhenius plots for 14 and 30 day D406 are shown together in Figure 8. Also, note the projected 300°C corrosion values for D406 after 14 days (0.16 μg Na_2O cm^{-2}) and 30 days (0.25 μg Na_2O cm^{-2}). An Arrhenius analysis was not performed for T806 after 30 days for reasons to be explained shortly. Arrhenius activation parameters calculated for the above tests are summarized in Table V.

Figure 7

Arrhenius Activation Energy Plots For Glasses D406 and T806 Glasses Exposed To Sulfur For 14 Days

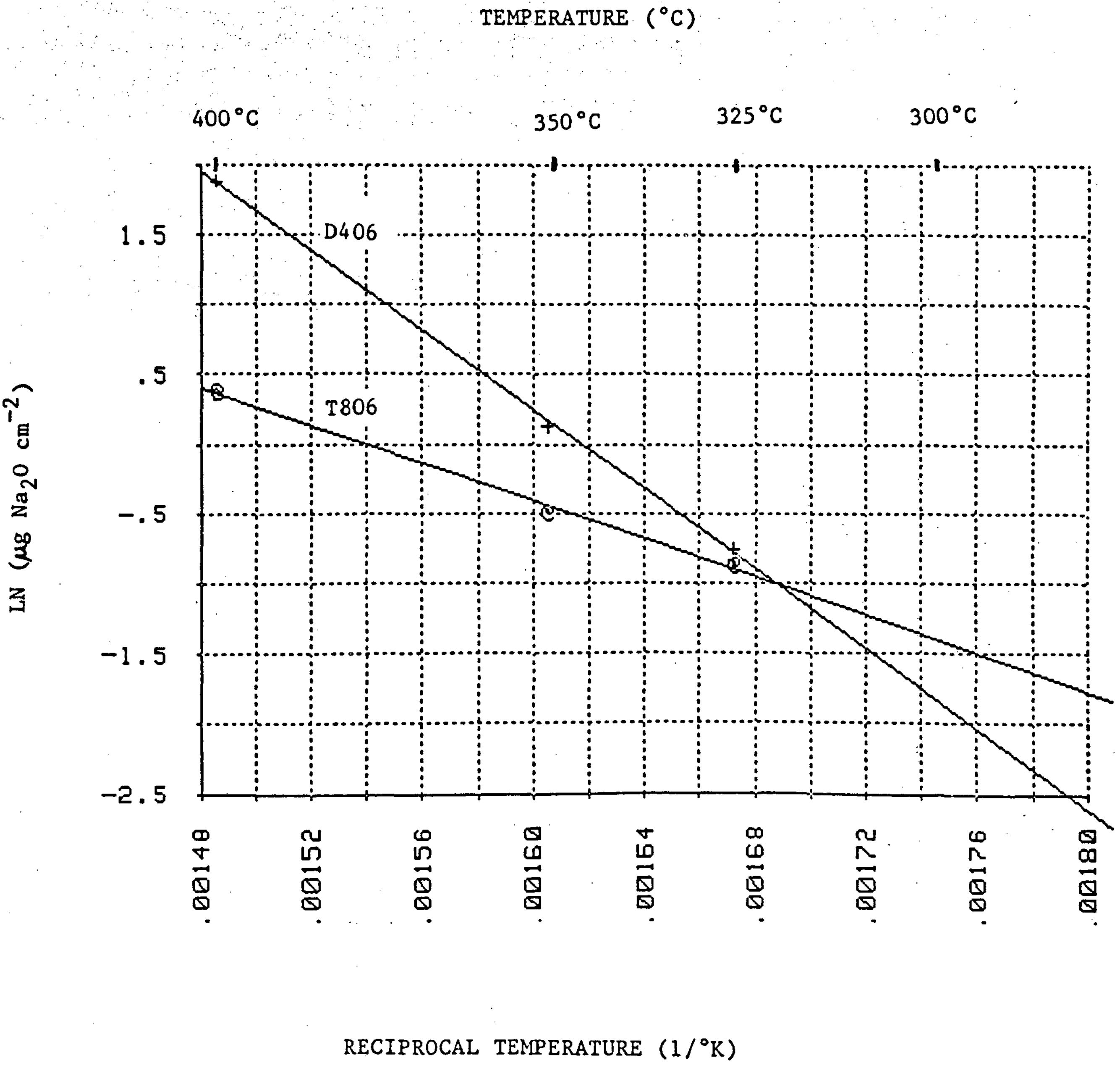


Figure 8

Arrhenius Activation Energy Plots For Glass D406
Comparative Results After 14 Days and After 30 Days

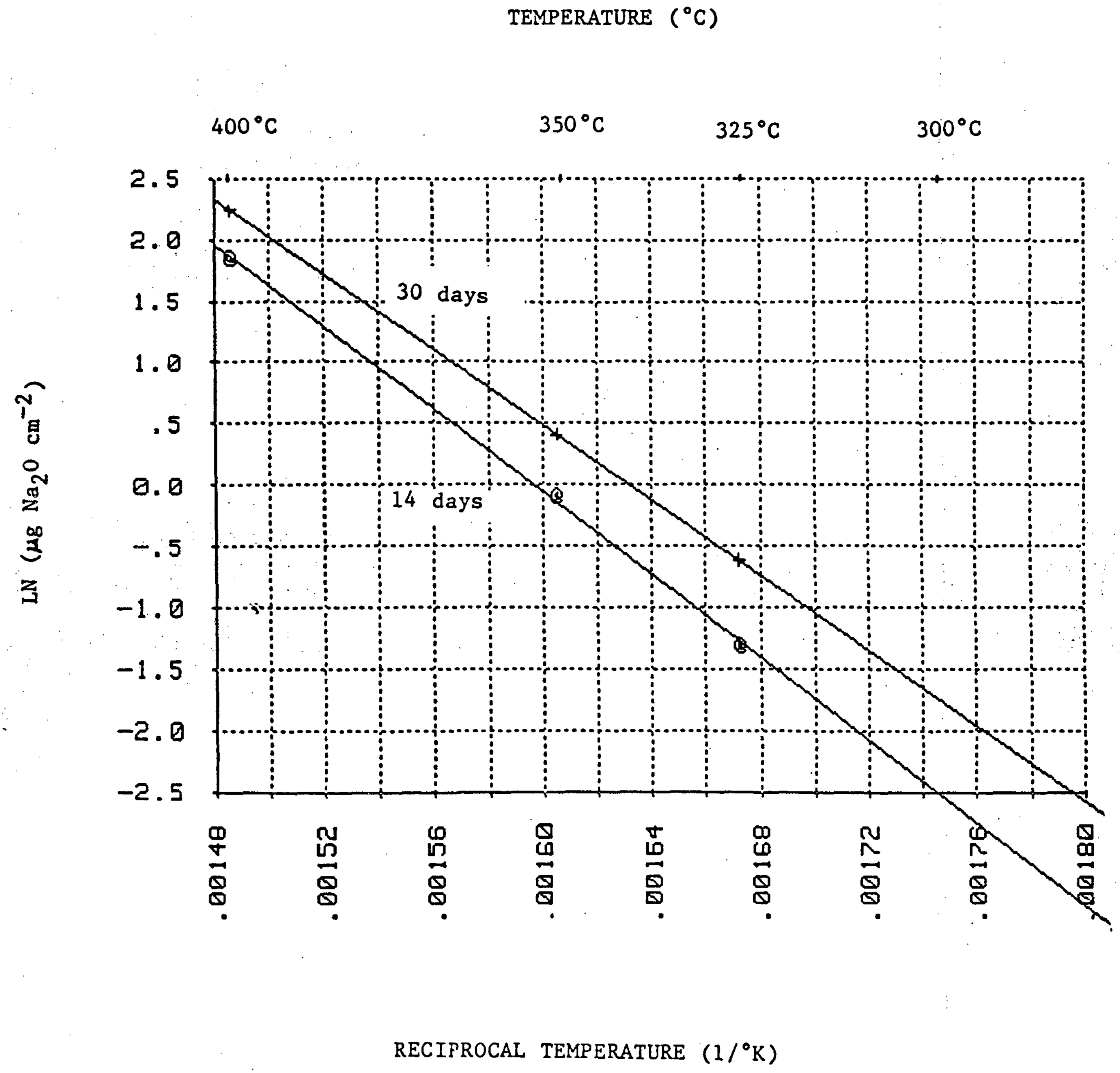


Figure 9

Sodium Oxide Loss From D406 Glass Versus $(\text{Time})^{1/2}$
At Various Exposure Temperatures To Sulfur

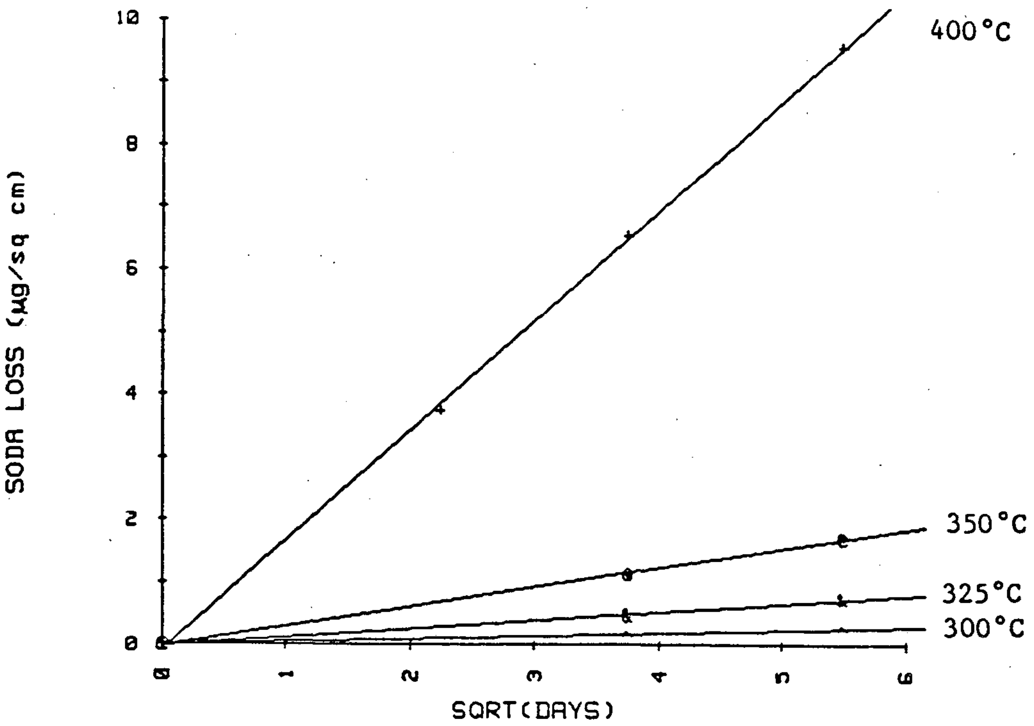


Figure 10

Sodium Oxide Loss From T806 Glass Versus $(\text{Time})^{1/2}$
At Various Exposure Temperatures To Sulfur

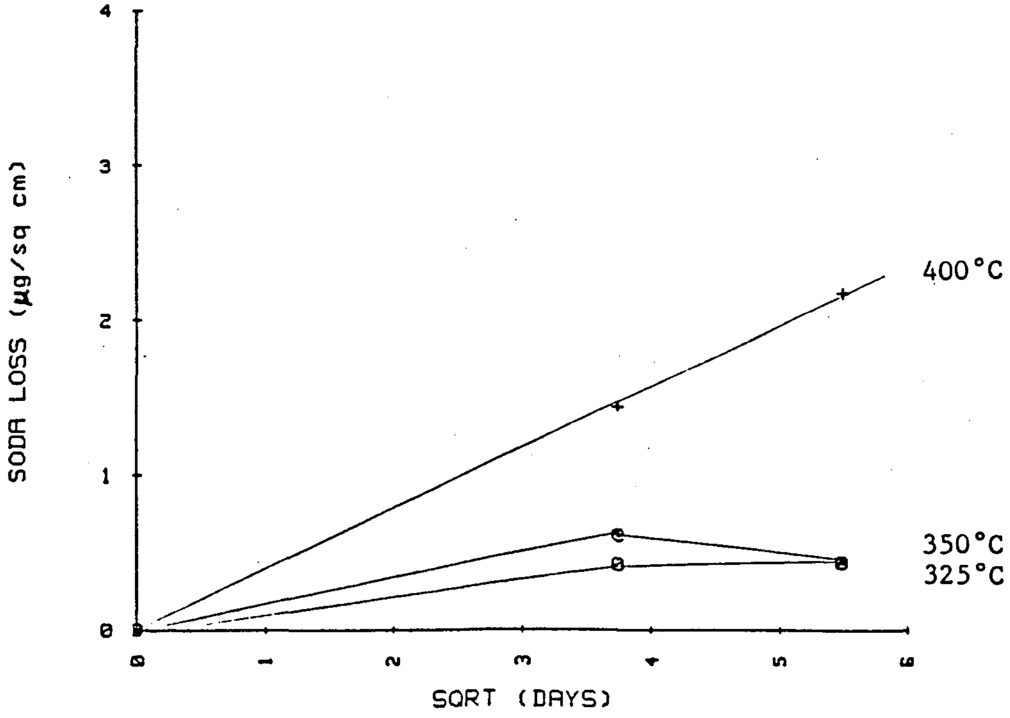


TABLE V

ARRHENIUS ACTIVATION PARAMETERS FOR GLASSES D406 AND T806

MEASUREMENTS AT 325, 350, AND 400°C

Time (Days)	Glass	Activation Energy (Kcal/mole)	Natural Log of Pre-exponential	D_0 (cm^2/sec)	τ_0 Characteristic Vibration Period (sec)
14	D406	56.3	22.972	1.4×10^2	6.3×10^{-18}
30	D406	54.8	22.790	4.5×10^1	2.0×10^{-17}
14	T806	26.7	10.404	1.6×10^{-9}	5.5×10^{-7}
30	T806	---	------		----------

The physical model used for calculation of activation energies is a continuous layer that becomes depleted in sodium oxide to give a smoothly varying concentration gradient. The flux of diffusing species was integrated over time to give a final expression for the total amount of sodium oxide diffusing (Q) from 1 cm^2 of glass surface in time t:

$Q = Q_0 \exp(-Ea/2RT)$ and $Q_0 = 2\, C_0\, [D_0 t/\pi\,]^{1/2} F$

where: $C_0 \equiv$ total concentration of possible diffusing species (O^{2-}) in atoms/cm^3

$F \equiv$ Fraction of species which actually participate, e.g. F may be less than 1 given a distribution of well depths such that some fall below the chemical potential of the solution phase contacting the glass

$t \equiv$ time (sec)

$T \equiv$ absolute temperature (°K)

$Ea \equiv$ activation energy (Kcal/mole)

$D_0 \equiv$ diffusion constant preexponential, e.g. $D = D_0 \exp[-Ea/RT]$

The expression for Q contrasts with expressions for <u>instantaneous rates</u> which are proportional to $e^{-Ea/RT}$. The derivation is reproduced in Appendix F. The extent of reaction is expected to increase with the square root of time. This is precisely what is seen for D406 at each of the three temperatures examined. Refer to Figure 9. Such a kinetic dependence speaks strongly for a rate controlling step involving solid state diffusion. The preexponential term of diffusion coefficients (D_0) is given by the rearranged expression of Q_0:

$$D_0 = \frac{\pi Q_0^2}{4C_0^2 t} \frac{1}{F^2}$$

Values of D_0 for both D406 and T806 are listed in Table V with F=1; all sodium oxide is assumed to react with sulfur according to Reaction I. Although the values of D_0 for D406 glass differ by a factor of ~3, the calculated diffusion coefficients at 400°C and 300°C differ by only 1% and 18% of one another, respectively, at these temperatures. The difference in D_0's is largely compensated for by the small differences in the activation energies.

Contrary to the assumption of total depletion of sodium oxide (F=1), the reaction with sulfur will stop (F<1) when the chemical potentials of sodium oxide in the glass and in the phase contacting the glass are equal. Notice that $D_0 \propto 1/F^2$. This means that for fixed Q_0, the value of D_0 increases by a factor of 100 when only 10% (F=0.1) of the O^{2-} species are able to participate in the sulfur reaction. We have insufficient data to determine the actual value of F.

At 400°C, the square root of time versus corrosion extent is linear for glass T806. Refer to Figure 10. However, this is not the case for corrosion temperatures of 325°C and 350°C where the extent of reaction has not changed (within experimental error) in the time period between 14 days and 30 days. The reason for this departure is not understood. One possibility is that some uncontrolled variable inhibited the later two sample sets. The experiment should be repeated to see whether this inhibition at lower temperatures is reproducible. If it is, one possibility would be the formation of a protective film at temperatures at or below 350°C. Given this departure from the experimental model, no attempt was made to calculate an activation energy for T806 after 30 days of sulfur exposure.

A characteristic vibration period can be calculated from D_0 and the atom hop distance. This quantity (τ_0) is given by:

$$\tau_0 = \frac{a^2}{D_0}$$

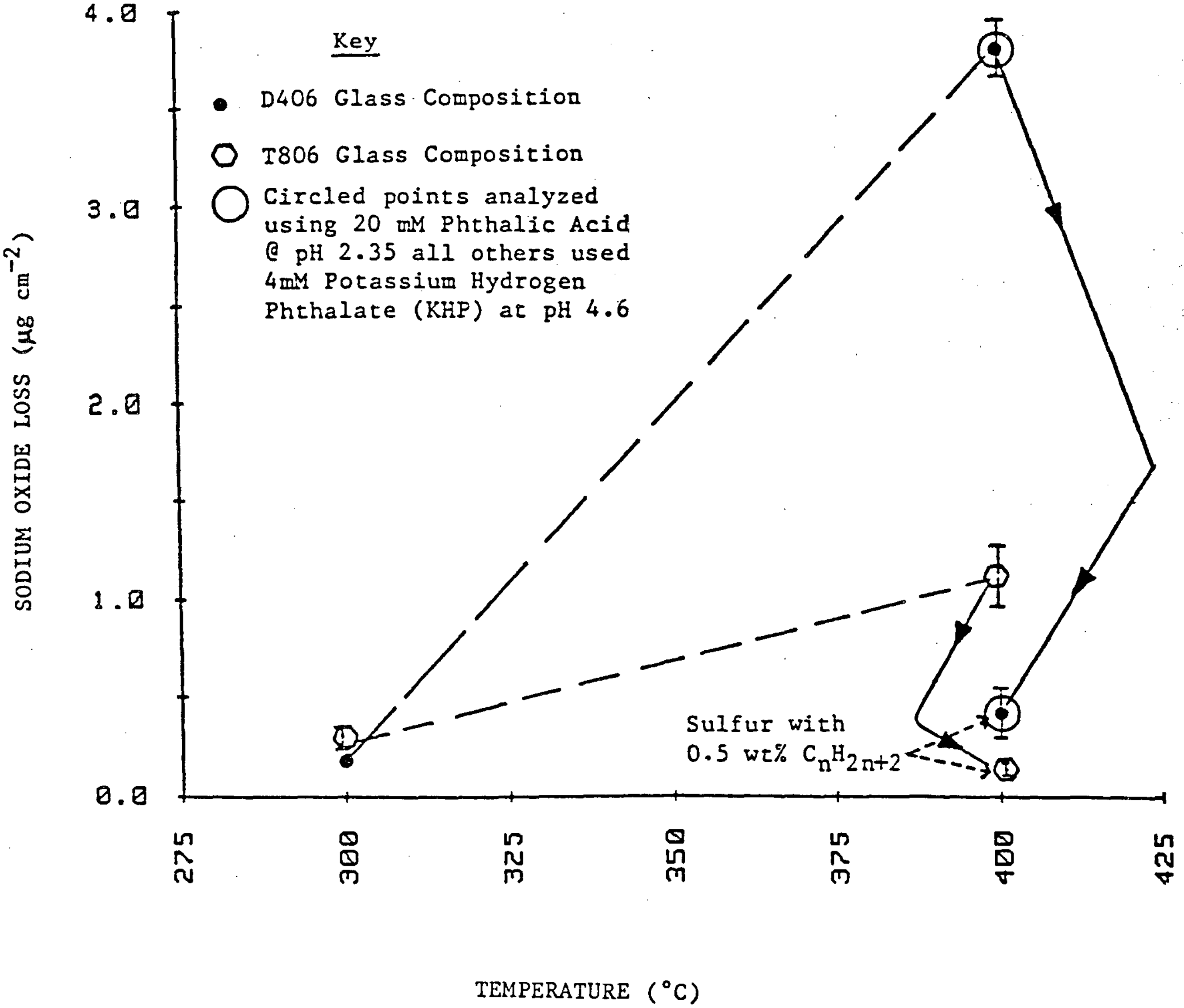
The calculated values are listed in Table V where a hop distance of 3A was assumed. The values obtained for D406 are on the order of 10^3 to 10^4 faster than expected for atomic vibrations. On the other hand, τ_0 for T806 is ~10^7 slower than expected for atomic vibrations. The extreme difference in τ_0 suggest that a fundamental difference may exist in the reaction mechanism of sulfur with sodium oxide in the two glasses. The very large τ_0 for T806 may suggest cooperative motion of more than one atom to affect reaction.

