



(NASA-CR-134706) DEVELOPMENT OF POTASSIUM  
ION CONDUCTING HOLLOW GLASS FIBERS  
Final Technical Report (Dow Chemical Co.)  
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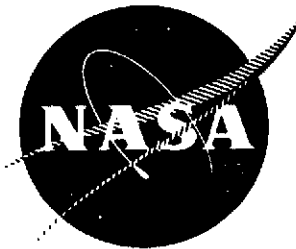
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FINAL TECHNICAL REPORT

October 21, 1974

DEVELOPMENT OF POTASSIUM  
ION CONDUCTING HOLLOW GLASS FIBERS

Contract No. NAS 3-16806



Sponsored by

National Aeronautics & Space Administration

Submitted by

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16. Abstract <p>Potassium ion conducting glasses, chemically resistant to potassium, potassium sulfide and sulfur, were made and their possible utility as the membrane material for a potassium/sulfur battery was evaluated. At least one satisfactory candidate was found. It possesses an electrical resistance of <math>1.3 \times 10^5 \Omega\text{-cm}</math> @ <math>300^\circ\text{C}</math>, which makes it usable as a membrane in the form of a fine hollow fiber. It's chemical and electrochemical resistances are excellent.</p> <p>The other aspects of the possible potassium sulfur battery utilizing such fine hollow fibers, including the header (or tube sheet) and a cathode current collector were studied. Several cathode materials were found to be satisfactory. None of the tube sheet materials studied possessed all the desired properties. Multi-fiber cells had very limited life time due to physical failure of fibers at the fiber/tube sheet junctions.</p> <p style="text-align: center;"><b>PRICES SUBJECT TO CHANGE</b></p>		
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TABLE OF CONTENTS

	<u>Page</u>
SUMMARY . . . . .	2
Technical Problems . . . . .	2
General Methodology . . . . .	2
Technical Results . . . . .	3
INTRODUCTION . . . . .	4
BACKGROUND . . . . .	6
RESULTS . . . . .	8
Glass Study and Selection . . . . .	8
Hollow Glass Fiber Fabrication . . . . .	11
Tubesheet Research . . . . .	13
Cathode Current Collector . . . . .	17
Multi-Fiber Cell Operation . . . . .	17
Cell Design . . . . .	18
CONCLUSION . . . . .	19
APPENDIX . . . . .	21
A. General Preparative Methods <sup>4</sup> . . . . .	21
B. Assembly of Single Fiber Cells . . . . .	23
C. Detailed Cell Design . . . . .	26
D. Comparison of K/S and Na/S Systems . . . . .	34

## SUMMARY

### Technical Problems

The main objective of this program is to define and characterize potassium ion conducting glasses suitable for hollow fiber electrolyte/separator use. As a desirable final goal, we shall demonstrate the feasibility of a long cycle life K/S secondary battery operating at 300°C with an energy density of 330 watt-hr./Kg (150 watt-hr./lb.) and a power density of 220 watts/Kg (100 watt/lb.). The actual design of an appropriate cell shall be made based on the properties of the glass so developed. Other essential parts of the cell, including the tubesheet and the cathode current collector, will also be studied and defined.

### General Methodology

Based on our previous knowledge in the analogous Na/S system, we made a search for the glasses in potassium borate/potassium halide system. Hand drawn fibers are used to make actual operating single-fiber cells to determine ionic conductances and chemical and electrochemical stability.

Tubesheet system search was again based on previous knowledge on the Na/S system. Parallel changes were made during the contract period as knowledge of needs increased.

Cathode materials, again previously known to us, were tested under operating conditions.

## Technical Results

In the glass membrane research, we have developed glasses that performed satisfactorily (T305) with the exception that present glass spinning techniques cannot be adapted to mass produce the desired fibers. The glasses that can be satisfactorily spun at present have good chemical resistance and have somewhat higher than desirable ionic resistance.