Suppression of Sulfate Formation by Organics

Sulfur corrosion of both glasses D406 and T806 via Reaction I is virtually stopped by the addition of 0.5 wt % of hydrocarbon polymer (poly(4-methyl-1-pentene)) to sulfur. Refer to Figure 11. One possibility we considered was that hydrogen sulfide, generated by the action of sulfur on organic impurities, retards Reaction I by competing for base on the glass surface. Specifically, one might envision an ion exchange reaction between sodium ion in glass and hydrogen from sulfanes (from

Figure 11

Effect of Temperature and Hydrocarbon Spiking on Sulfur Corrosion of Glasses D406 and T806



hydrogen sulfide and sulfur) to yield nonvolatile sodium polysulfides in excess of those formed via Reaction I. This is indeed the case as will be shown below.

$$\text{Na}^+\text{-from glass} + H_2S_x = \text{H}^+\text{-glass} + NaS_xH \xrightarrow{\text{Base}} Na_2S_x$$

A measurement of [polysulfide ion] to [sulfate ion] would confirm whether or not excess polysulfide ions are formed in the presence sulfanes. Since the chromatographic analyses are performed at pH 4.6 or lower, polysulfide ions will be fully protonated and thus not detectable by the conductivity detector. An alternative approach is to perform aerobic oxidation of polysulfides to thiosulfate, a detectable ion. Given the chain length of the polysulfide ion and the stoichiometry for conversion to thiosulfate, the ratio of polysulfide to sulfate may be determined. Since the reactions are carried out in excess sulfur, the polysulfide will be in equilibrium with sulfur and will have an average composition of sodium pentasulfide (9). During sample workup into deionized water, sufficient glass is dissolved to bring the workup solution to pH 9. The highest yield of thiosulfate to pentasulfide will occur in the presence of base and oxygen:

$$2\ Na_2S_5 + 6\ O_2 + 6\ NaOH = 5\ Na_2S_2O_3 + 3\ H_2O.$$

With the above stoichiometry, the three moles of sodium pentasulfide per mole of sodium sulfate via Reaction I would yield a molar ratio of 7.5 sodium thiosulfate to sodium sulfate in the aqueous solution. Since the observed ratios are significantly larger than 7.5 to 1.0, it appears that ion exchange must be occurring. The ratios are tabulated below in Table VI. More detailed information can be found in Appendix D, Table XXX.

TABLE VI

MOLAR RATIOS OF $S_2O_3^{2-}$ TO SO_4^{2-} AFTER OXIDATIVE WORKUP OF GLASS POWDERS EXPOSED TO ORGANIC SPIKED SULFUR

Glass	Exposure Temp.	$[S_2O_3]$ final/ $[SO_4]$ init
D406	300	------
D406	400	48
T806	300	77
T806	400	111

Stopping sulfate production by spiking with organics may not be beneficial since replacement of sodium ion with hydrogen ion could well generate internal stresses (10). In an effort to check for potential damage by either sulfate formation or ion exchange, capillaries of T806 glass were exposed to sulfur and to sulfur containing 0.5 wt% organic (18). No evidence of cracks was found for exposure temperatures of 300°C and 400°C with exposure times as long one month. Neither could cracking be induced by crushing one end and/or exposing the capillary to moist air in an attempt to aid cracking by stress corrosion. The particular batch of capillaries (C050852S) used in these experiments was prepared by melting and stirring well at 1200°C. Refer to Appendix G for more details regarding glass melt preparation and fiber spinning conditions. Previous work on capillaries (C082331L) giving cracks after sulfur exposure (19) were prepared with less stirring and melting at 1000°C.

Differing Sulfur Reactivity of T806 Glass As a Function of Glass Preparation Conditions

Two sets of conditions were used to prepare the T806 glass used in this work. Initially, the starting reagents were melted at 1000°C with one or two stirrings over an approximate 1 hr. heating period. It was noticed that stress bars (3mm x 3mm x 41mm) prepared from these melting conditions invariably showed more birefringence than glass prepared from identical starting reagents but with melting conducted at 1200°C with ten stirrings. Refer to Appendix H for more detailed information. Since comparisons were made after identical annealing conditions, we suspected the glass prepared at 1000°C with less stirring might be less uniform than that prepared at 1200°C with more stirring.

Somewhat after the above observation, it was noticed that sulfur corrosion leading to sulfate formation was more rapid with the T806 glass prepared at 1000°C. Two sets of side by side measurements were run with identical chromatographic conditions to eliminate any doubt of this difference. The results are shown below.

TABLE VII

SULFUR CORROSION MEASURED BY SULFATE FORMATION

5 DAYS EXPOSURE TO SULFUR AT 400°C

	Measured Sulfur Corrosion (μg Na_2O/cm^2)		Reactivity Ratio
Mesh Size	1000°C melt prepared glass	1200°C melt prepared glass	1000°C melt glass / 1200°C melt glass
+100-80	2.01 ± 0.04 (n=3)	1.06 ± 0.04 (n=3)	1.9
+140-100	2.4 ± 0.2 (n=2)	1.4 ± 0.2 (n=2)	1.7

Numbers following means are standard deviations and numbers in "( )" are the number of samples run.

The above reactivity differences were not caused by bulk composition differences or due to differences in specific surface area. The results of elemental analyses and specific surface area measurements for the very same batches of +140-100 mesh T806 glass powders used in the above reactivity comparisons are shown below:

Calcd. for Na_2O-1.1B_2O_3-1.3SiO_2; Na: 21.2%; Si: 16.9%; B: 11.1%; O:50.9%.
Found (1200°C melt) ; Na: 21.7% Si: 17.9%; B and O not run.
Found (1000°C melt) ; Na: 21.7%; Si: 17.9% ;B and O not run.

Specific surface area (3 point BET using Krypton; determinations by Quantachrome Corporation); 1200°C melt prepared glass: 593 cm^2/g; 1000°C melt prepared glass: 576 cm^2/g.

The present feeling is that the 1000°C melted T806 batches may contain composition differences from one region to the next while still having the same average bulk composition. Localized regions of greater sodium oxide content are expected to react more rapidly. As a follow up to this study, scanning Auger composition measurements at several locations on flat, polished T806 specimens will be run. Comparison of variations found on T806 prepared at each of the melting conditions may provide further evidence for the suspected composition variations in the 1000°C melt prepared T806 glass.

Differing Rates of Sulfate Production Dependent on Glass/Sulfur Ratio

Exposure of D406 glass powder (200 mg, +80-60 mesh, 51 cm^2) to sulfur for 6.5 days at 400°C resulted in a threefold reduction of sulfate production when the amount of sulfur was increased from 5 mg to 1000 mg. Refer to the upper line in Figure 12 . In analogy to sulfate suppression with organic spiked sulfur, it was wondered if small amounts of hydrogen

Figure 12

Effect of Changing Glass to Sulfur Ratio
D406 Glass (Fixed Mass = 200 mg) Exposed to Sulfur at 400°C

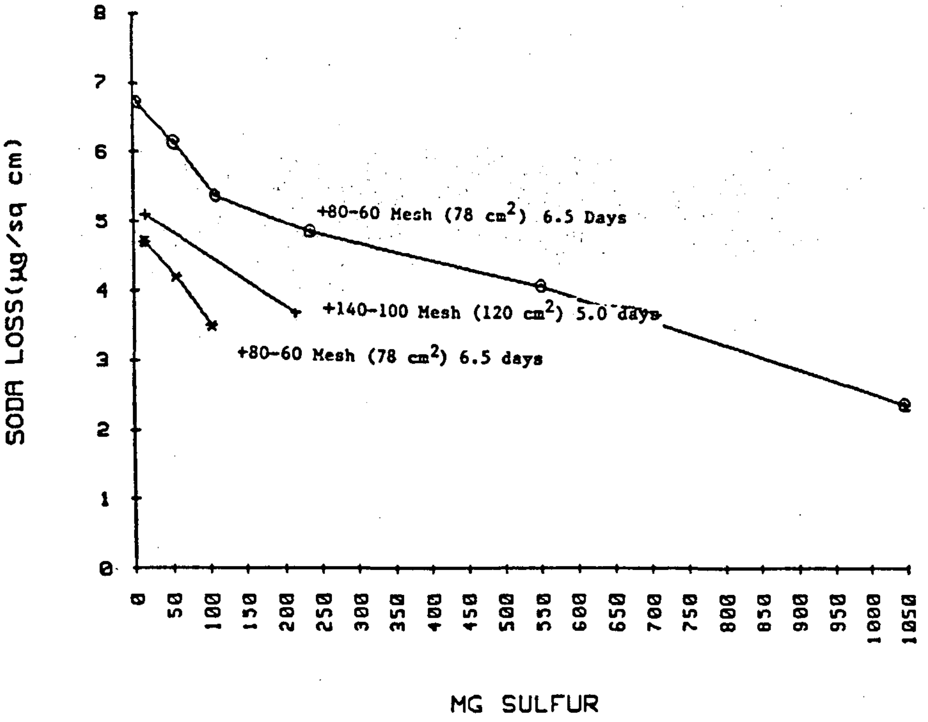
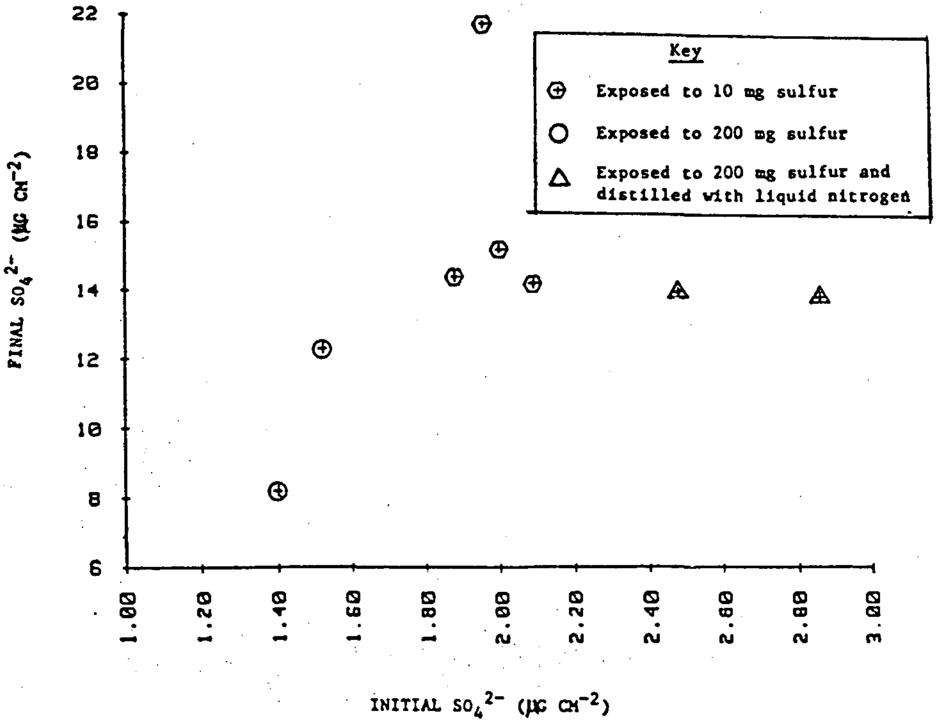


Figure 13

Comparison of Initial Sulfate From Sulfur Corrosion of D406 to
Subsequent Total Sulfate via Bromine Oxidation of the Workup Solution
Sulfur Exposed for 5 Days at 400°C



ion, generated from low level organic impurities in the sulfur, might be responsible sulfate retardation with increasing amounts of sulfur. Larger quantities of sulfur would presumably carry in more hydrogen ion to suppress sulfate production.

The experiment described here indicates some factor other than trace hydrogen sulfide is responsible for changes observed in sulfate production with different ratios of sulfur to glass powder. Two sample groups of D406 powder (200 mg, 51 cm^2) were exposed to either of two amounts of sulfur (10 mg and 200 mg) for five days at 400°C. Following in situ sulfur distillation and sample workup in deionized water, sulfate levels were determined. The amount of sulfate produced in samples having 10 mg of sulfur was 40% larger than those having 200 mg sulfur. These data are shown as the middle line of Figure 12. Following determination of initial sulfate content, the workup solutions were subsequently treated with excess bromine to oxidize sodium polysulfides (as well as any other sulfur species) to sulfate. Referring to Figure 13, it is seen that total sulfate reflecting the sum of initial sulfate and sodium polysulfides is essentially independent of the initial sulfate formed. If ion exchange were responsible for the reduced levels of sulfate (prior to bromine oxidation) in samples containing 200 mg of sulfur, additional polysulfide would have formed. If this happened, the additional polysulfide would be oxidized to give more sulfate so that the final to initial sulfate ratio would be greater.

An as yet unexplained phenomenon was observed in the above experiments. The amount of initial sulfate detected was affected by the in situ distillation procedure. Normal procedure has the tube end containing glass powder and sulfur inserted into a 300°C heater block with the opposite end exposed to ambient air. If the empty end is chilled in liquid nitrogen rather than ambient air, the amount of sulfate ion increases. Refer to data Table XXVII found in Appendix D for specific numbers and also to Figure 13. If the specimens are first distilled normally to give glass powder free of sulfur and the powder (still in the sealed tube) is again inserted into the heater block and the opposite end (the one containing sulfur) is chilled in liquid nitrogen, the sulfate level does not increase. However, normally distilled samples remixed with sulfur by heating in an upright position and subsequently distilled with liquid nitrogen give additional sulfate.

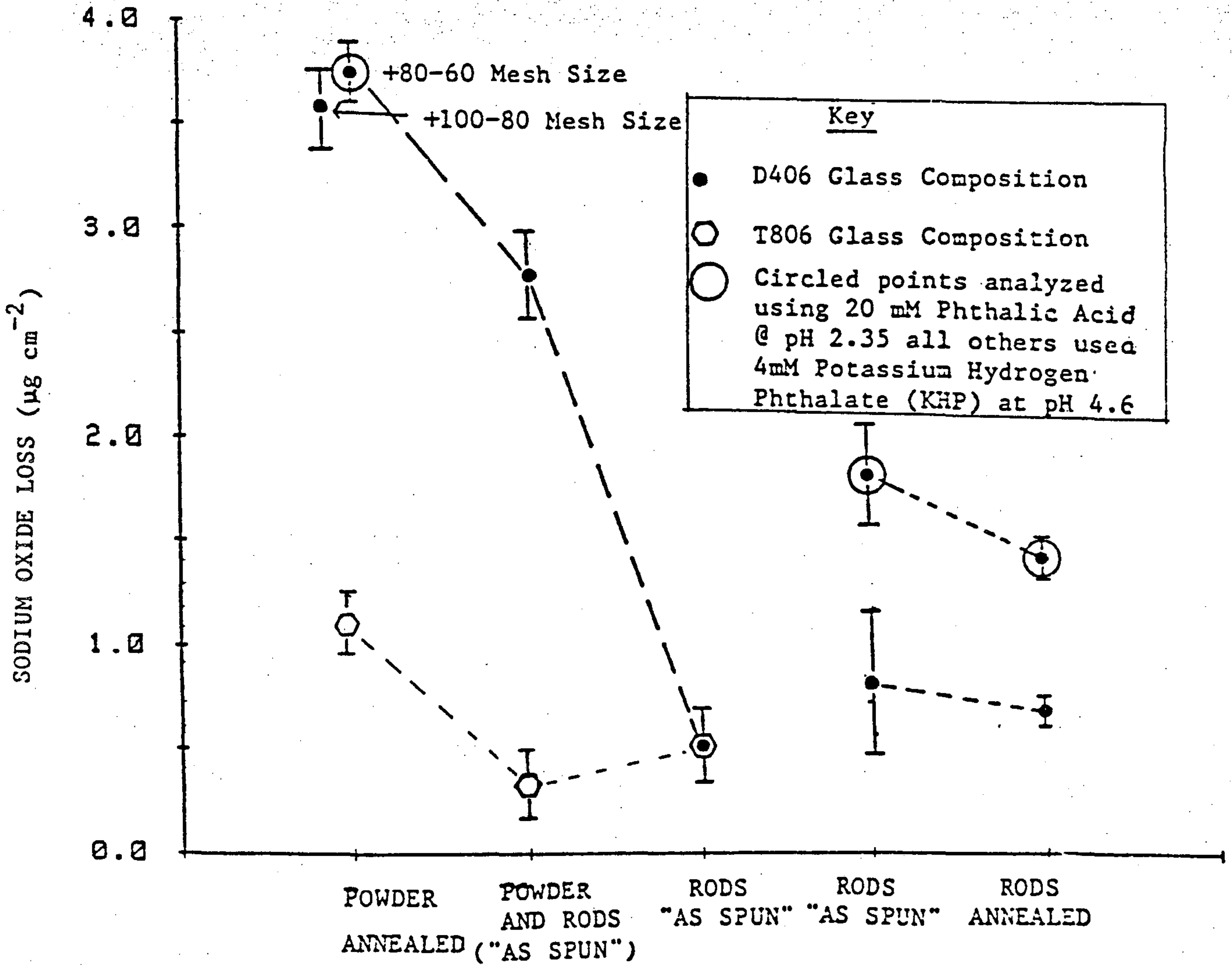
Contrasting Corrosion Rates For Powdered Glass Versus 80 um Rods

Figure 14 contrasts the degree of sulfur corrosion obtained with annealed glass powders to those obtained with 80 μm diameter rods both annealed and "as spun". Data are presented for both D406 and T806 glass compositions. The corrosion rates are significantly lower for the rods as compared to the powders for both glasses. Since the powder surface areas were accurately determined (within 2%) by 3 point BET analyses, some factor other than incorrect areas must be responsible for the observed differences.

We considered the possibility that the rods may somehow suppress the corrosion rate. Figure 14 shows the results of a preliminary experiment where the corrosion rates of mixed samples of rods and glass powder were

Figure 14

Sulfur Corrosion: Glass Powder Versus 80 µm Rods
5 Day Sulfur Exposure at 400°C



determined. The contribution from the high purity rods (max. 0.6 µg Na_2O/cm^2) was neglected and the corrosion rate was calculated solely on the mass of the glass powder; this gives a maximum number for the powder corrosion rate. Rates obtained for mixed samples of rods and powder are significantly less (24%) than for those obtained with powder only. We have no explanation for this at present.

Effect of Rod Thermal History

Comparative corrosion data are shown in Figure 14 for "as spun" and annealed glass rods. Two different chromatographic eluants were used in otherwise identical sample workups and analyses. The preferred eluant (4 mM KHP- pH 4.6) gives indistinguishable corrosion rates for "as spun" versus annealed rods. This is true for both D406 and T806 glasses. This eluant dissolves the glass more slowly and thereby reduces background sulfate contamination from low level contamination of starting glasses with sulfate.

DISCUSSION

A general trend observed is increasing sulfur-glass reactivity as the molar percentage of sodium oxide increases. This can be seen in 300°C data shown in Figure 6. The same general trend applies to the glasses at 400°C, with the exception of the highly reactive D406 glass. Two factors limit precise comparisons of the corrosion values reported. At 300°C, low level sulfate contamination of the starting glasses contributes an equivalent corrosion number of 0.1 µg cm^{-2}. This introduces a sizable uncertainty for the less reactive reactive glasses sulfur exposed at 300°C. The second factor is the statistical uncertainty of the corrosion values; 400°C measurements on sample groups of ten specimens gave coefficients of variation from 5% (D406) to 12% (LBB-40) with extreme values ranging from 8 to 20% of the mean, respectively. Corrosion values reported in the composition diagrams are based on single sample determinations except for D406 and T806. This is also true for values in the kinetic plots.

It was hoped that much larger differences of glass-sulfur reactivity would be observed when some threshold of sodium oxide content was exceeded; this was not the case. Given this result, it seemed most appropriate to pursue detailed comparisons of the two glasses of primary interest, D406 and T806, in order to either prove or reject the premise that Reaction I is responsible for early failure of T806 capillaries in sodium-sulfur cells.