We have developed marginally usable tubesheet materials which should be improved upon. However, we did develop a vital processing step in making a solder glass into a tubesheet precursory paste--i.e., a high packing density extrudable suspension of the solder glasses in an inert medium.

Cathode current collectors previously developed for the Na/S system were shown to work satisfactorily in the K/S system.

Based on T305, a cell design was made where the complete cell without insulation has an energy density of 300 watt-hr/Kg (137 watt-hr/lb.) at slow discharge rate and 264 watt-hr/Kg (120 watt-hr/lb.) at 220 watt-hr/Kg (100 watt/lb.) discharge rate. Another design was made for a lower power demand cell.

## INTRODUCTION

The need of a high energy density, high power density, infinitely rechargeable secondary battery cannot be overstated. Stationary power storage and motive power are among the larger scale needs for systems with performances similar to that which we can easily expect from both the sodium-sulfur and potassium-sulfur hollow glass fiber cells.

Development has been and is proceeding on a high energy density sodium sulfur secondary battery which uses the walls of fine hollow glass fibers as the electrolyte/separator. Use of thousands of these hollow glass fibers, bundled together in parallel and filled with sodium as the anolyte, and immersed in a mixture of sodium polysulfide and sulfur as catholyte, has resulted in a cell that has a very high energy per unit weight at a high power per weight of actual operational components.\*

This work is an outgrowth of the Na/S work. Having developed a Na<sup>+</sup> glass system that is stable under such physical and chemical conditions as in the Na/S hollow fiber system, we obtained funding to perform the present work from NASA to explore into the K/S system with analogous K<sup>+</sup> glasses.

---

\* At this writing we are able to fabricate Na/S multi-fiber test cells of ca 1000 fibers (nominal dimension 70 $\mu$  OD x 50 $\mu$  ID x 4.5 cm length), with a theoretical capacity of 0.3 a-hr. and operate them (charge/discharge cycling @ 1 hr rate) for 20-30 days routinely.

The need for this study in the K/S system stems from the following advantages over the analogous Na system.

- (1) Even though the theoretical energy density of the K & Na systems are comparable, (Appendix D) the higher voltage (~16%) of the K system allows the use of fewer units for the same voltage requirement which should decrease the amount of hardware needed.
- (2) The K/S system has a low melting eutectic @  $\sim K_2S_{3.5}$ . This would greatly facilitate the cooling down of the assembled cell.
- (3) Without a complete understanding of the failure mode of the Na/S cells, we may just find the K/S system possessing some unforeseen advantages.

This is the final report for Contract No. NAS 3-16806 which ended 5/27/74. Under the terms of the contract, we were to develop and study a  $K^+$  conducting glass that would be usable, in a hollow fiber form, as the electrolyte/separator of a K/S cell of energy density of 330 watt-hr/kg and a power density of 220 watts/kg. We were also to explore and select a tube sheet system and a cathode current collector to be used jointly with the developed glass system.

The contract also called for testing of fibers of the developed glass in conjunction with the developed tube sheet material - to this end the contractor had proposed to fabricate small multi-fiber cells which shall otherwise be essentially identical to a larger practical size cell.



Most terms of the contract were met. We had selected several candidates for glass composition of which one (T305) essentially satisfies all the conditions required. The only drawback is that its spinnability is only marginally satisfactory, and spinning methods and techniques have to be improved before it can be mass produced in the desired quantity. A cell design is made based on the conductivity of T305.

The cathode current collector, which was developed in the Na/S program, worked satisfactorily in the K/S system.

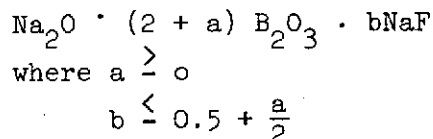
The tube sheet development met with most problems. Essentially, all the problems are now understood and most of them have been overcome.