D406 glass composition is one of the least reactive glass at 300°C but is the most reactive glass at 400°C. The calculated soda loss of 9.6 µg cm^{-2} corresponds to a soda depletion depth of approximately 0.2 µm assuming the soda is totally depleted within the reaction layer. This estimate was made by considering the sodium oxide loss from a single face of a 1 cm cube of D406 glass with density 2.3 g cm^{-3} being composed of 27.8 wt % soda. The cube contains 639,000 ug of soda. The arithmetic is as follows:

$$9.6\ \mu g\ cm^{-2}/639000\ \mu g\ cm^{-3} \times 10^{4}\ \mu m/cm = 0.15\ \mu m.$$

Partial soda depletion would necessarily correspond to greater reaction depths. A similar depth estimate for T806 with the same exposure conditions gives 0.033 μm from a sodium oxide loss of 2.2 $\mu g\ cm^{-2}$.

Both T806 and D406 have similar sulfur reactivities at 300°C given the limitations of direct measurement at 300°C. Since the sodium-sulfur cells operate at 300°C, we were interested in somewhat more reliable 300°C sulfur corrosion rates. Arrhenius activation plots were made for D406 and T806 in order project the extent of reactions; the estimates for D406 and T806 are 0.16 and 0.25 $\mu g\ cm^{-2}$ after 14 days of sulfur exposure at 300°C. (The significance of these numbers will be discussed shortly.) Also obtained from these analyses were the activation energies (Ea), preexponential terms (Q_0), and characteristic vibration periods (τ_0), and values of D_0. Refer to Table V. These numbers were used to calculate diffusion constants and penetration depths at 400°C and 300°C from the relationship:

$$D = (a^2/\tau_0)\ e^{-Ea/RT}$$

where "a" ,the atom hop distance, is estimated to be 3 A; and τ_0 is the reciprocal of attempt frequency. Since τ_0 is proportional to a^2, the atom hop distance taken does not affect the diffusion coefficient. The results are listed in Table VIII.

TABLE VIII

CALCULATION OF DIFFUSION CONSTANTS AND SODIUM OXIDE DEPLETION DEPTHS

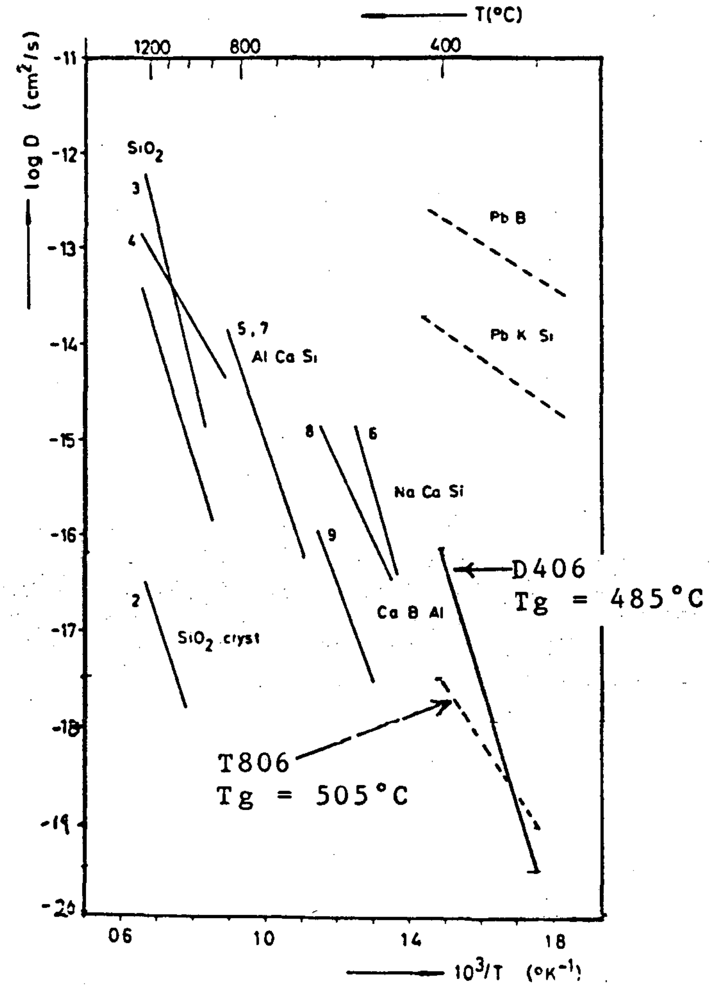
Temperature (°C)	Glass	Diffusion Constant cm^2/sec	30 day Depth* $[Dt]^{1/2}$	Na_2O loss $\mu g/cm^2$	Depth* from Na_2O
400°C	D406	6.4×10^{-17}	0.13 μm	9.6	0.15 μm
400°C	T806	3.4×10^{-18}	0.039	2.2	0.033
300°C	D406	4.0×10^{-20}	0.003	---	------
300°C	T806	9.8×10^{-20}	0.005	---	------

The symbol (*) refers to a total depletion depth. Refer to page 27 for a discussion of the effect of partial depletions on diffusion coefficients.

The temperature dependence of diffusion coefficients for sodium oxide (rate limited by O^{2-} diffusion) are shown plotted in Figure 15. Also shown in Figure 15 are diffusion coefficients for ^{18}O in the form of ^{18}O enriched oxides. Appendix K lists ^{18}O diffusivity studies for a variety of oxide containing glasses where the diffusion coefficient (D) is expressed as:

Figure 15

Oxygen-18 Diffusion in Glasses
Below the Transformation Temperature Tg
(Data From H. A. Schaffer: Ref 20)



$$D = D_0 e^{-Ea/RT}$$

Values of D_0 and Ea for several glasses are tabulated in Appendix K. Values of D_0 for D406 and T806 are given in Table V.

Inspection of Figure 7 shows the two glasses have equal sulfur reactivity and 320°C; at 300°C, T806 is estimated to be about 50% more reactive as determined by sulfate formation and the stoichiometry of Reaction I.

Given the above estimates of reactivity, it is appropriate see if they fit the experimental observations. Outer wall sulfur exposure of T806 (Lot C082381L) capillaries for 28 days at 300°C resulted in about five of fifteen capillaries developing longitudinally oriented cracks with opposing faces held open. This implies the development of a surface tensile layer; the loading moment being the product of stress and layer thickness. If we further assume it is caused sodium oxide loss, the required loss of sodium oxide per square centimeter to produce the observed crack face separation can be calculated. This is done by setting equal expressions that describe the moment required to hold the faces apart (Equation I) and the expression relating loading moment to moles of sodium oxide extracted (Equation II). The above expressions are derived in Appendix I.

Equation I: $\sigma_0 d_0 = E S (t/R)^2 (1/12\pi)$

Equation II: $\sigma_0 d_0 = \frac{E}{3} \frac{\Delta m}{\Delta A} \frac{\partial V}{\partial m}$

$$\frac{\Delta m}{A} = S\left(\frac{t}{R}\right)^2 \frac{1}{4\pi}\left(\frac{\partial V}{\partial m}\right)^{-1}$$

$$\frac{\Delta m}{A} = (10^{-4}\text{cm})\left(\frac{15\mu\text{m}}{32.5\mu\text{m}}\right)^2 \frac{1}{4\pi} \frac{1 \text{ mole Na}_2\text{O}}{24 \text{ cm}^3}$$

$$\frac{\Delta m}{A} = 7.1 \times 10^{-8} \text{ mole/cm}^2$$

$$\frac{\Delta m}{A} \times MW_{\text{Na}_2\text{O}} = \frac{4.4\mu\text{g Na}_2\text{O}}{\text{cm}^2}$$

where: R = average of outside and inside radii = 32.5 µm.
t = capillary wall thickness = 15 µm.
= crack face separation = 1 µm
E = Young's modulus of elasticity = 7.2×10^6 psi
A = area of exposed glass
$\partial V/\partial M$ = partial molar volume of sodium oxide = 26 cc/mole
σ_0 = tensile stress in layer
d_0 = tensile layer thickness

The calculated sodium oxide loss (4.4 $\mu g\ cm^{-2}$)* required to hold the crack faces apart by the observed 1 μm is significantly larger than than the sodium oxide losses experimentally determined. Since the discrepancy is well over an order of magnitude, it is safe to reject the hypothesis that sodium oxide loss via Reaction I is responsible for cracking T806 capillaries. This conclusion is supported by the failure to find cracks for similarly sulfur exposed T806 capillaries from a different batch (C050852S). The chief differences being the use of different and more pure starting materials (min. 99.999%), a higher melt temperature (1200 versus 1000°C), and more stirring (11 stirrings versus two stirrings). The limited results of cell lifetime testing (only four cells were run) using the latter batch of capillaries failed to show dramatic lifetime increases. Thus, it seems unlikely that Reaction I by itself is responsible for the early failure of sodium-sulfur cells where it is used as the electrolyte.

We also speculated that capillary cracking could result from an ion exchange between sodium ions in the glass and hydrogen ions in the sulfur melt, where H^+ is generated by sulfur decomposition of organics to sulfanes and carbon disulfide. Exposure of the latter batch of T806 capillaries to sulfur spiked with up to 0.5 wt% organic failed to produce cracks at either 300°C or 400°C for exposure times up to one month. Preliminary data in this report (Table VI) showed faster ion exchange rates for T806 than for D406. Had cracking been observed in either the sulfur or organic spiked sulfur, crack face separation would have provided a convenient assessment of loading moment. If future work is undertaken on the failure mechanism of T806 capillaries, it is strongly recommended that a technique be developed to check for the development of stresses in the capillaries. Caution would have to be exercised if photoelastic measurements were used. Schmitz reports formation of an altered glass layer possessing altered optical properties when E-glass is exposed to hydrogen ion (10).

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*The preceding calculation ignores the fact that the partial molar volume of soda decreases with decreasing soda content. Therefore, the calculated soda loss is smaller than that required for the 1 μm crack opening.

CONCLUSIONS

Thermodynamic calculations for Reaction I showed a basic glass (such as $Na_2O \bullet SiO_2$) could disproportionate sulfur while a glass with very low basicity would not.

Reaction I 4 Na_2O (from glass) + 3(x+1) S = Na_2SO_4 + 3 Na_2S_x

Prediction of reaction equilibria between sulfur and glasses throughout the Na2O/B2O3/SiO2 ternary system is not possible because necessary data to calculate corresponding sodium oxide activities are not available from the literature.

Sulfur reaction rates for 17 glass compositions in the ternary system $Na_2O/B_2O_3/SiO_2$ were determined at 300°C and 400°C by means of a sensitive anion chromatographic method. Although differences were measured in sulfur reactivity, no clearly superior glass composition was identified.

More detailed reactivity comparisons were run on glass compositions D406 and T806 that allowed calculation of activation energies, pre-exponential factors, and solid state diffusivities (presumably for sodium oxide). These data suggests different reaction mechanisms with sulfur for the two glasses. Corrosion depth estimates at 400°C were made from both measured quantities of reaction products and from an integrated sodium oxide flux expression. The reaction depths are 0.13 μm for D406 and 0.04 μm for T806 after 30 days at 400°C assuming 100% Na_2O depletion in the reaction layer. Reaction depths were estimated at 300°C also after 30 days exposure to sulfur: 0.003 μm for D406 and 0.005 μm for T806.

The following observations were also used to assess the likelihood of fiber failure caused by sulfur corrosion. In contrast to T806 capillaries sulfur exposed in a cell bundle containing Mo coated Al foil, no cracks were induced by sulfur exposure alone either at 300°C or 400°C. The crack face separation in the former case along with fiber dimensions and Young's modulus of elasticity allow an estimate of loading moment (average stress x thickness) to be made. The estimated extent of reaction at 300°C for T806 glass gives only about 10% of the loading moment estimated for capillaries sulfur aged in a cell bundle. Given insufficient levels of reaction and the small differences reaction rates, the hypothesis that sulfur reactivity alone is responsible for the early failure of T806 Na-S can be rejected. These data suggest that other factors such as the Mo coated Al foil may be involved in the failure of T806 glass capillaries.

Additional aspects of the glass/sulfur reactivity are summarized here.

1. For a given surface area of glass powder, sulfur reactivity increases with decreasing mass of sulfur.

2. The form and preparation method of the glass are important. Given identical surface areas, powdered glass is significantly more

reactive (ca.7x for D406 at 400°C) than smooth glasses surfaces such as found in 80 µm O.D., annealed, spun rods. Powdered T806 glass melted at 1000°C is about twice as reactive than that melted 1200°C; differences in surface area were shown not to be the cause for the latter.

3. The sulfur reaction is retarded by the addition of hydrocarbons which decompose in sulfur to yield hydrogen sulfide and carbon disulfide.

4. Glass T806 ion exchanges H^+ for Na^+ more rapidly than D406 at 400°C. Although the above ion exchange will introduce surface tensile stresses, T806 capillaries failed to crack when exposed to sulfur deliberately spiked with hydrocarbons.

SUGGESTIONS FOR ADDITIONAL RESEARCH

Work performed in this report fails to support the hypothesis that early failure of cells using glass composition T806 is caused by sulfur exposure alone. It is important to determine if T806 cells fail as a result of intrinsic reactivity with cell reactants (and/or products) or if these failures are the result of some other factor. For example, should failure be induced by the presence of aluminum foil, switching to a different cathode could allow the use of this T806 glass having improved chemical resistance, as discussed below.

Glass composition T806 shows superior corrosion resistance to metallic sodium (5) and to sodium trisulfide (5) at 300°C. The importance of these experimental findings will now be considered. Consider first the improved resistance to metallic sodium. Our present glass electrolyte, D406, will not survive freeze-thaw when a filled, undischarged cell is held at 300°C for times as short as two days prior to cooling (11). Sodium exposure of D406 glass causes a large reduction of capillary tensile strength (1). Stresses caused by sodium expansion upon melting are sufficient to burst the sodium weakened capillaries (12). Since T806 capillaries are significantly stronger after sodium aging (67 Kpsi versus <u>ca.</u> 15 Kpsi after 30 days), odds are that cells using T806 glass capillaries are much more likely to survive thermal cycle.

Although neither T806 or D406 (13) glasses are damaged by sodium tetrasulfide exposure, sodium trisulfide exposure is a different story. During rapid discharge, as would occur in the case of high power cells, cell terminal potential falls below that which guarantees the absence of sodium trisulfide. Studies of D406 glass exposed to sodium trisulfide showed a serious loss of tensile strength (13), surface damage (2), and significantly reduced cell lifetimes for cells discharged to a cathode composition of sodium trisulfide and then held in open circuit (6).

Neither tensile strength measurements (5) or surface examination via SEM showed detectable damage to T806 glass upon exposure to sodium trisulfide. These findings suggest T806 may be a better candidate for use in high power cells.

What follows are a few proposed experiments that may help identify factor(s) responsible for reduced lifetimes of cells using T806 glass as the electrolyte. The first proposal is to cycle dianode T806 cells in Na_2S_X. The cell configuration is: Na/glass/Na_2S_X/glass/Na. This arrangement eliminates the metallic cathode foil, Mo coated Al. Times to failure for a number of such cells are of particular interest. If the dianode T806 cells consistently last longer than the typical two week lifetimes observed for Na/S cells using T806 glass electrolyte, this may be an indication that the aluminum foil is involved in the early failure of cells using T806 electrolyte.

Our reason for suspecting the aluminum foil goes back to the initial observation of longitudinal cracks in T806 capillaries while <u>exposed to sulfur</u> <u>in a cell bundle</u> (14). In contrast, no cracks were observed upon exposure to sulfur alone (15,16). The most obvious difference in the two experiments is that capillaries in a cell bundle are in close proximity to the cathode foil, i.e., Mo coated Al. (There is some evidence that this cathode foil plays a significant role in the life limiting process in sodium-sulfur cells using D406 as the glass electrolyte (17): mean cell lifetimes increased from about 40 days to 150 days by air baking the foil for 24 hr. at 300°C.)

A second experiment to probe the effect of the aluminum foil is to test for leaks while sulfur exposing T806 capillaries in rolled cell bundles. A possible arrangement is as follows. An evacuated anode cup of an assembled cell is monitored via a mass spectrometer for sulfur while the exterior fiber surfaces are sulfur exposed at 300°C. This could be done by sulfur filling a glass case cell and subsequently inserting the cell into an evacuated heating chamber; the anode fill tube would be left open and the sulfur fill would be tube closed. Any capillaries developing a leak would allow sulfur to enter the vacuum manifold and be detected by a quadrupole mass spectrometer. Provision for heating the manifold and spectrometer tube must be made to assure sufficient sulfur vapor for detection. Rolled bundles could be fabricated with and without aluminum foil for comparison of times to leak development. Thus the role of the foil could be investigated. This arrangement would allow tests on a statistically significant collection of capillaries comparable to that used in a Na/S cell.

Another possibility regarding sulfur related, early failure modes for T806 is localized attack at the "test tube" seals forming the closed capillary ends. A number of missing seal ends were observed while inspecting sulfur exposed capillaries for longitudinal cracks. As an example, one of fourteen sealed fiber ends separated after sulfur exposure at 300°C for thirty-four days (15). Inspection of the fiber ends prior to sulfur exposure showed all sealed ends present.

The last mentioned experiment could be incorporated as part of the experiment where capillaries are monitored for leaks while sulfur exposed. At the conclusion of the leak experiment, sulfur could be removed from the fiber exterior and foil (if used) by vacuum distillation. Prior to unrolling the bundle for inspection, melted dye would be pressurized into the capillaries via the anode cup (dye testing) and then allowed to cool. Observation of dye at a failure site (fiber ends in this experiment) would eliminate any confusion caused possible capillary breakage as a result of unrolling the bundle.

The experiments suggested above should comment upon whether or not the cell foil is involved in the early failure of T806 Na/S cells. If it is, a less reactive, substitute foil could be tried. It is conceivable that Na/S cells having superior lifetimes as well as the ability to survive thermal cycle after exposure to 300°C could be made. Presently it is felt that thermal cycle of T806 cells held open circuited at 300°C should be possible. Work to date suggests that this highly improbable for D406 Na/S cells. Additional work will be required to investigate the possibility of thermal cycle of T806 Na/S cells after being charged and discharged.

APPENDIX A

ION CHROMATOGRAPHIC TECHNIQUE AND COMMENTS ON WORKUP CHEMISTRY

1. Test of Ion Chromatographic Method

One of the initial checks of the experimental technique run was the reaction of anhydrous sodium carbonate (1.114 mg, 10.5 μmoles) with sulfur (110 mg, 3430 μmoles) in a sealed, evacuated Pyrex ampule for three days at 400°C. The balanced reaction is given below:

Reaction II $4\ Na_2CO_3 + 16\ S = Na_2SO_4 + 3\ Na_2S_5 + 4\ CO_2$

After in situ distillation, the solid reaction residue was diluted to 10.0 ml with deionized water and filtered. One portion of the filtrate was analyzed immediately (Chromatogram 1), another portion was adjusted to pH 4 with Dowex cation exchange resin after standing 1 hr (Chromatogram 2). Refer to Figure 16 for the chromatograms. The results are summarized in Table IX.

TABLE IX

Standing Time Prior to Analysis	Mass SO_4^{2-} (μg) (Calc: 252)	Mass $S_2O_3^{2-}$ (μg) (Calc: 883)
0 hr	---	---
1 hr	233	190
29 hr	247	433

These results show that 92% of the expected mass of thiosulfate ion from Reaction II were found at the 1 hr analysis time. Thiosulfate ion is produced from the air oxidation of sodium pentasulfide, Reaction III.

Reaction III $3\ Na_2S_5 + 4.5\ O_2 = 3\ Na_2S_2O_3 + 12\ S$

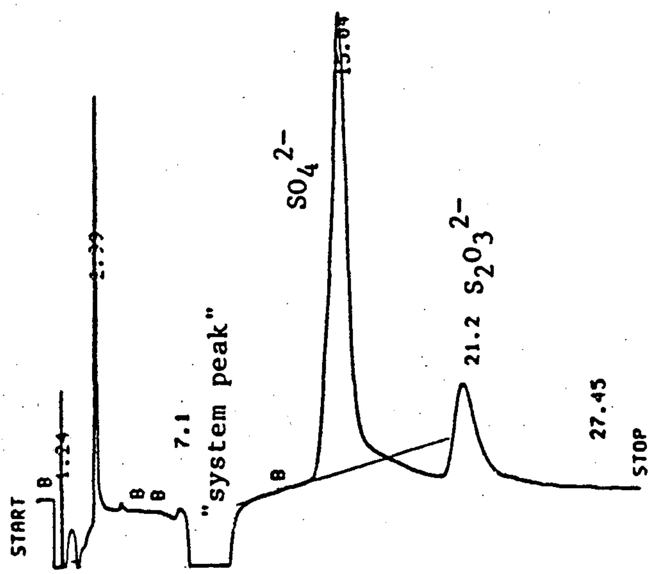
2. Aerobic Oxidation of Polysulfides at Neutral pH

A second experiment was run to check the rate of solution oxidation of sodium tetrasulfide to sodium thiosulfate. The possibility of further oxidation to sulfate ion was of potential concern. Sodium tetrasulfide (115 mg, 661 μmole) was dissolved into 100 ml deionized water and then diluted further by a factor of five to give a 1.32 μM solution or 17.9 ppm solution based on the weight of tetrasulfide ion. The results are tabulated in Table X.