#### BACKGROUND

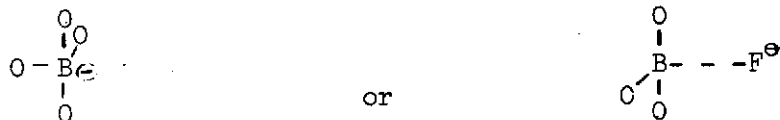
For the purpose of use as the electrolyte/separator in a potassium-sulfur cell, a glass must possess as a minimum of the following properties:

- A. Chemically resistant to all ingredients concerned - K; S;  $K_2S_x$ .
- B. Possess reasonable potassium ion conductance - would like to have a resistivity of  $\leq 5 \times 10^4 \Omega\text{-cm}$ , but up to several times that is still usable based on electrical requirement of the cell.
- C. Must not be electronically conductive,  $S^{=}$  ion conductive, or  $K^{\circ}$  permeable.

As a background knowledge, we at Dow have long known Na<sup>+</sup> conducting glasses and their chemical resistance to the corresponding ingredients (i.e., Na; S; Na<sub>2</sub>S<sub>x</sub>) related to glass compositions. We have known the "basic" glasses such as Na<sub>2</sub>O · 3SiO<sub>2</sub> are reactive toward S at elevated temperatures. These reactions result in local stresses that tend to crack the fine hollow glass fibers. The glass used in the Na/S cell at the time this contract started were of general composition.



Ideally, these glasses would be devoid of any O<sup>-</sup> sites, i.e., all formal negative charges would be assigned to either



The F<sup>-</sup> seems well supported by the trigonal boron atoms when used in moderation (not to exceed  $\frac{B_{\text{trig}}}{4}$  and, of course, the use of NaF increases the mole percent of Na<sup>+</sup> and, hence, decrease the resistivity of Na<sup>+</sup>, e.g.



We have made analogous potassium glasses. One of them, K<sub>2</sub>O · 2B<sub>2</sub>O<sub>3</sub> · 0.3KF · 0.1 MgF<sub>2</sub> was under static K/S test (i.e., in a single fiber cell with no current flow) for >5 months without noticeable degradation. The resistivity, however, was 4 x 10<sup>5</sup> Ω-cm and we would like to drop that value somewhat. We have also noticed that corresponding K glasses tend to crystallize more easily than the Na analogs at 300°C.

## RESULTS

### Glass Study and Selection

The criteria of selection of glass for use as fibers are conductance and longevity under actual operating conditions. No other test is as valuable as testing the performance of actually operating single fiber cells (SFC) under various conditions.

The SFC are made from manually drawn fibers of the glass under test. These fibers are generally 400 - 800 microns O.D. with O.D./W.T. between 4 and 10 and are fabricated into working cells as described in the Appendix B.

The advantages and limitations of the SFC include:

1. The glass can be studied in the absence of undue stresses - e.g. tube sheet.
2. Conductance can be measured to within several percent error.
3. Various catholyte compositions and temperatures can be used, though one cannot change catholyte composition effectively in any one test.
4. Failure can be noted rapidly and decisively.

5. One should realize, however, prolonged imbalance of charge/discharge could lead to an artificial failure. Also, the cathode lead of SS347 is not indefinitely stable, hence, generally 4 - 6 months is the extent of these studies.
6. Sublimation of sulfur is always a "side reaction".
7. The design of the SFC can only make use of large (>300 micron I.D.) fibers, hence we have used them only for manually drawn fibers.

The initial group of glasses suggested for studies included:

T104 K	$K_2O \cdot 2.14 B_2O_3 \cdot 0.5 KF$
T101 S20 K	$K_2O \cdot 2B_2O_3 \cdot 0.5 KF \cdot 0.2 SiO_2$
T301	$3K_2O \cdot 7B_2O_3 \cdot 1.6 KF$
T301.5	$3K_2O \cdot 6.5B_2O_3 \cdot 0.5 Al_2O_3 \cdot 1.6 KF$
T301.5 (0.1 R)	$3K_2O \cdot 6.5B_2O_3 \cdot 0.5 Al_2O_3 \cdot 1.5 KF \cdot 0.1 RbF$

The last two being attempts to lower ionic resistivity by enlarging the anionic network.

Single fiber tests were run on those five glasses. The catholyte used on the initial test was  $K_2S_x$  prepared by reacting anhydrous  $K_2CO_3$  with purified sulfur (see Appendix on general preparatory methods) and the summarized results are as follows:

<u>Glass</u>	$\rho \times 10^{-5} / \Omega\text{-cm @ } 300^\circ\text{C}$ <u>Individually</u>	<u>Individual Cell</u> <u>Life Span (Days)</u>
T104K	2.5	20, 36, 40, 60
T101 S20K	1.5	7, 17, 18, 24, 28, 45
T301	2.5	22, 80, 110, >200
T301.5	2.5	15, 45, 65
T301.5 (0-1R)	2.5	2, 4

As can be seen, the most attractive candidates are T301 (relative longevity), and T101 S20K (conductance). We have also noticed that all these fluoride

containing glasses have tendencies to crystallize when held at moderate temperatures ( $\sim 600^\circ\text{C}$ ), hence, again based on knowledge in the Na analog, we went ahead and explored the other halides. Of the various glasses tried, T305 ( $\text{K}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 0.2 \text{SiO}_2 \cdot 1/12 \text{K Br}$ ) looked attractive. It was added onto the list of glass candidates, and SFC's were made from this glass. It turned out to have the following properties:

1. Crystallization tendency greatly reduced, probably machine spinnable into hollow fine fibers with the then fiber spinning technique.
2. Ionic resistivity acceptable ( $\sim 1.5 \times 10^5 \Omega\text{-cm}$  @  $300^\circ\text{C}$ ).
3. Moisture sensitivity at room temperature much less than the other glasses studied.
4. SFC performance on longevity excellent ( $>5$  months on all 4 SFC's).

The superiority of T305 over all the compositions in both conductance and longevity singled it out as the composition of choice. We started looking at several glasses near its compositional vicinity for better ionic conductance. We found further additions of KBr did increase the conductance, but decreased the life time drastically. Since additional  $\text{K}_2\text{O}$  is not even a likely possibility (crystallization tendency increases drastically), we went ahead and tested T305 at a higher temperature ( $320^\circ\text{C}$ ). The resistivity at that temperature is  $7 \times 10^4 \Omega\text{-cm}$ , and again the longevity (of four starts, one failed @ three months, one @ four months, and two @  $>5$  months) even at this elevated temperature, suggested that this glass is a hopeful candidate.

In order to improve drawability, we have made a number of other glasses. Of those T318 ( $\text{K}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 0.4 \text{SiO}_2 \cdot 0.16 \text{KCl}$ ) seems to be a good candidate, even though it had a higher resistance ( $\rho \approx 2.2 \times 10^5 \Omega\text{-cm}$  @  $300^\circ\text{C}$ ). The non-halide containing glasses T323 ( $\text{K}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 0.3 \text{SiO}_2$ ) and T325 ( $\text{K}_2\text{O} \cdot 2.1 \text{B}_2\text{O}_3 \cdot 0.2 \text{SiO}_2$ ) promise good drawability but they would have a predicted resistivity of  $> 4 \times 10^5 \Omega\text{-cm}$ .