Figure 16

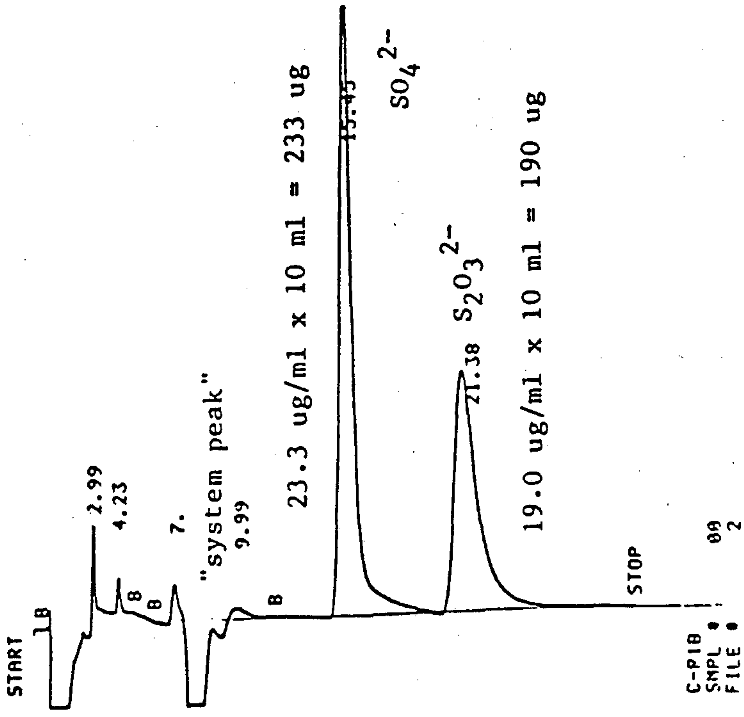
Ion Chromatographic Analysis of Nonvclatile Residue from the Reaction of Sodium Carbonate and Sulfur at 400°C

Chromatogram #1
No cation exchange resin added.



```
C-R1B
SMPL #       00
FILE #        2
REPT #      291
METHOD       41

#   NAME   TIME        CONC      MK      AREA
0          1.24       0.4737              3769
0          2.99       4.6789             37137
0         15.04      73.5883            584076
0         21.2       21.1019     V      167488
0         27.45       0.1569     V        1245
      TOTAL          99.9999            793709
```

Chromatogram #2
Cation exchange resin added.



23.3 ug/ml x 10 ml = 233 ug

19.0 ug/ml x 10 ml = 190 ug

```
C-P1B
SMPL #       00
FILE #        2
REPT #      292
METHOD       41

#   NAME   TIME        CONC      MK      AREA
0          2.99       2.1125             14468
0          4.23       0.7049              4828
0          7.         1.4538              9957
0          9.99       1.293               8855
0         15.45      56.0763            384055
0         21.38      38.3592            262714
      TOTAL          99.9999            684879
```

TABLE X

AEROBIC OXIDATION OF SODIUM TETRASULFIDE IN DISTILLED WATER

Standing Time Prior to Analysis	Mass SO_4^{2-} (µg) (Calc: 0 ug)	Mass $S_2O_3^{2-}$ (µg) (Calc: 179)[a]
1 hr	2.2	76
2 hr	3.7	90
21 hr	4.7	103

Notes: (a) Calculated for 10. ml of solution.

3. Reproducibility of Injections of Sulfate and Thiosulfate Ions

The mean and standard deviation of four identical injections of an aqueous standard solution 10.0 ppm each of sulfate ion and thiosulfate was determined. The reproducibility for repeated injections is good.

TABLE XI

REPRODUCIBILITY OF INJECTED STANDARDS: SULFATE AND THIOSULFATE IONS

Injection No.	ppm SO_4^{2-}	ppm $S_2O_3^{2-}$
1	10.2	9.1
2	10.1	9.8
3	10.0	9.8
4	10.1	9.4
Mean	10.1	9.5
SDev.	0.08	0.34
CV	0.8%	3.5%

4. Reproducibility of Sulfate Analyses on Identically Prepared, Separate Samples of Glass Powder Exposed to Sulfur

Summary data are shown in Table XII for the same glass (LBB-40) under two different workup conditions. Statistical data are also presented for D406 glass.

TABLE XII

REPRODUCIBILITY OF RESULTS FROM SULFUR EXPOSURE AND WORKUP

EXPOSURE CONDITIONS: 5 DAYS AT 400°C

Glass	Workup Solution	Mean Na_2O loss ($\mu g\ cm^{-2}$)	Std. Dev.	95% Conf. limits on Mean	Number of Samples
LBB-40[1]	Eluant 1	1.69	0.13	1.53-1.85	5
LBB-40[2]	Eluant 2	1.89	0.23	1.74-2.05	11
D406[3]	Eluant 3	3.64	0.17	3.54-3.74	13

Eluant Systems

(1) 0.4 mM phthalic acid and 4.0 mM potassium hydrogen phthalate.
(2) 4 mM potassium hydrogen phthalate; pH 4.6.
(3) 20 mM phthalic acid; pH 2.30.

Notes:

1. Mesh size +140-100; 593 cm^2/g.
2. Mesh size +80-60; 256 cm^2/g.
3. Two mesh sizes (+100-80 and +80-60) were used but gave results independent of mesh size.

5. Extraction Techniques and Estimated % Sulfate Not Extracted

The initial workup method for sulfur exposed glasses used two aqueous extractions for a combined volume of 5.0 ml. Refer to the Experimental section for details of the procedure. In one experiment (LBB-40, 5 days at 400°C), a second set of extractions was performed giving an additional 9% of sulfate ion. The percentage of sulfate ion missed in the first pair of extractions is probably less than 9% because of the way the liquid is separated from the glass powder; it is drawn off with a syringe. Thus, some sulfate solution remains behind and is taken into the second set of extractions.

The current technique for sulfate extraction is as follows: the powder, previously separated from sulfur via in situ distillation, is quickly added to 20 ml of stirred eluant or deionized water contained in a 25 ml Erlenmeyer flask. The resulting solution is used to twice rinse the pyrex tube in which the sulfur exposure was performed. In order to prevent the workup solution from becoming alkaline, it is important to add the exposed glass to the eluant. A discussion of how the workup solution pH can affect the analyses will follow shortly. After stirring for 20 sec, the stirring is stopped and the solution is drawn off with a syringe fitted with a long needle. The solution is filtered through a 0.2 μm milipore filter before either (1) immediate injection into the ion chromatogram port or (2) treatment with the hydrogen form of Dowex cation resin (pH adjustment) prior injection. Note, the anion exchange chromatographic column can be damaged by basic solutions.

6. Comments on Extraction Solution pH

The method used for aqueous extraction of glasses in reaction workups may result in an alkaline solution depending on the soda content of the glass. Both unexposed and sulfur-exposed LBB-40 glass give pH 9 solutions following the workup extraction procedure using deionized water. An approximate estimate of base dissolving from the glass can be obtained by the volume of eluant required to prevent the solution from going basic. More than 48 μeq of base were found in the workup solution of LBB-40 sulfur exposed only 7 days at 300°C. The total sulfate ion in this solution was 28 μg or ca. 0.3 μmoles.

7. Workup Solution Chemistry as a Function of pH

We shall attempt to justify that the sodium sulfate measured by our initial workup procedure adequately represents the amount of sodium sulfate formed by the sulfur-glass reaction and is not appreciably changed by any subsequent oxidative reactions. What we need to examine is the fate of sodium pentasulfide generated from the sulfur-glass reaction:

Ampoule Reaction: $4\ Na_2O + 16\ S = Na_2SO_4 + 3\ Na_2S_5$

The following equations are the expected aerobic oxidations of sodium pentasulfide under three likely workup conditions: in the absence of base, in the presence of base, and in the presence of pH 4 buffer.

No Base: $Na_2S_5 + 3/2\ O_2 = Na_2S_2O_3 + 3\ S$

With Base: $2\ Na_2S_5 + 6\ O_2 + 6\ NaOH = 5\ Na_2S_2O_3 + H_2O$

Reaction III; $Na_2S_2O_3 + 2\ O_2 + 2\ NaOH \xrightarrow{\text{slow}} 2\ Na_2SO_4 + H_2O$

PH 4 Buffer: $Na_2S_5 + 2\ H^+ = H_2S_5 \longrightarrow H_2S + 4\ S$

$Na_2S_5 + 3/2\ O_2 = Na_2S_2O_3 + 3\ S$

Two equal weight samples of sodium carbonate (1.11 mg, 10.5 μmole) were reacted with sulfur (400°C) in sealed ampules. One was worked up in 5.0 ml deionized water and the other in 10 ml of 0.0016 N NaOH. Recalling that four moles of sodium carbonate are required per mole of sodium sulfate, the expected mass of sulfate ion is 252 μg. The masses of reaction products found versus time are tabulated below.

TABLE XIII

THE EFFECT OF WORKUP SOLUTION pH ON DETECTED REACTION PRODUCTS

Standing Time Prior to Analysis	Mass SO_4^{2-} (μg)	Mass $S_2O_3^{2-}$ (μg)
RESULTS FROM DEIONIZED WATER WORKUP		
0 hr	---	---
1 hr	233	190
29 hr	247	433
RESULTS FROM BASIC AQUEOUS SOLUTION		
1 hr	290	188
29 hr	445	755

Notice that under the simulated worst workup condition of basic, aerobic environment, the rate of sulfate formation from polysulfide accounts for no more than 15% error after one hour. Currently, all workups are performed with 20 ml of eluant. This is particularly important on 300°C samples where low levels of sulfate are formed.

8. Sodium Thiosulfate - Not a Direct Product of Sulfur Exposure

The sodium thiosulfate found in neutral or basic workup solutions is believed to be exclusively formed during the workup procedure. In fact we considered the possibility of the following concurrent reaction between glass and sulfur (21):

$$3\ Na_2O + 12\ S = Na_2S_2O_3 + 2\ Na_2S_5$$

However, mildly acidic workup with immediate analysis shows no detectable thiosulfate, suggesting the above reaction does not occur in the sealed ampule. Thiosulfate is stable over a few hours in 4 mM KHP eluant system (pH 4.6)

9. Thiosulfate Formation - Function of pH in Deionized Water Workup

Glasses giving alkaline aqueous extracts were observed to give larger ratios of thiosulfate to sulfate when reacted with sulfur and subjected to the deionized water workup. This observation is consistent with aerobic oxidation of sodium polysulfides under alkaline workup conditions.

$$2\ Na_2S_5 + 6\ O_2 + 6\ NaOH = 5\ Na_2S_2O_3 + 3\ H_2O$$

With the above stoichiometry, the three moles of sodium pentasulfide per mole of sodium sulfate (from the sulfur-glass reaction) would yield a molar ratio of 7.5 sodium thiosulfate to sodium sulfate in the aqueous workup solution.

10. Comments Regarding Species Not Detected by Ion Chromatography

There are number of sulfur species which are not detectable under the current ion chromatographic technique. Some of these are: $S_4O_6^{2-}$ (from oxidation of thiosulfate), $S_2O_6^{2-}$ (dithionate), and $^{-2}O_3S$-S_n-SO_3^{2-} (the polythionate series where n= 1, 2, 3 etc.). The content of such species was demonstrated to be negligible.

The following work was performed to estimate what fraction of such species might exist. After determining the quantities of sulfate and thiosulfate present in the workup solution, elemental bromine was added until bromine color persisted so that all species were oxidized to sulfate. As an example, 1 µl (3.1 mg) of bromine was added to a 25 ppm ($S_4O_6^{2-}$) solution. The calculated concentration via the reaction below is 42.9 ppm sulfate ion versus 42. ppm measured.

$$S_4O_6^{2-} + 7\ Br_2 + 10\ H_2O = 4\ SO_4^{2-} + 12\ Br^- + 20\ H^+$$

The oxidation was complete in less than five minutes. A similar reaction can be written for the oxidation of polysulfides to sulfate, for example consider sodium pentasulfide:

$$S_5^{2-} + 16\ Br_2 + 20\ H_2O = 5\ SO_4^{2-} + 32\ Br^- + 40\ H^+$$

From Reaction I (the ampule reaction between glass and sulfur) each mole of sulfate is accompanied by three moles of polysulfide. The subsequent bromine oxidation of the solution will generate "3x" moles of sulfate ion where "x" is the number of sulfur atoms in the polysulfide chain. Consider the outcome of bromine oxidation of a workup solution containing 1 eq. of sulfate and 3 eq. of pentasulfide; fifteen additional equivalents of sulfate will be generated at the conclusion of the oxidation. Figure 17 shows final sulfate levels plotted against initial sulfate levels. Values of "x" were calculated for a number of D406 glass powder samples sulfur exposed for five days at 400°C. The values of "x" were calculated for several samples and are shown in Figure 18.

Since the reactions were carried out in excess sulfur, we expected to find "x" close to five because of the known equilibrium between polysulfides and sulfur. Surprisingly, the majority of samples gave values of "x" in the range between 1.8 and 2.4. Two possibilities are as follows. First, if the equilibrium between sulfur and polysulfides is rapid during the 300°C in situ sulfur distillation, polysulfides could be shifted to low values of "x" by sulfur removal. This hypothesis was tested by measuring the total sulfate content after bromine oxidation of a sodium polysulfide before and after having undergone the distillation process. Second, exchange of sulfide ion for oxygen ion may occur in the glass. Such an exchange would effectively prevent sulfide ion from reacting with sulfur to generate longer polysulfide chains.

Figure 17

Comparison of Initial Sulfate From Sulfur Corrosion of D406 to Subsequent Total Sulfate via Bromine Oxidation of the Workup Solution Sulfur Exposed for 5 Days at 400°C

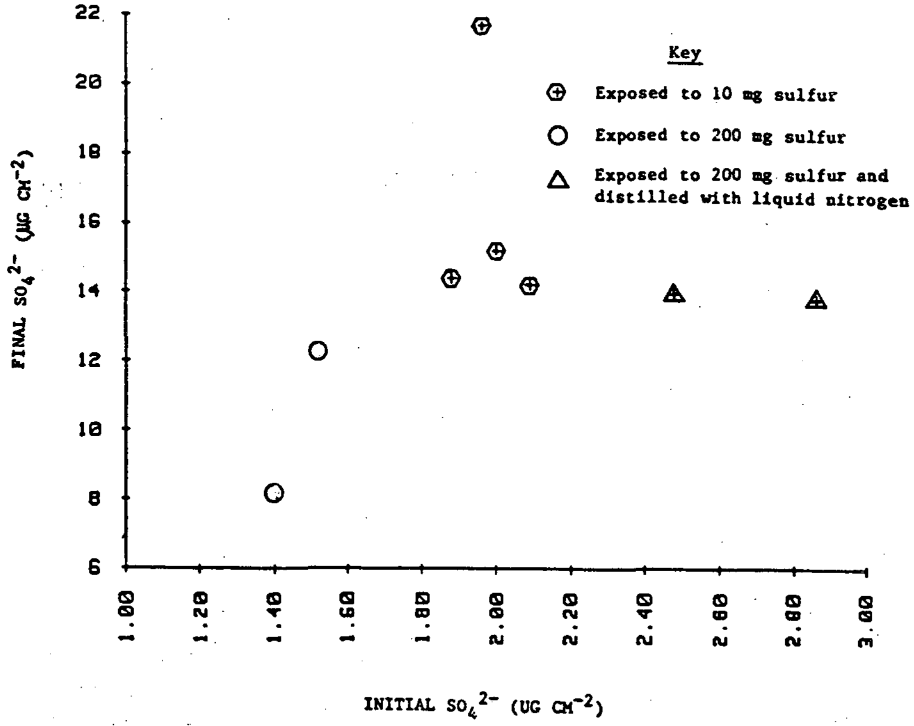


Figure 18

Calculated "x" in Na_2S_x from Above Figure D406 Glass Exposed to Sulfur for 5 Days at 400°C

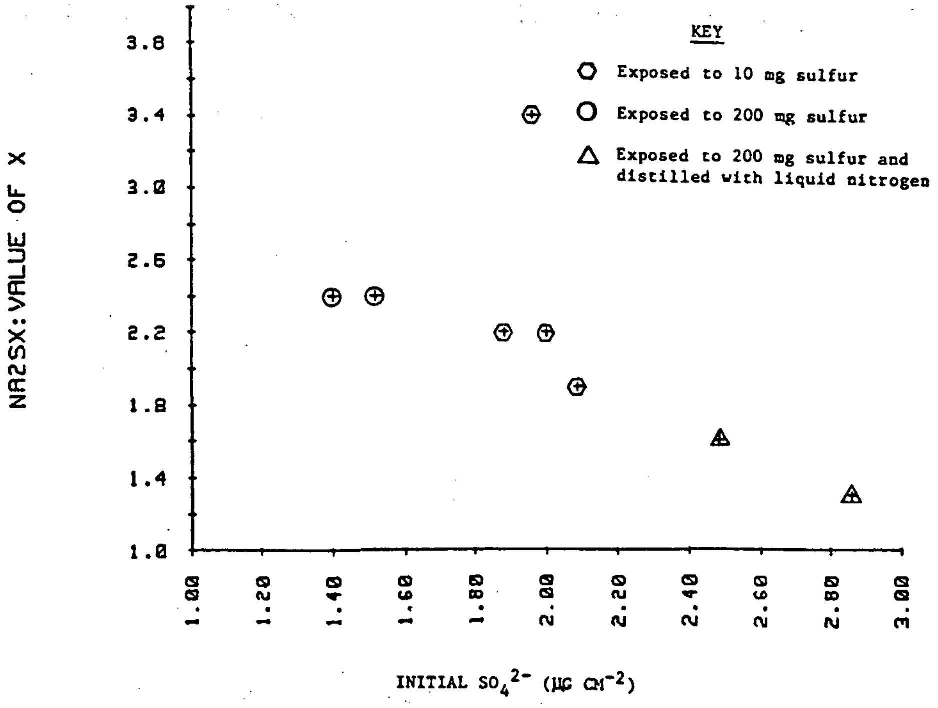


Figure 19

Calculated "x" in Na_2S_x From Exposure of T806 Glass to Sulfur for 5 Days at 400°C

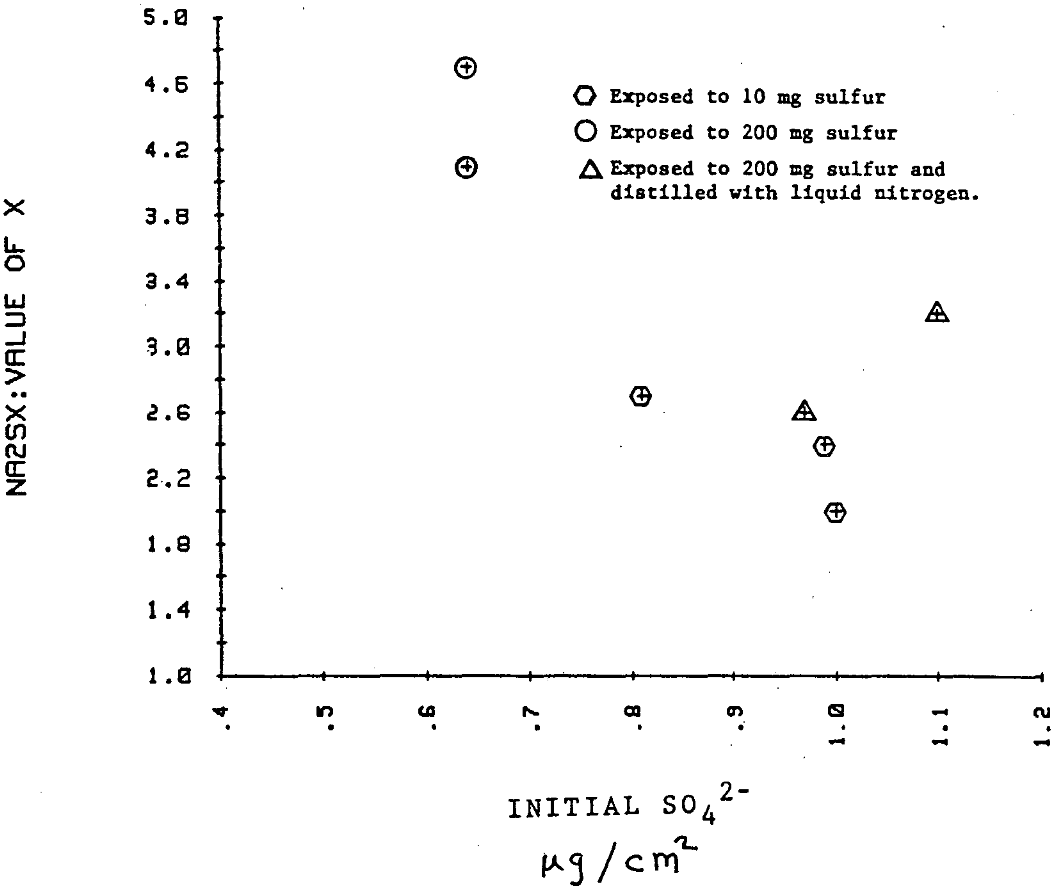


Table XXXII of Appendix D summarizes the results of an experiment where Na_2S_4 is subjected to in situ distillation at 300°C. The value of "x" decreased from 4.0 to 3.4 after 0.5 hr of distillation on two duplicate samples. Since the standard distillation time is also 0.5 hr, sulfur removal from Na_2S_s seems unlikely to account for the low values of "x" in Na_2S_x generated by sulfur exposure of D406 glass.