Some of the physical and electrochemical data of T305 and T318 include:

	T305	T318
$\alpha$ (Thermal expansion coeff.)	$140 \times 10^{-7}/^{\circ}\text{C}$	$138 \times 10^{-7}/^{\circ}\text{C}$
Tg (Glass transition Temp.)	$> 440^{\circ}\text{C}$	$> 440^{\circ}\text{C}$
$\rho$ @ 300 $^{\circ}\text{C}$ (Resistivity)	$1.5 \times 10^5 \Omega\text{-cm}$	$2.2 \times 10^5 \Omega\text{-cm}$

### Hollow Glass Fiber Fabrication

The standard technique and equipment used are those developed for the Na glass. It is a batch process where glass (see Appendix) is loaded into a nickel melt tank fitted with a boron nitride (Union Carbide) spinnerette. The tank is then purged with nitrogen and heated to ca 900 $^{\circ}\text{C}$  to melt the glass to a rather fluid state. Dry  $\text{N}_2$  is purged through the melt for several hours to substantially remove all the dissolved  $\text{H}_2\text{O}$ . The tank is then evacuated to aid deseeding (bubble-removal) the glass for about 1/2 hour and repressurized with  $\text{N}_2$ . The glass thus dried and degassed is spun into hollow fibers through the said BN spinnerette.

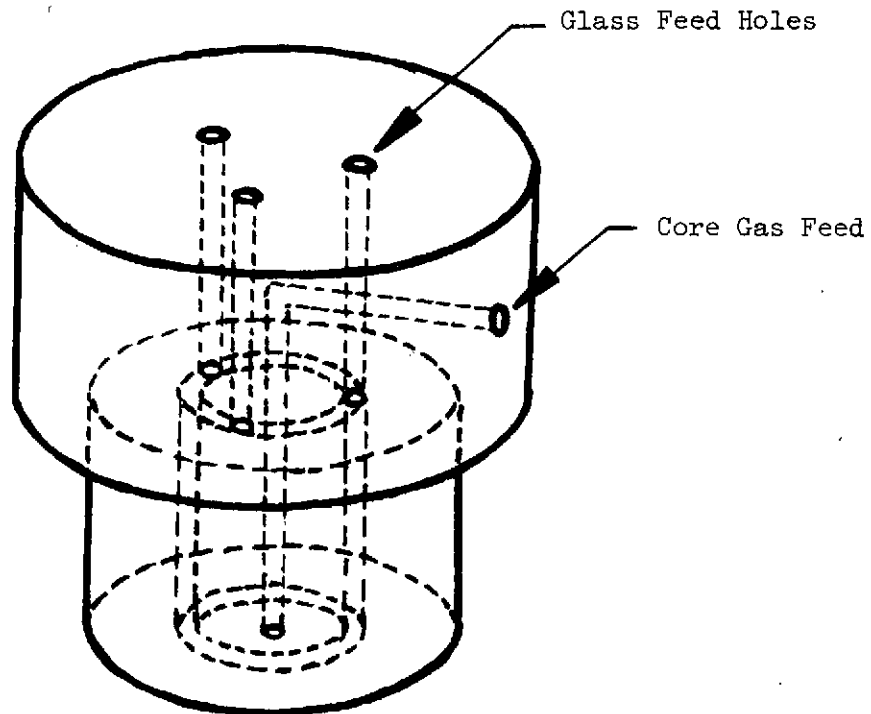


Fig. I Boron Nitride Spinnerette

A total of four spin runs were made; two on T305 and one each on T406K and T318.

The two runs on T305 were thought to be satisfactory at the time those runs were made. The glass was marginal in its tendency to crystallize under spinning conditions (glass @ spinnerette 700°C), and when crystals did form on the spinnerette surface, we simply interrupt the operation and dissolve off the crystals with a small stream of water. We found that the fibers thus spun contained minute seeds (bubbles), and theorized those were due to the fact that the glass was not deseeded properly. Rods, as well as fibers of sizes ranging from 60 micron x 20 micron to 80 micron x 60 micron were spun and collected. At the time, we thought those were usable and were going to improve on the deseeding steps.

The development on the parallel sodium project revealed shortly after that the seeds in the glass fibers were highly detrimental to their life times as a component in operating cells and, it was also discovered that seeds are actually introduced directly or indirectly from surface hydrolysis of the boron nitride spinnerette. This then, meant that we could not use the washing process and, hence, cannot use T305 until our spinning process is improved.