Similar calculations of "x" in Na_2S_x generated by exposing T806 glass to excess sulfur are shown in Figure 19. Notice that samples exposed to 200 mg sulfur with ambient cooling of the empty end of the distillation tube give $x \geq 4$. Presently, we are unsure of mechanisms responsible for: (1) lower values of "x" when less sulfur is used and (2) formation of more sulfate when the empty end of the distillation tube is liquid nitrogen chilled during the in situ sulfur distillation.

APPENDIX B

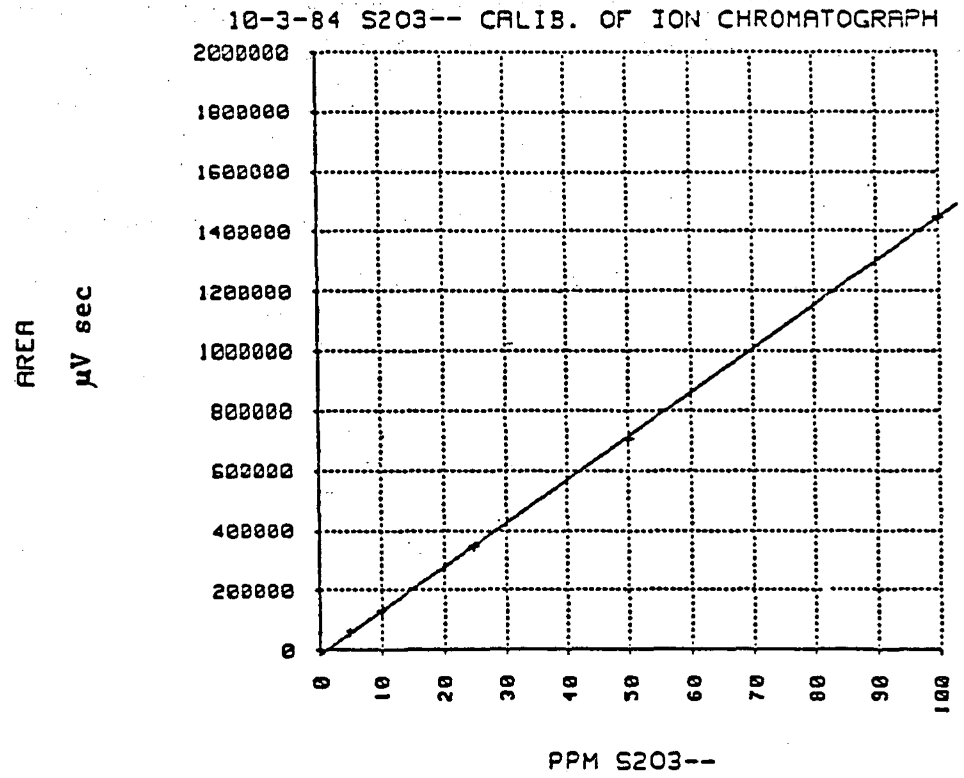
SHIMADZU C-R1B INTEGRATOR PARAMETER SETTINGS

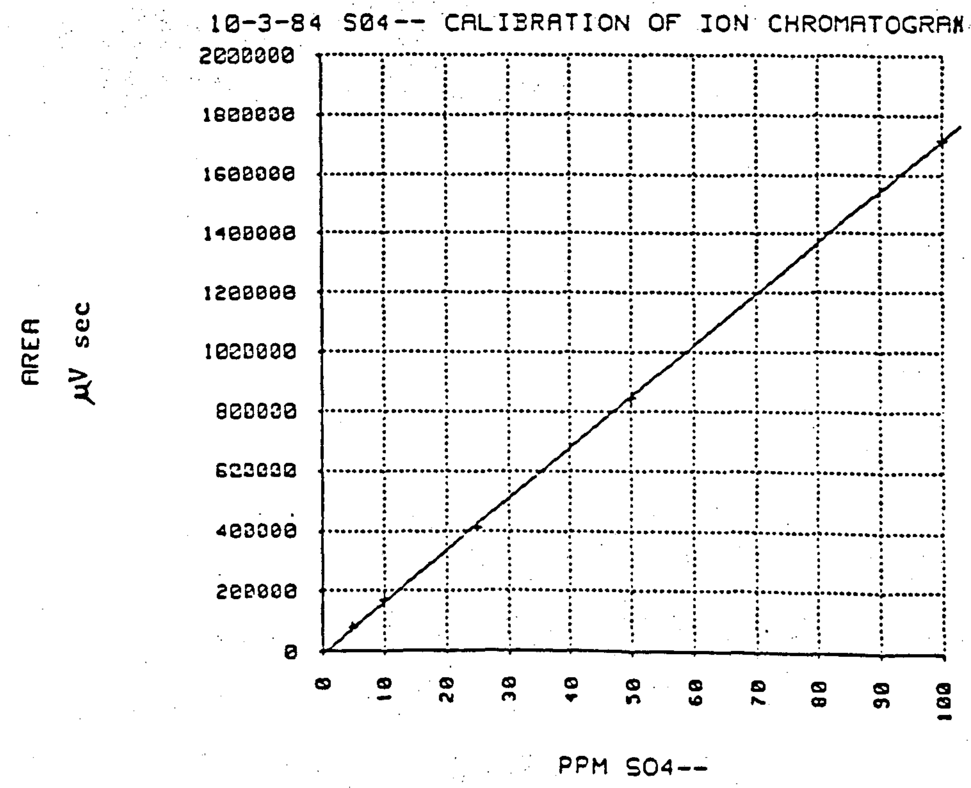
```
CAL PM    2
WIDTH          7
SLOPE       130.8
DRIFT          0
MIN AR      1000
T-DBL          5
LOCK           0
STP TM        25
ATTEN          2
SPEED          4
METHOD        41
SPL WT       100
IS WT          1
```

```
TIME-P    2
   MAX        6

   #    TIME    NAME        DATA

   1    0.2   B               0
   2    5     B               0
   3    6     B               0
   4   12     B               0
```

APPENDIX C

CALIBRATION PLOTS FOR ION CHROMATOGRAPH





APPENDIX D

TABLE XIV

ION CHROMATOGRAPHIC ANALYSIS OF SULFUR SOAKED D406 GLASS

Glass	Sample Form	Temp. (°C)	Aging Time (Days)	Sample Mass (mg)	Surface Area (sq. cm)	Mass Sulfate (µg)	Mass Thiosulfate (µg)	Mass (1) Soda/sq cm (µg/sq cm)	Workup Code
D406	Powder(2)	400°C	4.5	210	81.9	79	73	2.5	DI
D406	Powder	400°C	13.5	212	82.7	163	143	5.1	DI
D406	Powder	400°C	28.	206	80.3	193	0	6.2	E1 (Note 3)
Pyrex	Powder	400°C	28	200	78.0	1.0	0	0.03	E1 (Note 3)
D406	Powder	300°C	4.5	193	75.3	5.5	18	0.19	DI
D406	Powder	300°C	13.5	207	80.7	11.0	21	0.35	DI
D406	Powder	300°C	28.	216	84.2	10.3	0.0	0.32	E1 (Note 3)

Workup Codes:

<u>DI-Deionized water.</u>	Aqueous glass extract filtered, allowed to stand for 1 hr prior to acidification with cation exchange resin (hydrogen form), refiltered and analyzed immediately.
<u>DI-time:</u>	As above, but filtered glass extract allowed to stand for time listed prior to acidification with cation resin.
<u>E1-Eluant 1:</u>	Glass powder extracted with eluant (4.0 mM potassium hydrogen phthalate, 0.4 mM phthalic acid, pH = 3.85), filtered, treated with cation exchange resin, refiltered and analyzed immediately.
<u>E2-Eluant 2:</u>	As above, but the extraction is performed with 4 mM potassium hydrogen phthalate adjusted to pH 4.6 with potassium hydroxide.
<u>E3-Eluant 3:</u>	As above, but the extraction is performed with 20 mM phthalic acid (pH 2.3).

TABLE XIV NOTES

(1) This is the mass of sodium oxide that would be lost per square centimeter of glass surface based on the following equation and the number of moles of sodium sulfate found by analysis.

$$4\ Na_2O + 16\ S = Na_2SO_4 + 3Na_2S_5$$

(2) The +100-80 mesh glass powder has a specific surface area of 390 cm^2/g as determined by 3 point BET analysis using Krypton. The surface area determinations were performed by Quantachrome Corporation.

(3) These samples were worked up by the addition of 5 ml of an aqueous solution containing 4 mM potassium hydrogen phthalate and 0.4 mM phthalic acid. The pH of the solution before addition to the glass sample is 3.85 and is approximately 5 after addition to the glass sample. Workup using acidic conditions decomposes sodium polysulfides to hydrogen sulfide and sulfur. Subsequent exposure to air does not result in the generation of sodium thiosulfate since the starting polysulfides are decomposed under the acidic workup conditions.

TABLE XV

ION CHROMATOGRAPHIC ANALYSIS OF SULFUR SOAKED D406 GLASS SERIES

EXPOSURE TEMPERATURE = 400°C

Glass Powder Mesh	Aging Time (Days)	Sample Mass (mg)	Surface Area (sq. cm)	Extract Volume (cc) /Time (sec)	Mass Sulfate (µg)	Mass Thiosulfate (µg)	Mass (1) Soda/sq cm (µg/sq cm)	Workup Code
+100-80	5.0	218	85.0	10cc/20sec	122.	0.0	3.70	E2
+100-80	5.0	201	78.4	10 / 20	104.	0.0	3.42	E2
						MEAN (N=2) =	3.56 + 0.20	
+100-80	5.0	211	82.2	20 / 15	120.	0.0	3.77	E3
+100-80	5.0	209	81.5	20 / 20	110.	0.0	3.48	E3
+100-80	5.0	202	78.7	20 / 20	101.	0.0	3.31	E3
+100-80	5.0	200	78.0	20 / 20	112.	0.0	3.70	E3
+100-80	5.0	210	81.9	20 / 20	116.	0.0	3.65	E3
						MEAN (N=5) =	3.58 + 0.19	
+80-60	5.0	210	53.8	20 / 20	77.7	0.0	3.72	E3
+80-60	5.0	210	53.8	20 / 20	82.5	0.0	3.95	E3
+80-60	5.0	208	53.2	20 / 20	73.6	0.0	3.56	E3
+80-60	5.0	208	53.2	10 / 20	78.4	0.0	3.80	E3
+80-60	5.0	212	54.2	20 / 20	77.9	0.0	3.70	E3
+80-60	5.0	216	55.3	20 / 20	63.0	0.0	[2.93]	E3
						MEAN (N=6) =	3.61 + 0.36	
						MEAN (N=5) =	3.75 + 0.14	

Workup Codes:

<u>E2-Eluant 2:</u> Glass powder extracted with eluant 2 (4.0 mM potassium hydrogen phthalate adjusted to pH 4.5 with potassium hydroxide), filtered, treated with cation exchange resin (hydrogen form), refiltered and analyzed immediately.

<u>E3-Eluant 3:</u> As above except the extraction is done with eluant 3 (20 mM phthalic acid, pH 2.30)

Notes: Refer to Table XIV Notes for note 1.

TABLE XVI

ION CHROMATOGRAPHIC ANALYSIS OF SULFUR SOAKED T806 GLASS

Glass(2)	Sample Form	Temp. (°C)	Aging Time (Days)	Sample Mass (mg)	Surface Area (sq. cm)	Mass Sulfate (µg)	Mass Thiosulfate (µg)	Mass (1) Soda/sq cm (µg/sq cm)	Workup Code
T806a	Powder(2)	400	5	93	36.3	30	100	2.1	DI-3 min
T806b	Powder(2)	400	5	93	36.3	30	255	2.1	DI-2 hr
T806	Powder(2)	400	5	87	33.9	22	0.0	1.7	E -3 min
T806	Powder(3)	400	6.5	201	51.5	41	172	2.1	DI
T806a	Powder(3)	400	14	209	53.5	65	461	3.1	DI
T806b	Powder(3)	400	14	209	53.5	113	350	(5.4)	DI-24 hr
T806	Powder(3)	300	6.5	210	53.8	16	133	0.64	
T806a	Powder(3)	300	14	190	48.6	13	132	0.69	DI
T806b	Powder(3)	300	14	190	48.6	16	175	(0.89)	DI-24 hr

Subscripts "a" and "b" refer to the same sample, but the aqueous glass extracts were divided into two portions for separate workups.

Workup Codes:

<u>DI-Deionized water:</u> See Table XIV Workup Codes for explanation

<u>E1-Eluant 1:</u> Glass powder extracted with eluant 1 (4.0 mM potassium hydrogen phthalate, 0.4 mM phthalic acid, pH = 3.85), filtered, treated with cation exchange resin, refiltered and analyzed immediately.

Notes: (1) Refer to Table XIV notes.
(2) A melting temperature of 1000°C for 1.5 hr was used in glass preparation. Two to three stirrings were used. Refer to Appendix H under preparation of Samples T806 A and B for more details.
(3) Powder mesh size: +100-80; area estimate: 390 cm^2 g^{-1}.
(4) Powder mesh size: +80-60; area estimate: 256 cm^2 g$_{-1}$.

TABLE XVII

ION CHROMATOGRAPHIC ANALYSIS OF SULFUR SOAKED T806 GLASS

T806 GLASS BATCH PREPARED BY MELTING REAGENTS AT 1200°C WITH EXTENSIVE STIRRING

Glass(2)	Sample Form	Temp. ('C)	Aging Time (Days)	Sample Mass (mg)	Surface Area (sq. cm)	Mass Sulfate (µg)	Mass Thiosulfate (µg)	Mass (1) Soda/sq cm (µg/sq cm)	Workup Code
T806	Powder(3)	400	5	208.0	53.2	19.5	0.0	0.94	E2
T806	Powder(3)	400	5	207.0	53.0	21.6	0.0	1.05	E2
T806	Powder(3)	400	5	206.	52.7	23.4	0.0	1.14	E2
T806	Powder(3)	400	5	201.	51.5	21.5	0.0	1.08	E2
T806	Powder(3)	400	5	205.	52.5	27.7	0.0	1.36	E2
							MEAN (N=5) =	1.11 + 0.16	
T806	Powder(3)	300	5	200.	51.2	4.8	0.0	0.24	E2
T806	Powder(3)	300	5	200.5	51.3	7.2	0.0	0.36	E2
T806	Powder(3)	300	5	206.	52.7	4.9	0.0	0.24	E2
T806	Powder(3)	300	5	209.	53.5	6.7	0.0	0.32	E2
T806	Powder(3)	300	5	207.5	53.1	6.0	0.0	0.29	E2
T806	Powder(3)	300	5	210.5	53.9	7.4	0.0	0.35	E2
T806	Powder(3)	300	5	214	54.8	8.4	0.0	0.40	E2
T806	Powder(3)	300	5	200.5	51.3	6.6	0.0	0.33	E2
							MEAN (N=8) =	0.32 + 0.06	

Workup Codes:

E2-Eluant 2: Glass powder extracted in 20 ml eluant (4.0 mM potassium hydrogen phthalate, pH = 4.6) with 20 sec stirring in an Erlenmeyer flask, filtered, and analyzed immediately. Note, pH adjustment with Dowex cation resin was not required.

Notes: (1) Refer to Table XIV notes.
(2) Glass batch prepared on 5/08/85. 1200°C melt temperature with 10 stirrings.
(3) Powder mesh size: +80-60; area estimate: 256 cm^2 g^{-1}.

TABLE XVIII

ION CHROMATOGRAPHIC ANALYSIS OF SULFUR SOAKED T806 GLASS

SULFUR REACTIVITY VERSUS PRIOR GLASS MELT PREPARATION

Glass	Sample Form	Temp. (°C)	Aging Time (Days)	Sample Mass (mg)	Surface Area (sq. cm)	Mass Sulfate (μg)	Mass Thiosulfate (μg)	Mass (1) Soda/sq cm (μg/sq cm)	Workup Code
T806/n	Powder(2)	400	5	201.	78.4	32.2	0.0	1.06	E2
T806/n	Powder(2)	400	5	213.	83.1	32.5	0.0	1.01	E2
T806/n	Powder(2)	400	5	207.	80.7	34.3	0.0	1.10	E2
								MEAN = 1.06 + 0.05	
T806/o	Powder(2)	400	5	204.5	79.8	63.7	0.0	2.06	E2
T806/o	Powder(2)	400	5	213.	83.1	64.0	0.0	1.99	E2
T806/o	Powder(2)	400	5	202.	78.8	62.6	0.0	2.05	E2
								MEAN = 2.03 + 0.04	
T806/n	Powder(3)	400	5	111.5	66.1	39.9	0.0	1.56	E2
T806/n	Powder(3)	400	5	111.0	65.8	32.2	0.0	1.26	E2
								MEAN = 1.41 + 0.21	
T806/o	Powder(4)	400	5	105.0	60.5	58.7	0.0	2.50	E2
T806/o	Powder(4)	400	5	108.0	64.0	53.1	0.0	2.14	E2
								MEAN = 2.32 + 0.25	

Workup Codes:

E2-Eluant 2: Glass powder extracted in 20 ml eluant (4.0 mM potassium hydrogen phthalate, pH = 4.6) with 20 sec stirring in an Erlenmeyer flask, filtered, and analyzed immediately.

/n Glass batch prepared on 5/08/85. 1200°C melt temperature with 10 stirrings.
/o Glass batch prepared by melting at 1000°C and stirring twice.

Notes: (1) Refer to Table XIV note 1.
(2) Powder mesh size: +100-80: measured area: 390 cm^2 g^{-1}.
(3) Powder mesh size: +140-100: 590 cm^2 g^{-1} by 3 point BET.
(4) Powder mesh size: +140-100: 576 cm^2 g^{-1} by 3 point BET.

TABLE XIX

ION CHROMATOGRAPHIC ANALYSIS OF SULFUR SOAKED LBA GLASS SERIES

SULFUR EXPOSURE TEMPERATURE = 400°C

Glass(2)	Aging Time (Days)	Sample Mass (mg)	Surface Area (2) (sq. cm)	Mass Sulfate (µg)	Mass Thiosulfate (µg)	ug $S_2O_3^{2-}$ -------- µg SO_4^{2-}	Mass (1) Soda/sq cm (µg/sq cm)	Workup Code
LBA-45	7	234	91.3	166.	0.0	---	4.7	E2
LBA-40	7	211	82.3	86.	0.0	---	2.7	E2
LBA-35	7	220	85.8	66.	0.0	---	2.0	E2
LBA-33.3	7	227	88.5	55.3	0.0	---	1.6	E2
PYREX	7	200	78.0	2.5	0.0	---	0.08	E2
LBA-45	17	210	81.9	107.	0.0	---	3.4	E2
LBA-40	17	204	79.6	115	0.0	---	3.7	E2
LBA-35	17	208	81.1	99.5	0.0	---	3.2	E2
LBA-33.3	17	210	81.9	99.4	0.0	---	3.1	E2
LBA-45	40	205	80.0	244	0.0	---	7.9	E2
LBA-40	40	221	86.2	191	0.0	---	5.7	E2
LBA-35	40	203	79.2	145	0.0	---	4.7	E2
LBA-33.3	40	198	77.2	108	0.0	---	3.5	E2
LBA-45	64	210	81.9	285	0.0	---	9.0	E2
LBA-40	64	200	78.0	232	0.0	---	7.7	E2
LBA-35	64	217	84.6	158	0.0	---	4.8	E2
LBA-33.3	64	200	78.0	116	0.0	---	3.8	E2

Compositions	Glass	Na_2O	"Si_2O_4"	B_2O_3
	LBA-45	0.45	0.275	0.275
	LBA-40	0.40	0.300	0.300
	LBA-35	0.35	0.325	0.325
	LBA-33.3	0.333	0.333	0.333

Workup Codes: Refer to Table XIV.

Refer to Table XIV Notes for (1) and (2).

TABLE XX

ION CHROMATOGRAPHIC ANALYSIS OF SULFUR SOAKED <u>LBA GLASS SERIES</u>

SULFUR EXPOSURE TEMPERATURE = 300°C

Glass(2)	Aging Time (Days)	Sample Mass (mg)	Surface Area (2) (sq. cm)	Mass Sulfate (µg)	Mass Thiosulfate (µg)	ug $S_2O_3^{2-}$ -------- µg SO_4^{2-}	Mass (1) Soda/sq cm (µg/sq cm)	Workup Code
LBA-45	7	218	85.0	21.9	0.0	---	0.66	E-2
LBA-40	7	230	89.7	16.6	0.0	---	0.48	E-2
LBA-35	7	225	87.7	13.4	0.0	---	0.39	E-2
LBA-33.3	7	203	79.2	11.5	0.0	---	0.37	E-2
LBA-45	18	223	86.9	23.6	0.0	---	0.70	E-2
LBA-40	18	222	86.6	14.6	0.0	---	0.43	E-2
LBA-35	18	216	84.2	10.0	0.0	---	0.31	E-2
LBA-33.3	18	225	87.7	9.4	0.0	---	0.28	E-2
LBA-45	28	202	78.8	20.5	0.0	---	0.67	E-2
LBA-40	28	197	76.8	11.6	0.0	---	0.39	E-2
LBA-35	28	223	86.9	9.6	0.0	---	0.28	E-2
LBA-33.3	28	199	77.6	9.0	0.0	---	0.30	E-2
LBA-45	65	198	77.2	21.6	0.0	---	0.72	E-2
LBA-40	65	203	79.2	13.1	0.0	---	0.43	E-2
LBA-30	65	201	78.4	13.5	0.0	---	0.44	E-2
LBA-33.3	65	198	77.2	12.2	0.0	---	0.41	E-2

<u>Compositions</u>

<u>Glass</u>	Na_2O	"Si_2O_4"	B_2O_3
LBA-45	0.45	0.275	0.275
LBA-40	0.40	0.300	0.300
LBA-35	0.35	0.325	0.325
LBA-33.3	0.333	0.333	0.333

Workup Codes: Refer to Table XIV.

Refer to Table XIV Notes for notes (1) and (2).

TABLE XXI

ION CHROMATOGRAPHIC ANALYSIS OF SULFUR SOAKED LBB GLASS SERIES

SULFUR EXPOSURE TEMPERATURE = 400°C

Glass (Note 2)	Aging Time (Days)	Sample Mass (mg)	Surface Area (sq. cm)	Mass Sulfate (µg)	Mass Thiosulfate (µg)	ug $S_2O_3^{2-}$ -------- µg SO_4^{2-}	Mass (1) Soda/sq cm (µg/sq cm)	Workup Code
LBB-40	6.5	207	80.7	50	86	1.7	1.6	E1-I
LBB-40	6.5	206	80.3	46	309	6.7	1.5	DI
LBB-40	7	218	85.0	73	390	5.3	2.2	DI
LBB-35	7	294	115.	77	255	3.3	1.7	DI
LBB-30	7	207	80.7	37	75	2.0	1.2	DI
LBB-25	7	213	83.1	15	0	0.0	0.47	DI
Pyrex	7	200	78.0	2.5	0	0.0	0.08	DI
LBB-40	15.0	232.5	90.7	132	284	2.1	3.8	DI
LBB-35	13.5	192	74.9	116	338	2.9	4.0	DI
LBB-30	15.0	275	107.	57	169	3.0	1.4	DI
LBB-25	12.5	196	76.4	19	0	0.0	0.64	DI
LBB-40a	27	204	79.6	113	190	1.7	3.7	DI
LBB-40b	27	204	79.6	123	657	5.3	4.0	DI-5 days
LBB-35a	27	202	78.8	138	193	1.4	4.5	DI
LBB-35b	27	202	78.8	138	545	3.9	4.5	DI-5 days
LBB-30a	27	232	90.5	53.0	173	3.3	1.5	DI
LBB-30b	27	232	90.5	90.3	95.2	1.0	2.6	DI-5 days
LBB-25a	27	250	97.5	28.5	0.0	0.0	0.75	DI

Compositions	Glass	Na_2O	"Si_2O_4"	B_2O_3
	LBB-40	0.40	0.200	0.400
	LBB-35	0.35	0.217	0.433
	LBB-30	0.30	0.233	0.467
	LBB-25	0.25	0.250	0.500

Workup Codes: Refer to Table XIV.

Note: E1-I means that insufficient eluant was used, resulting in a basic workup solution.

Refer to Table XIV Notes for (1) and (2).

TABLE XXII

ION CHROMATOGRAPHIC ANALYSIS OF SULFUR SOAKED <u>LBB GLASS SERIES</u>

SULFUR EXPOSURE TEMPERATURE = 300°C

Glass (Note 2)	Aging Time (Days)	Sample Mass (mg)	Surface Area (sq. cm)	Mass Sulfate (µg)	Mass Thiosulfate (µg)	ug $S_2O_3^{2-}$ / µg SO_4^{2-}	Mass (1) Soda/sq cm (µg/sq cm)	Workup Code
LLB-40	7	233	90.9	28	193	6.8	0.79	DI
LBB-35	7	262	102.2	27	145	5.4	0.68	DI
LBB-30	7	202	78.8	5.5	<5	---	0.18	DI
LBB-25	7	209	81.5	4.0	0	0.0	0.13	DI
LBB-40	13.5	234	91.3	(52.5)	45.5	0.87	(1.5)	E-70 hr.
LBB-40	13.5	240	93.6	30.5	327	10.7	0.84	DI-70 hr.
LBB-35	9	242	94.4	21	159	7.6	0.57	DI
LBB-30	10.5	257	100.2	6.5	0	0.0	0.17	DI
LBB-40a	26	248	96.7	26.5	161	6.1	0.71	DI
LBB-40b	26	248	96.7	(106)	180	1.7	(2.8)	DI-7 days
LBB-35a	26	191	74.5	12.5	79.5	6.4	0.43	DI
LBB-35b	26	191	74.5	(27.0)	185.	6.9	(0.94)	DI-7 days
LBB-30a	26	196	76.4	2.2	1.9	0.87	0.07	DI
LBB-30b	26	196	76.4	(21.5)	0.0	0.0	(0.73)	DI-7 days
LBB-25	26	200	78.0	6.5	0.0	0.0	0.22	DI-7 days

Samples with "b" suffix were allowed to stand 7 days prior to acidification with ion exchange resin.

<u>Compositions</u>	<u>Glass</u>	Na_2O	"Si_2O_4"	B_2O_3
	LBB-40	0.40	0.200	0.400
	LBB-35	0.35	0.217	0.433
	LBB-30	0.30	0.233	0.467
	LBB-25	0.25	0.250	0.500

Workup Codes: Refer to Table XIV.

Refer to Table XIV Notes for (1) and (2).

TABLE XXIII

ION CHROMATOGRAPHIC ANALYSIS OF SULFUR SOAKED LBC GLASS SERIES

SULFUR EXPOSURE TEMPERATURE = 400°C

Glass$^{(2)}$	Aging Time (Days)	Sample Mass (mg)	Surface Area (2) (sq. cm)	Mass Sulfate (μg)	Mass Thiosulfate (μg)	ug $S_2O_3^{2-}$ -------- μg SO_4^{2-}	Mass (1) Soda/sq cm (μg/sq cm)	Workup Code
LBC-40	5	194	75.7	53	510	9.6	1.8	DI-3 hr
LBC-35	5	214	83.5	43	321	7.5	1.3	DI-5 hr
LBC-30	5	226	88.1	16.0	65.5	4.1	0.47	DI-24 hr
LBC-40	14.5	198	77.2	107	0.0	---	3.6	E1
LBC-35	14.5	194	75.7	62.8	0.0	---	2.1	E1
LBC-30	14.5	205	80.0	48.5	0.0	---	1.6	E1
LBC-27.2	14.5	193	75.3	22.6	0.0	---	0.77	E1
LBC-40	30.5	219	85.4	156	0.0	---	4.7	E2
LBC-35	30.5	201	78.4	100	0.0	---	3.3	E2
LBC-30	30.5	218	85.0	80	0.0	---	2.4	E2
LBC-27.2	30.5	212	82.7	51	0.0	---	1.6	E2
PYREX	30.5	208	81.1	2.7	0.0	---	0.09	E2

Workup Codes: Refer to Table XIV.

Notes: (1) Refer to Table XIV Notes for (1) above.
(2) Glass powder mesh size: +100-80; 390 cm^2 g^{-1}.

Compositions

Glass	Na_2O	"Si_2O_4"	B_2O_3
LBC-40	0.40	0.150	0.450
LBC-35	0.35	0.1625	0.4875
LBC-30	0.30	0.175	0.525
LBC-27.2	0.272	0.182	0.546

TABLE XXIV

ION CHROMATOGRAPHIC ANALYSIS OF SULFUR SOAKED LBC GLASS SERIES

SULFUR EXPOSURE TEMPERATURE = 300°C

Glass(2)	Aging Time (Days)	Sample Mass (mg)	Surface Area (1) (sq. cm)	Mass Sulfate (µg)	Mass Thiosulfate (µg)	ug $S_2O_3^{2-}$ -------- µg SO_4^{2-}	Mass (2) Soda/sq cm (µg/sq cm)	Workup Code
LBC-40	14	225	87.8	27.0	0.0	---	0.79	E1
LBC-35	14	216	84.2	6.7	0.0	---	0.21	E1
LBC-30	14	195	76.1	3.6	0.0	---	0.12	E1
LBC-27.2	14	204	79.6	3.6	0.0	---	0.12	E1
LBC-40	28	225	87.8	26.0	0.0	---	0.76	E2
LBC-35	28	197	76.8	11.5	0.0	---	0.39	E2
LBC-30	28	210	81.9	5.5	0.0	---	0.17	E2
LBC-27.2	28	190	74.1	7.7	0.0	---	0.27	E2
LBC-40	62	230	89.7	27.5	0.0	---	0.79	E2
LBC-35	62	194	75.7	18.0	0.0	---	0.61	E2
LBC-30	62	204	79.6	9.0	0.0	---	0.31	E2
LBC-27.2	62	230	89.7	14.7	0.0	---	0.42	E2

Notes: (1) Refer to Table XIV Notes for (1) above.
(2) Glass powder mesh size: +100-80; 390 cm^2 g^{-1}.

<u>Compositions</u>

Glass	Na_2O	"Si_2O_4"	B_2O_3
LBC-40	0.40	0.150	0.450
LBC-35	0.35	0.1625	0.4875
LBC-30	0.30	0.175	0.525
LBC-27.2	0.272	0.182	0.546

TABLE XXV

ION CHROMATOGRAPHIC ANALYSIS OF SULFUR SOAKED <u>LBD GLASS SERIES</u>

SULFUR EXPOSURE TEMPERATURE = 400°C

Glass	Aging Time (Days)	Sample Mass (mg)	Surface Area (2) (sq. cm)	Mass Sulfate (µg)	Mass Thiosulfate (µg)	ug $S_2O_3^{2-}$ -------- µg SO_4^{2-}	Mass (1) Soda/sq cm (µg/sq cm)	Workup Code
Pyrex	5	200	78.0	6	0	0.0	0.2	DI
LBD-39	11	199	77.6	103	253	2.5	3.4	DI
LBD-35	11	176	68.6	103	200	1.9	3.9	DI
LBD-31	11	206	80.3	64.5	143	2.2	2.1	DI
LBD-39	27	196	76.4	126	75	0.60	4.3	E1-I
LBD-35	27	201	78.4	148	7.5	0.05	4.9	E1-I
LBD-31	27	243	94.8	89	0.0	0.00	2.4	E1

Workup Codes:

<u>E1-Eluant 1:</u> Glass powder extracted with eluant (4.0 mM potassium hydrogen phthalate, 0.4 mM phthalic acid, pH = 3.85), filtered, treated with cation exchange resin, refiltered and analyzed immediately.

<u>E1-I:</u> As above, but added in portions rather than all at once. Final pH <u>ca.</u> 5, but cannot guarantee that the mixture remained acidic during the multiple extractions.

<u>Compositions</u>

Glass	Na_2O	"Si_2O_4"	B_2O_3
LBD-39	0.39	0.061	0.549
LBD-35	0.35	0.065	0.588
LBD-31	0.31	0.069	0.621

<u>Notes:</u> (1) Refer to Table XIV Notes for (1) above.
(2) Glass powder mesh size: +100-80; 390 cm^2 g^{-1}.

TABLE XXVI

ION CHROMATOGRAPHIC ANALYSIS OF SULFUR SOAKED LBD GLASS SERIES

SULFUR EXPOSURE TEMPERATURE = 300°C

Glass	Aging Time (Days)	Sample Mass (mg)	Surface Area (2) (sq. cm)	Mass Sulfate (µg)	Mass Thiosulfate (µg)	ug $S_2O_3^{2-}$ -------- µg SO_4^{2-}	Mass (1) Soda/sq cm (µg/sq cm)	Workup Code
LBD-39	9	227	88.5	36.5	110.5	3.0	1.1	DI
LBD-31	9	192	74.9	10.5	1.3	0.12	0.36	DI
LBD-39	15	207	80.7	44.5	156	3.5	1.4	DI
LBD-35	15	234	91.3	30.5	149	4.9	0.86	DI
LBD-31	15	209	81.5	11.0	21	0.52	0.35	DI
LBD-39	27	187	72.9	48.0	172.	3.6	1.7	DI-1 day
LBD-35	27	202	78.8	23.0	168	7.3	0.75	DI-1 day
LBD-31	27	177	69.0	10.5	35.0	3.3	0.39	DI-1 day

Notes: (1) Refer to Table XIV Notes for (1) above.
(2) Glass powder mesh size: +100-80; 390 cm^2 g^{-1}

Refer To Table A2 for workup notes.

Compositions	Glass	Na_2O	"Si_2O_4"	B_2O_3
	LBD-39	0.39	0.061	0.549
	LBD-35	0.35	0.065	0.588
	LBD-31	0.30	0.069	0.621

TABLE XXVII

DETERMINATIONS OF "X" IN Na_2S_x PRODUCED BY SULFUR EXPOSING

D406 GLASS 5 DAYS AT 400°C

Mass Glass(1) (mg)	Glass Surface Area (cm^2)	Mass Sulfur (mg)	Initial(2) SO_4^{2-} (µg)	Na_2O(3) loss (µg-cm^{2-})	Final(4) SO_4^{2-} (µg)	Ratio $\frac{SO_4^{2-}\text{ final}}{SO_4^{2-}\text{ initial}}$	Calculated(5) Value of "X" in Na_2S_x
218.5	55.8	16	109.3	5.0	1210	11.3	3.36
215.5	55.2	14	115.4	5.4	782.8	6.8	1.93
200.0	21.2	12	165.2	8.3	942.9	5.7	1.57
211.0	54.0	14	101.4	4.9	780.5	7.7	2.23
200.8	51.4	10	102.9	[5.2](6)	779.5	7.6	[2.2]
210.0	53.8	10	141.8	[6.8]	--	--	--
217	55.5	19	142.9	[7.1]	1,018.	6.6	[1.87]
210.0	53.8	220	75.1	3.6	617	8.2	2.4
211.0	54.0	206	81.2	3.9	662	8.2	2.4
217.5	55.6	215	73.6	3.4	--	--	--
200	51.2	206	127.8	[6.4]	723	5.7	[1.57]
210.5	53.9	200	153.8	[7.4]	741	4.8	[1.27]
159	40.7	202	156.4	[4.5]	709	9.9	[2.97]
141.0	36.1	230	90.1	[7.1]	641	6.4	[1.8]

NOTES FOR TABLE XXVII

(1) Glass powder mesh size: +80-60; 256 $cm^2\ g^{-1}$.

(2) Sample extracted 20 sec with 20 ml deionized water. Solution pH adjusted to *ca.* 5-6 with Dowex cation exchange (hydrogen form) followed by immediate chromatographic analysis (4 mm KHP, 0.4 mm PA, pH 3.8).

(3) Determined from measured SO_4^{2-} and stoichiometry of Reaction 1:

$$4\ Na_2O + 3(X+1)S \ = \ Na_2SO_4 + 3Na_2S_x$$

(4) Determined by chromatographic analysis after treatment with excess $Br_2(l)$, 1-2 µl.

(5) Calculated from:

$$X = \frac{1}{3}\left[\frac{SO_4^{2-}\ \text{final}}{SO_4^{2-}\ \text{init}} - 1\right]$$

Assumes no sulfur containing species other than SO_4^{2-} and S_x^{2-}.

(6) Numbers reported in brackets are for samples where the in situ sulfur distillation was performed with liquid nitrogen cooling of the empty section of the sample tube. Normal in situ distillation has this end at ambient temperature.

TABLE XXVIII

DETERMINATIONS OF "X" IN Na_2S_x PRODUCED BY SULFUR EXPOSING

T806 GLASS 5 DAYS AT 400°C

Mass Glass(1) (mg)	Glass Surface Area (cm^2)	Mass Sulfur (mg)	Initial(2) SO_4^{2-} (μg)	Na_2O(3) loss ($\mu g\text{-}cm^{-2}$)	Final(4) SO_4^{2-} (μg)	Ratio $\frac{SO_4^{2-}\text{ final}}{SO_4^{2-}\text{ initial}}$	Calculated(5) Value of "X" in Na_2S_x
197	117	13.5	94.7	2.1	874	9.2	2.73
198	117	10	120.1	2.6	827	6.9	1.97
130	77.1	11	76.7	2.5	620	8.1	2.37
175	103.8	230	66.1	1.65	1,013	15.3	4.77
218	129.3	200	82.8	1.65	1,092	13.2	4.07
202.5	120.1	200	116	[2.5]	1,036	8.9	[2.63]
242	143.5	230	143.5	[2.8]	1,508	10.5	[3.17]

Notes:

(1) Glass powder mesh size: +140 - 100; 593 $cm^2\ g^{-1}$.

Refer to Table XXVII for notes (2) - (5).

TABLE XXIX

CHANGE IN "X" FOR Na_2S_x UNDER IN SITU SULFUR DISTILLATION CONDITIONS (300°C VACUUM)

DATA FOR Na_2S_4

Mass Na_2S_4 (mg)	Distillation Time (hr)	Calc. Yield(1) (Theory) SO_4^{2-} (mg)	SO_4^{2-} found after Br_2 oxid. (mg)	% Found / Theory	Calculated Value of "X" in Na_2S_x	Comment
16.7	0	36.83	36.5	99.1	3.96	CONTROL
17.2	0	37.93	38.0	100.1^8	4.01	CONTROL
20	0.5	44.11	37.8	85.6^9	3.43	
19	[0.5]^2	41.90	35.5	84.7^3	3.39	
23	[0.75]	50.72	39.4	77.6^8	3.11	
28	16.0	61.75	39.2	63.4^8	2.54	

Notes:

(1) S_x^{2-} oxidized to X SO_4^{2-} by Br_2. For X = 4, we have:

$$\underset{\text{FW } 174.236}{Na_2S_4} + 13\ Br_2 + 16\ H_2O = 4\ SO_4^{2-} + 26\ Br^- + 32\ H^+ + 2\ Na^+$$

$$\text{wt}\quad SO_4^{2-}/Na_2S_4 = 4(96.0616)/174.236 = 2.2053$$

(2) Brackets indicate that empty end of distillation tube was kept at liquid nitrogen temperature during distillation.

TABLE XXX

ANALYSIS OF D406 GLASS EXPOSED TO SULFUR (200 mg) CONTAINING 1 mg POLY-(4-METHYL-1-PENTENE) FOR 5 DAYS

Oxidation Code(1)	Mass Glass(2) (mg)	Glass Surface Area cm^2	Sulfur Exp. Temp (°C)	Mass SO_4^{2-} Init.(3) (µg)	Mass SO_4^{2-} Final(4) (µg)	Mass $S_2O_3^{2-}$ Init.(3) (µg)	Mass $S_2O_3^{2-}$ Final(4) (µg)	Mass Ratio $\frac{S_2O_3^{2-}\text{ Final}}{SO_4^{2-}\text{ Initial}}$	Na_2O(5) Loss µg/cm^2
I	210.0	53.8	300	9	12.5	25	107	11.9	0.43
I(a)	204.7	52.4	400	10.9	36.3	45.2	586	53.8	
II(b)	204.7	52.4	400	10.9	27.6	45.2	633	58.1	0.54

Suffixes (a) and (b) refer to different portions of workup solutions from one glass sample.

Notes:

(1) Oxidation Codes: (I) saturated with O_2 for 10 min prior to pH adjustment with Dowex cation exchange resin.
(II) Workup solution exposed to air overnight, then saturated with O_2 for 10 min prior to pH adjustment.

(2) Glass powder mesh size: +80 - 60; 256 cm^2 g^{-1}.

(3) Initial values are those obtained immediately after extraction of glass powder with deionized water (20 ml for 20 sec) follwed with pH adjustment to ca. 5-6.

(4) Values obtained after oxidation of basic workup solution as per "Oxidation Code". Solution pHs adjusted to ca. 5-6 before Ion Chromatographic analysis. (Eluant: 4 mm KHP; 0.4 mm PA; pH 3.8).

(5) Calculated from Initial Sulfate and stoichiometry of Reaction I.

TABLE XXXI

ANALYSIS OF T806 GLASS EXPOSED TO SULFUR (200 mg) CONTAINING 1 mg POLY-(4-METHYL-1-PENTENE) FOR 5 DAYS

Oxidation Code(1)	Mass Glass(2) (mg)	Glass Surface Area cm^2	Sulfur Exp. Temp (°C)	Mass SO_4^{2-}		Mass $S_2O_3^{2-}$		Mass Ratio $\frac{S_2O_3^{2-}\text{ Final}}{SO_4^{2-}\text{ Initial}}$	Na_2O(5) Loss $\mu g/cm^2$
				Init.(3) (µg)	Final(4) (µg)	Init.(3) (µg)	Final(4) (µg)		
II	211	54.0	300	9.8	21.1	40.5	259	12.3	0.47
				9.8	38.1	40.5	892	91.0	
II	200	51.2	400	17.3	30	78.3	1220	70.5	0.87
	200	51.2	400	17.3	40.4	78.3	2196	126.9	
	215		400	10.9(6)	--	57.4	---	---	0.51

Refer to Table XXX for note (1) - (5).

(6) Sample workup with 20 ml 2% formaldehyde (H_2CO); H_2CO complexes sodium sulfite and thereby prevents the normally rapid oxidation to sulfate by atmospheric oxygen. It may also slow solution oxidation of $S_2O_3^{2-}$ to SO_4^{2-}.

APPENDIX E

INFRARED ANALYSIS OF SULFUR EXPOSED T806 GLASS

One of two identically sulfur exposed (400°C, 6.5 days) T806 glass samples (200 mg), was cleaned by in situ distillation and submitted for diffuse reflectance infrared fourier transform spectroscopy (DRIFT). The concentration of sodium sulfate (60 μg/200 mg, 0.03 wt%) is insufficient for detection by DRIFT. Notice also that the small mass change would be very difficult to detect on a standard analytical balance.

SPECIAL ANALYTICAL REPORT WC-84-92

DECEMBER 11, 1984

C. A. NIELSEN, CENTRAL RESEARCH, WALNUT CREEK

FT-IR ANALYSIS FOR SULFATE ON SULFUR EXPOSED GLASS

INTRODUCTION: The reaction of sulfur with the glass hollow fibers used in the Sodium-Sulfur batteries is suspected to result in shortened lifetimes of these devices. Diffuse reflectance infrared spectroscopy is a technique requiring minimum sample preparation and would be able to detect oxidized sulfur compounds in the low percentage levels. The depth of penetration of the infrared radiation into the glass particles is a complicated mathematical function. I would guess it to be on the order of 50 microns for these glasses over the spectral range of 2600 cm^{-1} to 2000 cm^{-1} (the sulfur-oxygen overtone region).

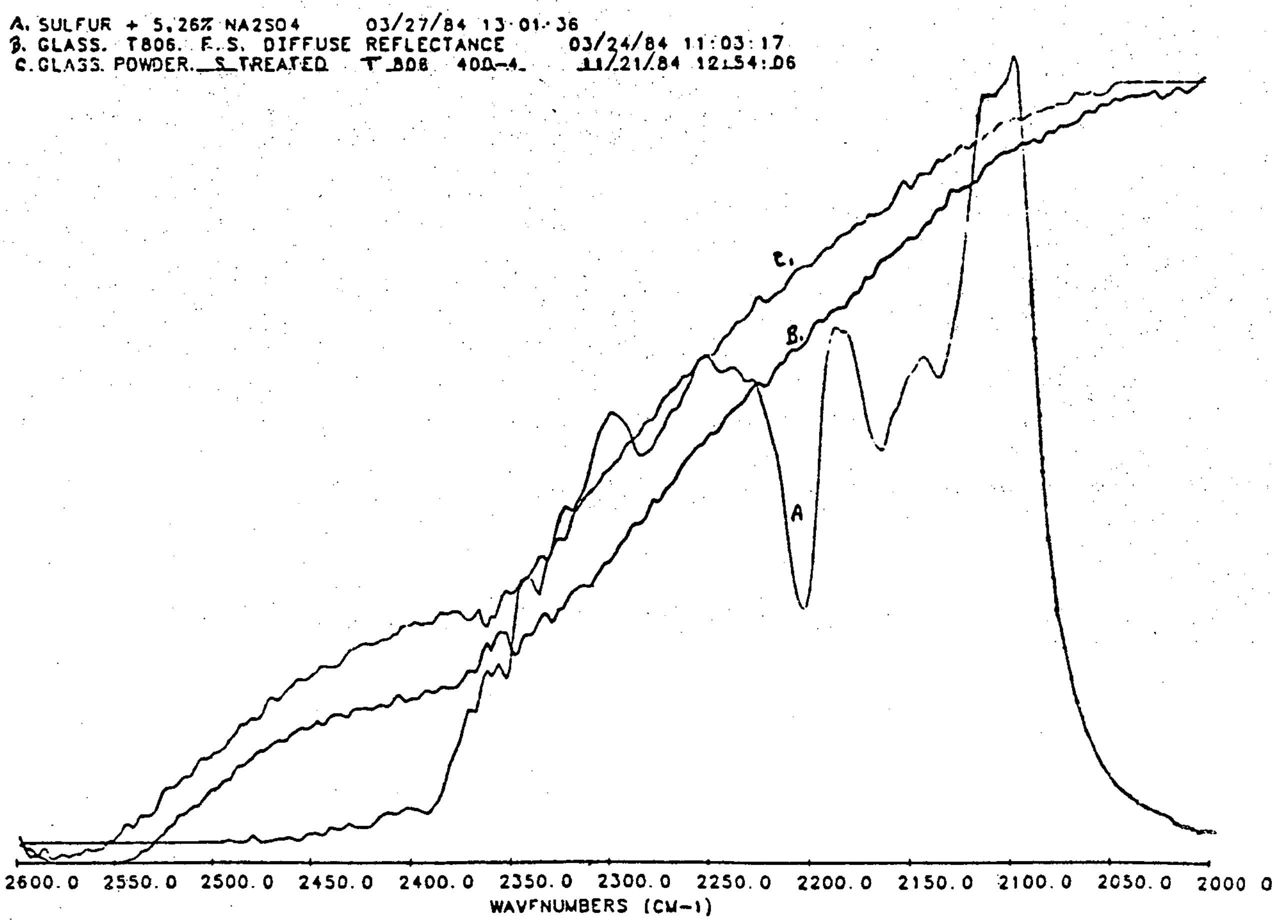
EXPERIMENTAL: A Nicolet 5-DX fourier transform infrared spectrometer was used with a Barnes Analytical diffuse reflectance accessory. One hundred scans at 4 cm^{-1} resolution, instrument gain of 8, were averaged and ratioed against a KBr background. One glass sample, T-806, 400-4, known to be relatively high in sulfate, was run as received and again diluted with KBr (about 1:20). These spectra were compared to spectra of unexposed, annealed sample of T-806 glass. A sample of sulfur containing 5.25% Na_2SO_4 was also run in order to get some idea of the relative sensitivity.

RESULTS: Three spectra are superimposed in Figure 1: the spectra of T-806, 400-4, of the untreated T-806 and of Sulfur containing 5.26% Na_2SO_4. The Kubelka-Munk transformation of the spectra were not done; the presentation is in Absorbance units. However, since we see no absorbance due to sulfate this refinement would be academic. Assuming the absorption due to Sulfate in the glass to be the same as in the sulfur we would place an approximate lower limit of 1% for this technique without going to extremely long acquisition times.

M. D. YEAMAN, ANALYTICAL LABORATORIES, WALNUT CREEK

APPENDIX E- CONTINUED

INFRARED ANALYSIS OF SULFUR EXPOSED T806 GLASS



APPENDIX F

DERIVATION OF AN EXPRESSION FOR THE TOTAL AMOUNT OF SODIUM OXIDE DIFFUSING OUT OF GLASS IN TIME "t"*

$$D = \frac{a^2}{\tau_0} e^{-Ea/kT}$$

Where:
$D \equiv$ diffusion constant (cm^2/sec)
$a \equiv$ atom hop distance (cm) for diffusing species
$Ea \equiv$ activation energy (erg/atom)
$k \equiv$ Boltzman's constant (erg/(atom - °K))
$\tau_0 \equiv$ [attempt frequency]$^{-1}$ (sec)

$$\text{Flux} = \frac{\text{atoms}}{\text{cm}^2\ \text{sec}} = J$$

$$J = D \frac{\partial c}{\partial x} = \left[\frac{a^2}{\tau_0} \exp(-Ea/kT)\right] \frac{\partial c}{\partial x}$$

$$Q = \int_0^t J dt = \text{total Na}_2\text{O diffusing in time "t"}$$

Let $c = c(x,t)$

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \qquad \text{Eq. 1}$$

Now $c(x,t) = c_0$ = concentration of diffusing species, e.g. Na_2O, in molecules/cm^3

Boundary Conditions: $c(0,t) = 0 \quad t>0 \quad$ Eq. 2
$c(x,0) = c_0 \quad x<0 \quad$ Eq. 3

---

*Derived by Lowell Hazelton, Dow Chemical U.S.A., Central Research-Walnut Creek, CA

Let $c = F(x)T(t)$

$$\frac{1}{T(t)} \frac{\partial T(t)}{\partial t} = D \frac{1}{F} \frac{\partial^2 F}{\partial x^2}$$

$$\frac{dT(t)}{T(t)} = Kdt$$

$$\ln T(t) = Kt + c$$

$$T(t) = ce^{Kt} \qquad K<0$$

$$\frac{1}{F} \frac{\partial^2 F}{\partial x^2} = \frac{K}{D}$$

$$F = Ae^{ax} \quad : \quad a^2 = \frac{K}{D} \quad \Longrightarrow \quad a = \pm i \sqrt{\frac{-K}{D}}$$

<u>or</u> $F = A\sin \alpha x + B\cos \alpha x$

$$c = e^{kt} (A\sin \alpha x + B\cos \alpha x)$$

where $k = -K, \quad \alpha = \sqrt{\frac{k}{D}}$

from Eq. 2, $B = 0$

or $c = Ae^{-kt}\sin \alpha x$

$$c(x,0) = \int_0^\infty A(\alpha)\sin(\alpha x)d\alpha$$

where $A(\quad) = \frac{2}{\pi} \int_0^\infty c(x,0)\sin(\alpha x)dx$

from $c(x) = c_0 \Longrightarrow A(\alpha) = \frac{2}{\pi} \frac{C_0}{\alpha}$

$$c(x,t) = \frac{2}{\pi} c_0 \int_0^\infty e^{-kt} \frac{1}{\alpha} \sin(\alpha x)\, d\alpha \quad ; \quad k = D\alpha^2$$

$$= \frac{2}{\pi} c_0 \int_0^\infty e^{-D\alpha^2 t} \frac{1}{\alpha} \sin(\alpha x)\, d\alpha$$

Flux: $$J = D \left.\frac{\partial c}{\partial x}\right|_{x=0} = D \frac{2c_0}{\pi} \left.\int_0^\infty e^{(-D\alpha^2)t} \cos(\alpha x)\, d\alpha \right|_{x=0}$$

$$= \frac{1}{2} \frac{2Dc_0}{\pi} \sqrt{\frac{\pi}{Dt}} \left. e^{\frac{-x^2}{4Dt}} \right|_{x=0}$$

$$= c_0 \sqrt{\frac{D}{t}} \left. e^{\frac{-x^2}{4Dt}} \right|_{x=0} = \sqrt{\frac{D}{\pi t}}\, c_0$$

$$Q = \text{total } Na_2O = \int_0^t J\,dt = 2 \cdot \sqrt{\frac{D}{\pi}}\, t^{1/2} c_0 \quad \text{in } \frac{\text{molecules}}{\text{cm}^2}$$

if $D = \frac{a^2}{\tau} = \frac{a^2}{\tau_0} e^{-Ea/kT}$ Where τ is the reciprocal of success frequency

$$Q = 2c_0 a \sqrt{\frac{t}{\pi \tau_0}}\, e^{-Ea/2kt} \equiv Q_0 e^{-Ea/2kT}$$

where $$\tau_0 = \frac{4c_0^2 a^2 t}{\pi\, Q_0^2 \left[\frac{N_A}{m\ Na_2O\ (\mu g)}\right]^2}$$ Eq. 4

Note units of Q are $\frac{\mu g}{cm^2}$

Now, $$\ln Q = \ln \left[2c_0 a \sqrt{\frac{t}{\pi \tau_0}} - \frac{Ea}{2kT} \right]$$

$$\ln Q = A + B\left(\frac{1}{T}\right)$$

Now A and B are found from the least squares fit of the Arrhenius activation energy plot.

$$Q_0 = e^A$$

$$B = \frac{-Ea}{2k} \quad \text{or} \quad -\frac{Ea'}{2R} \quad \text{Where } Ea' \cong \text{cal/mole and } R = 1.98 \ \frac{\text{cal}}{\text{mole°K}}$$

$$Ea' = (-2R)B$$

As an example, take the following for T806 ($Na_2O \cdot 1.1\ B_2O_3 \cdot 1.3\ SiO_2$):

$$c_0 = \frac{\rho}{\text{mass } Na_2O} = \frac{2.3 \text{ g cm}^{-3}}{(62 + 76.6 + 78.1)\text{g}/N_A} = 6.4 \times 10^{21} \text{ molecules } Na_2O/\text{cm}^3$$

$$a = 3\ \text{Å} = 3 \times 10^{-8} \text{ cm}$$

$$t = 14 \text{ days} = 1.21 \times 10^6 \text{ sec}$$

$$\tau_0 = 10^{-13} \text{ sec}$$

$$Q_0(\text{T806}) = \left[\frac{4(6.4 \times 10^{21} \text{ molecules } Na_2O/\text{cm}^3)(3 \times 10^{-8} \text{ cm})^2 (1.21 \times 10^6 \text{ sec})}{\pi \left(\frac{6.02 \times 10^{23} \text{ molecules/mole}}{62 \times 10^6\ \mu\text{g } Na_2O/\text{mole}} \right)^2 \quad (1 \times 10^{-13} \text{ sec})} \right]^{1/2}$$

$$= 7.8 \times 10^7\ \mu\text{g } Na_2O/\text{cm}^2$$

	Q_0	τ_0	Ea'
Observed T806:	3.3×10^4	5.5×10^{-7} sec	26.7 Kcal/mole
Observed D406:	9.5×10^9	6.3×10^{-18} sec	56.3 Kcal/mole

APPENDIX G

PREPARATION OF T806 CAPILLARY LOTS CO50852L AND CO82331L

A. Capillary lot CO50852L - Glass Preparation

Wt, compound, source.

66.05g, SiO_2, Johnson MattLog Chem /0856
40.35g, Na_2CO_3, Johnson MattLog Chem /0861
93.6g, $Na_2B_4O_7$, Johnson MattLog Chem / 0875

Note, reagent purities 99.999% or better, puratronic grades.

Powders mixed 1 hour by tumbling and subsequently melted and mixed (11 times) over a 5 hour period at 1200°C in covered Pt-Au (5% Au) alloy crucible.

Glass Batch Code: G042550L
Reference Book: C-0052 p. 10

B. Capillary lot C082331L - Glass Preparation

Refer to Appendix H in the section title "Sample Preparation (T806A and T806B)".

C. Comparative "spinning" conditions.

	CO50852L	CO82331L
Hold temperature prior to spinning	1000°C	1100°C
Hold time prior to spinning	18 hr	18 hr
Tank bottom temperature	1000°C	1000°C
Heat shield temperature	841°C	840°C
Spinnerette temperature	809°C	812°C
Draw rate	75 m/min	75 m/min
Notebook references	C0052:10	C001:30

APPENDIX H

PREPARATION OF T806 GLASS STRESS BARS AND BIREFRINGENCE INSPECTION

This note describes the preparation of three rectangular "stress" bars (3 mm x 3 mm x 41 mm) prepared from glass composition T806 (Na_2O-1.1B_2O_3-1.3SiO_2). Details of sample preparation, grinding, and annealing conditions will be given shortly. Birefringence measurements were made by passing white light through the length of the specimens. Specimens were placed between crossed Polaroid filters with a first order blue tint plate inserted between the specimen and the analyzing Polaroid filter of the microscope. The tint plate gives a blue colored background and enhances the sensitivity for birefringence (22). Since birefringence is observed in two identically prepared, carefully annealed samples (T806A and T806B), composition gradients affecting the index of refraction are suspected. The third sample (T806C) was melted at a higher temperature (1200°C versus 1000°C) and was mixed more thoroughly (ten versus three stirrings). Birefringence is reduced in the latter sample. Comparative measurements of Rayleigh scattering on these three samples were attempted, but were unsuccessful due to the presence of bubbles in the glass. However, the "light path" could not be seen through any of the specimens indicating the glass was "relatively" uniform.

Experimental

Reagents

Na_2O-SiO_2	(PQ Metso Anhydro Beads #2408)
Na_2O-$2Si_2O_3$	(PQ SS20)
B_2O_3 Boric Anhydride Powder	(J.T. Baker Lot 404343)

Sample Preparation (T806A and T806B)

Na_2O-SiO_2 (106.2 g, 0.87 mol), Na_2O-$2Si_2O_3$ (33.8 g, 0.186 mol), and B_2O_3 (76.6 g, 1.1 mols were weighed into a glass container. The powders were mixed for approximately 5 minutes by tumbling the sealed container end for end. The mixed powder was placed in a platinum crucible (uncovered) and was held at 1000°C for 1.5 hr. The glass melt was stirred three separate times while at temperature. Glass sticks were cast by pouring the hot melt directly onto aluminum V-shaped troughs initially at room temperature.

The sticks so obtained were vacuum annealed for 2 hr. at 500°C and cooled at a rate of 1°C $min.^{-1}$ to room temperature. Sample grinding was performed under kerosene in a dry room (ca. 5% relative humidity) on a Raytech-Shaw facet machine using four progressively finer diamond mesh wheels (180, 600, 1200, 3000 mesh). The surface finish is smooth to approximately 5 µm after the final polishing. Dichloromethane was used for glass surface cleaning and rinsing to avoid possible reaction with boron trioxide; alcohols and water should be avoided since they may form boron esters or hydroxides, respectively.

Significant color shifts were observed when the bars were examined for birefringence; the probable cause being either unrelieved stress or glass inhomogeneity. In order to eliminate possible residual stresses, the bars were then reannealed (in vacuum) using the following schedule: temperature increased from 40°C to 540°C over 5 hr., held 4 hr. at 540, cooled at 0.5°C min.$^{-1}$ to 380°C (125°C below Tg) and further cooled to room temperature at a rate of 1°C min.$^{-1}$; this annealing schedule is defined as <u>Schedule A</u> for future reference. The two specimens marked "T806A" and "T806B" are for these reannealed specimens. Both specimens still show significant birefringence (23); sample "T806A" shows greater shifts $[(N_2-N_1)_{max} = (12 + 1.5) \text{ X } 10^{-6}]$ than "T806B" $[(N_2-N_1)_{max} = (6.0 + 0.8) \times 10^{-6}]$. The birefringence shifts were estimated by the use of a Michel-Levy scale of birefringence (24); the retardation (R) can be calculated by the following equation:

$$N_2-N_1 = R/t$$

where "t" is the the optical path length through the specimen (41 mm for these specimens). Both samples were prepared from the same glass melt and were annealed and reannealed together in the same container. The differences in birefringence are believed to be caused by glass inhomogeneity rather than by residual stresses since the same final annealing schedule (Schedule A) gives significantly reduced birefringence for more thoroughly mixed glass, refer to Sample "T806C" described below.

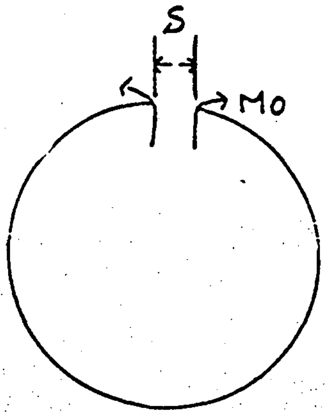
<u>Sample Preparation (T806C)</u> (18).

Na_2O-SiO_2 (183.9 g, 1.51 mols, (Na_2O-$2Si_2O_3$) (58.6 g, 0.322 mol), and B_2O_3 (132 g, 1.90 mols) were weighed into a glass jar and were mixed by tumbling end for end over a 90 min. period. The powder was placed in a covered platinum-gold (5% gold) crucible for melting at 1200°C. At approximately 20 min. intervals, the crucible was removed and the glass melt was vigorously stirred for 100-150 strokes. Ten such stirrings were performed for a total fusing time of 3.5 hr. Glass sticks (15 mm x 10 mm x 275 mm) were cast by pouring into a chrome plated nickel, V-shaped trough. The sticks were annealed according to Schedule "A" defined previously.

Using a diamond saw cooled with kerosene, a specimen was cut to approximately 10 mm x 10 mm x 43 mm and the ends were lapped to a 3000 mesh finish for inspection by birefringence. Shifted colors were observed along the saw cut surface and to a lesser extent within the bulk of the sample. Reannealing according to Schedule "A" eliminated virtually all birefringence. The specimen was ground to final size (3 mm x 3 mm x 41 mm) and subsequently examined by birefringence. Significant color shifts color shifts were again observed. Reannealing once more according to Schedule "A" again nearly eliminates all birefringence $[(N_2-N_1)_{max} = (3.0 + 0.8) \times 10^{-6}]$ - Sample "T806C".

APPENDIX I

Part 1: Estimate of Residual Stress in a Surface Layer Due to Opening of a Cracked Tube

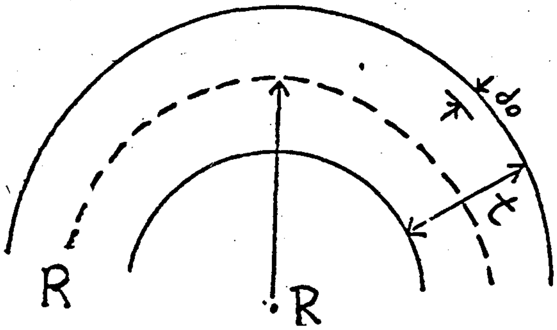


$$S = \frac{2\pi M_o R^2}{E' I}$$

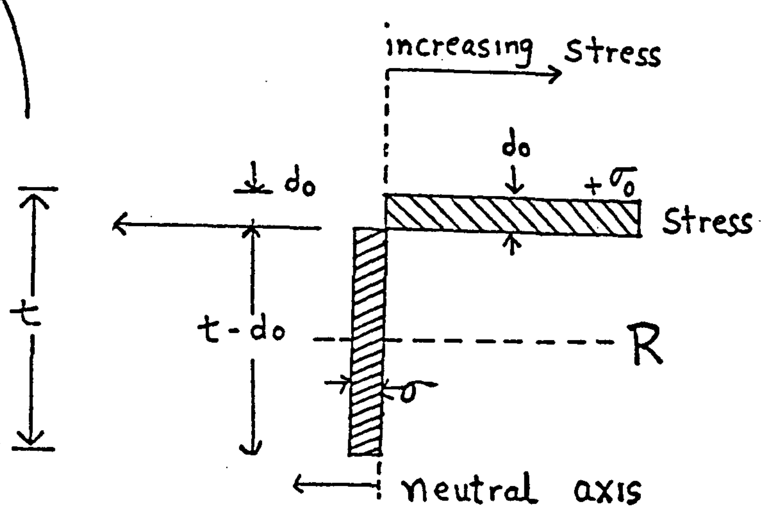
R = mean radius; $E' = \frac{E}{1-v^2}$; v = poisson's ratio; $I = \frac{1}{12} t^3$;

t = wall thickness

Assume :



Surface tensile stress (σ_0) in this layer of depth d_o



$$\sigma_0 \; d_0 = \sigma \, (t-d_0)$$

$$\sigma \sim \sigma_0 \, \frac{d_o}{t}$$

for d<<t

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*Derived by Dow Consultant Professor Iain Finnie.

$$M_0 = \sigma_0 \; d_0 \frac{t}{2}$$

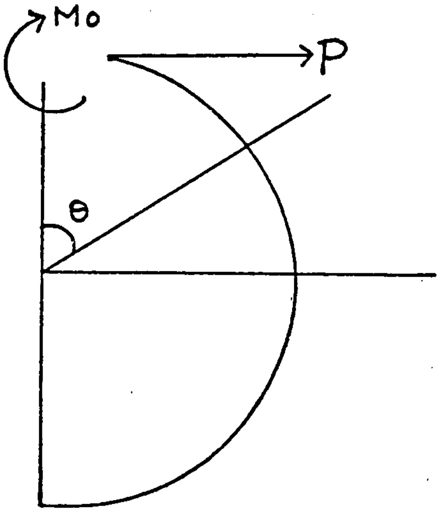
$$\sigma_0 \, d_0 = \frac{2M_0}{t}$$

$$\text{but } M_0 = \frac{\delta E'I}{2\pi R^2}$$

$$\sigma_0 \, d_0 = \frac{\delta E'I}{2\pi R^2} \left(\frac{t^3}{12}\right)\left(\frac{2}{t}\right)$$

$$\sigma_0 \, d_0 = \delta \left(\frac{t}{R}\right)^2 \frac{E'}{12\pi}$$

Derivation of δ, M_0 relationship



$$M_\theta = M_0 + PR(1-\cos\theta)$$

Strain Energy $\quad U = \int_0^\pi \frac{[M_0 + PR(1-\cos\theta)]^2}{2EI} R\,dE$

(For 1/2 a ring)

$$\frac{\delta}{2} = \frac{\partial u}{\partial P} = \frac{1}{EI}\int_0^{\pi} [M_0 + PR(1-\cos\theta)]\, R(1-\cos\theta)\, Rd$$

$$\frac{\delta}{2} = \frac{M_0R^2}{EI}\int_0^{\pi} (1-\cos\theta)\, d\theta$$

$$\delta = \frac{2\pi M_0 R^2}{EI}$$

Solving for M_0 gives: $M_0 = \frac{\delta EI}{2\pi R^2}$

Part 2: Derivation of loading moment caused by sodium oxide abstraction from glass.

$$\Delta V = \Delta M \left(\frac{\partial V}{\partial M}\right)$$

where $\frac{\partial V}{\partial M}$ is the partial molar volume of sodium oxide in a glass.

ΔV = differential volume change
ΔM = differential moles lost
Moment $= \sigma d = E \frac{\Delta L}{L} d$

$$\sigma d = E\left(\frac{1}{3}\frac{\Delta V}{V}\right) d$$

$$\sigma d = \frac{E}{3}\,\frac{\Delta M \frac{\partial V}{\partial M}}{Ad}\, d$$

$$\sigma d = \frac{E}{3}\left(\frac{\Delta M}{A}\right)\left(\frac{\partial V}{\partial M}\right)$$

$\frac{\partial V}{\partial M} \sim 24 \frac{cm^3}{\text{mole } Na_2O}$ for glass T806.

Refer to Appendix J.

APPENDIX J

MEASUREMENT OF GLASS DENSITIES AND PARTIAL MOLAR VOLUMES OF Na_2O IN GLASSES

Table XXXII summarizes the results of density measurements on 15 glasses. In addition, the volumes of 1g glass matrix (Si_2O_4 & B_2O_3) containing m moles of Na_2O are calculated, e.g. total glass weight greater than 1 gm. The latter volumes are plotted and curve fitted to first and second degree polynomials. The polynomial coefficients and slopes, which give the partial molar volume of Na_2O are tabulated in Table XXXIII. In all but the LBA series, the second degree polynomials give better fits to the data, as evidenced by larger values of the F statistic. Notice that the partial molar volume of Na_2O nearly doubles from the lowest to the highest levels of sodium oxide in the LBB and LBC series.

We will approximate $\partial V/\partial m_{Na_2O}$ for T806 using the LBB glass series data which are nearest to T806.

$$Na_2O \cdot 1.1\ B_2O_3 \cdot 1.3\ SiO_2$$

$$Na_2O \cdot 1.1\ B_2O_3 \cdot 0.65\ Si_2O_4$$

$$\text{cation \% } Na^+ = \frac{1}{2.75} = 0.364$$

$$F \simeq \frac{Si_2O_4}{Si_2O_4 + B_2O_3} = \frac{0.65}{1.75} = 0.371$$

$$\text{Moles } Na_2O \text{ in 1 gm matrix} = \frac{i}{100 - i} \left[F \cdot MW_{Si_2O_4} + (1-F) \cdot MW_{B_2O_3}\right]^{-1}$$

$$= 6.46 \times 10^{-3} \text{ moles} = 6.46 \text{ mM}$$

$$\left.\frac{\partial V}{\partial M}\right._{LBB} = \text{mMoles } Na_2O \cdot 2 \cdot 2.187 - 4.26$$

$$= (6.46)\ (2)\ (2.187) - 4.26 = 24 \text{ cm}^2/\text{mole}$$

Figure 20 is a typical plot of volume versus moles Na_2O in 1 g of matrix. The line passing through the points is the second degree polynomial fit of glass volume to mMol Na_2O. The slope of this line, evaluated at various values of Na_2O, gives the partial molar volume of sodium oxide at specific compositions. Refer to Table XXXIV.

Figure 20

Graph of Glass Volume$^{(1)}$ Versus Moles of Sodium Oxide
Slope Gives Partial Molar Volume of Sodium Oxide
Data For LBB Glass Series

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POLYNOMIAL MODEL:  Y=A(M)*X^M+A(M-1)*X^(M-1)+...+A(1)*X+A(0)
Coefficients:
   A(0)=.521794113
   A(1)=-4.2590144
   A(2)=2187.15426

Source          Df          SS             MS            F

Regression       2         .004           .002       2073.191
Residual         1         .000           .000
Total            3         .004
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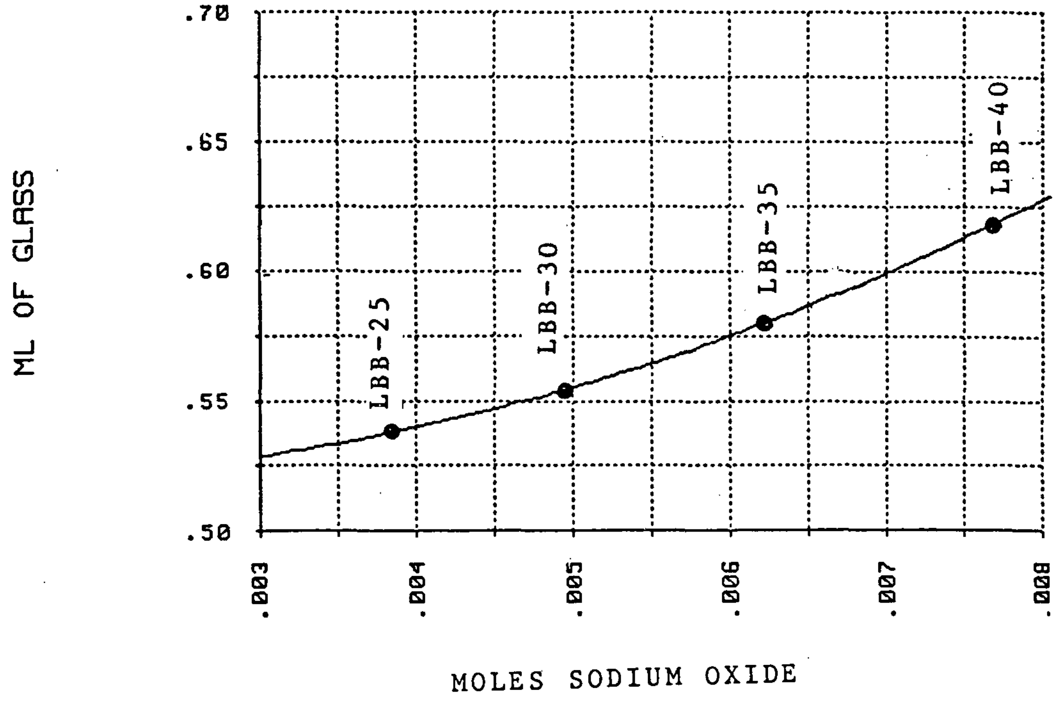

(1) Where the volume is for 1 gm of matrix containing the calculated number of moles of sodium oxide as listed in TABLE XXXIII.

TABLE XXXII

GLASS DENSITIES

	MEASURED QUANTITIES				CALCULATED PARAMETERS			
	Air Weights		Liquid Weights					
Glass Type	Hanger & glass (W_1)	hanger (W_2)	Hanger & glass (W3)	hanger (W4)	Volume(2) Glass ml	Glass(2) Density	mMoles Na_2O(4) in 1 gm Matrix	Volume(5) 1 gm Matrix with Na_2O
LBA-33.3	3.8382	1.9124	2.9407	1.7552	0.7996	2.409	5.26	0.5530
-35	5.6443	1.9114	4.0533	1.7540	1.5483	2.411	5.67	0.5606
-40	4.7196	1.9115	3.4878	1.7555	1.1619	2.417	7.02	0.6127
-45	4.9455	1.3201	3.4605	1.2276	1.5039	2.411	8.61	0.6737
LBB-25	3.5135	1.2704	2.5172	1.1764	0.9745	2.302	3.84	0.5380
-30	4.3600	1.2703	3.0553	1.1776	1.3090	2.360	4.94	0.5535
-35	4.3259	1.2701	3.0480	1.1776	1.2803	2.387	6.21	0.5803
-40	4.6267	1.2694	3.2325	1.1765	1.4054	2.389	7.69	0.6182
LBC-27.2	4.1675	1.2699	2.9111	1.1754	0.9745	2.302	3.84	0.5555
-30.0	5.2964	1.2693	3.6101	1.1776	1.3090	2.360	4.94	0.5651
-35.0	4.5926	1.2701	3.1987	1.1776	1.2803	2.387	6.21	0.5940
-40	4.4728	1.2693	3.1286	1.1765	1.405	2.389	7.69	0.6333
LBD-31	4.2130	1.3198	2.9507	1.2280	2.2886	2.289	6.02	0.6001
-35	4.0225	1.3198	2.8478	1.2276	2.3117	2.312	7.22	0.6262
-39	4.9096	1.3199	3.3827	1.2275	2.3170	2.317	8.57	0.6609

NOTES FOR TABLE XXXII

(1) Liquid weights measured in tributyl phosphate (TBP): d = 0.9259.

(2) $W_{glass\ in\ air} = W_1 - W_2 = W_A$; $W_{glass\ in\ TBP} = W_3 - W_4 = W_L$ $V_{glass} = (W_A - W_L)/\rho_{TBP}$

(3) Glass density = $\dfrac{W_A}{V_{glass}} = \dfrac{W_A}{W_A - W_L} \times 0.9259$

(4) Moles Na_2O in 1 gm glass matrix:

$$M_{Na_2O} = \frac{i}{100 - i}\left[F \cdot MW_{"Si_2O_4"} + (1 - F)\, MW_{B_2O_3}\right]^{-1}$$

where i is "cation %" Na^+ as designated from last digits of glass code, e.g. LBB40 gives i = 40.

$$F \equiv \frac{M_{Si_2O_4}}{M_{Si_2O_4} + M_{B_2O_3}}$$

The values of f are; LBA: F = 1/2; LBB: F = 1/3; LBC: 1/4; LBD: F = 1/10.

Refer to Table II in RESULTS SECTION for compositions.

(5) Volume of 1 gm glass matrix containing $Na_2O = (1\ gm + M_{Na2O}*62)/\ _{glass}$. These volumes are plotted against M_{Na2O} and are fitted to first and second order polynomials. The derivatives give:

$$\frac{\partial V}{\partial M_{Na_2O}}$$

, the partial molar volume of sodium oxide. Note that using 1 g matrix instead of 1 mole matrix merely shifts the curve downward along the y-axis but doesn't change the slope.

TABLE XXXIII

SUMMARY OF PARTIAL MOLAR VOLUME OF Na_2O IN THE GLASS SERIES

	$Volume_{glass} = ax + b$					$Volume_{glass} = a\,x^2 + bx + c$			
Glass	a(2) cm^3/mole	b	"F" Statistic	moles(1) Na_2O 10^3X	$V/_m$ = 2ax + b cm^3/mole	"a"	"b"	"c"	"F" Statistic
LBA-33.3	36.8	0.356	592.5	5.26	31.7	1501.05	+15.92	0.426	239.8
LBA-35.0	"	"	"	5.67	32.9	"	"	"	"
LBA-40	"	"	"	7.02	37.0	"	"	"	"
LBA-45	"	"	"	8.61	41.8	"	"	"	"
LBB-25	21.05	0.453	139.8	3.84	12.5	2187.15	-4.26	0.522	2073.9
-30	"	"	"	4.94	17.3	"	"	"	"
-35	"	"	"	6.21	22.9	"	"	"	"
-40	"	"	"	7.69	29.4	"	"	"	"
LBC-27.2	22.19	0.452	278.4	4.53	15.5	1862.98	-1.38	0.523	993.7
-30.0	"	"	"	5.19	18.0	"	"	"	"
-35.0	"	"	"	6.53	23.0	"	"	"	"
-40.0	"	"	"	8.08	28.7	"	"	"	"
LBD-31	23.91	0.455	454.7	6.02	19.9	1550	1.2217	0.5366	--
-35	"	"	"	7.22	23.6	"	"	"	"
-39	"	"	"	8.57	27.8	"	"	"	"

Notes:

(1) This is 1000X the number of moles of Na_2O contained in 1 gm glass matrix consisting of B_2O_3 and Si_2O_4.

(2) $\frac{\partial V}{\partial M_{Na_2O}} = a$

APPENDIX K

SILICON AND OXYGEN DIFFUSION IN OXIDE GLASSES

DATA FROM H. A. SCHAFFER - Ref. 20

tracer	composition,oxides-wt%	D_o(cm^2/s)	Q(kcal/mol)	T(°C)
^{31}Si	40.5 Si,20.9 Al,38.5 Ca	10^2	70	1365-1430
^{18}O	40 20 40	10^4-10^9	95±20	1370-1530
^{18}O	41.09 19.72 39.84	(9.2±2.2)x10^1	59.6±2.7	1320-1540
^{30}Si	40.0 19.6 40.3	1-10^{-3}	55±10	660- 760
^{18}O	40 20 40	7.5x10^{-3}	59	765- 845
^{18}O	39.24 21.24 39.52	$(2.8^{+2.2}_{-1.2})$x10^{-3}	57.7±1.2	625- 830
^{18}O	PbO	5.4 x10^{-5}	22.4	490- 650
^{30}Si	79.6 Pb, 20.3 Si	10^{-11}-2x10^{-12}	8.5±2	320- 400
^{18}O	88 Pb, 12 B	$(6^{+10}_{-\ 3})$x10^{-10}	11±1	275- 425
^{18}O	62 Pb, 27 Si, 7 K	$(1^{+2}_{-0.5})$x10^{-10}	12±1	275- 425
^{18}O	B_2O_3	2.5x10^{-2}	32.8±8	351- 650
^{18}O	60.9 B,18.4 Al,20.7 Ca	(5.2^{+8}_{-3})x10^{-5}	46.6±1.5	500- 600
^{18}O	42.5 23.2 34.3	(9.5^{+3}_{-2})x10^{-7}	35.4±0.4	475- 600
^{18}O	SiO_2	4.3x10^{-6}	56	900-1250
^{18}O	SiO_2, quartz	3.7x10^{-9}	55	1010-1220
^{18}O	SiO_2	1.5x10^{-2}	71	925-1225
^{18}O	SiO_2	2x10^{-9}	29	850-1250
^{18}O	86.5 Si,13.5 Na	5x10^{-10}	24	550- 700
^{18}O	72 Si,12 Ca,16 Na	2x10^3	66.5	460- 525

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