In view of the fact that T406, the Na glass we used at that time, can be spun for hours without crystals we tried a spin run with its potassium analog T406K ( $K_2O \cdot 2B_2O_3 \cdot 0.16 KCl \cdot 0.2 SiO_2$ ). However, there is no significant difference between it and T305.

Glasses T317 ( $K_2O \cdot 2B_2O_3 \cdot 0.16 KCl \cdot 0.3 SiO_2$ ) and T318 ( $K_2O \cdot 2B_2O_3 \cdot 0.16 KCl \cdot 0.4 SiO_2$ ) were made and crystallization at 650°C was qualitatively tested against T406 as a standard. This indicated that T317 is probably spinnable and T318 definitely spinnable.

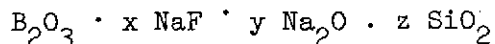
In our spin run with T318, we found that the drawing itself was very satisfactory - a continuous drawing of over four (4) hours with no crystallization, no breaks. However, there were still seeds in the glass,

presumably due to the higher viscosity of this glass (compared to T406) which makes the deseeding step inadequate. Size controls were good. We collected a substantial quantity of 70 micron x 50 micron fibers.

### Tube Sheet Research

This concept of paralleling thousands of fine hollow fibers requires a tube sheet, or header, to common the interiors of all the fibers into a compartment separate from the exteriors of same. In effect, our design calls for ring-sealing all the fibers at the open ends and then potassium filling the fibers. This tube sheet, therefore, will be exposed to potassium metal on one side, and sulfur vapor and possibly potassium polysulfide on the other.

From previous knowledge in the Na/S system, we have learned that a tube sheet system stable toward both S and Na are solder glasses of general composition.



These solder glasses can be prepared and made into a high density extrudable paste through a series of grinding, spheroidization and surface treatments. This paste can be applied and rolled into a tube sheet precursor and finally heated to cure to a solid glass tube sheet. The tube sheet will have the following properties:

1. Chemically inert.
2. Non-porous.
3. Does not chemically weaken the glass fibers they hold together.



Two other criteria must be satisfied for a solder glass tube sheet to be usable for a particular fiber:

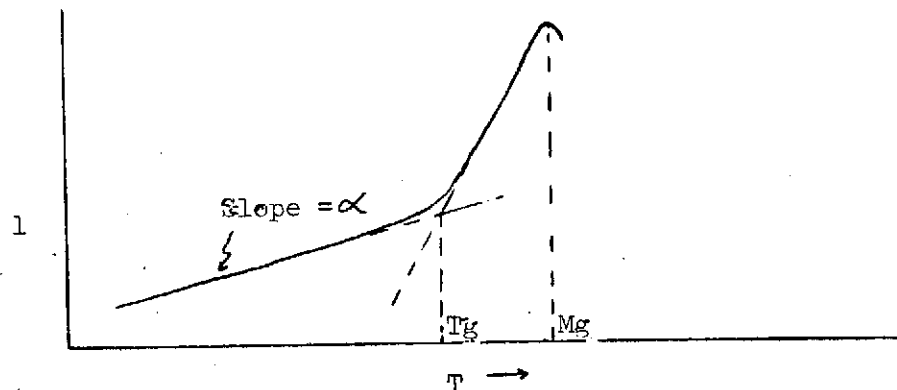
1. The curing, or sintering, temperature of the solder glass must not be so high that the glass fibers begin to deform, or roughly, Mg (Mg is not a well defined term; we shall define it in our own terms, see later in paragraph) for solder glass must be below Tg for fiber glass.
2. Thermal expansion coefficient of the two glasses must be reasonably closely matched so that the mechanical stress at the junction will remain substantially below the tensile strength of the fiber wall.

In addition, for obvious reasons, we would like the tube sheet not to deform at operating temperatures, i.e., Tg of tube sheet  $>300^{\circ}\text{C}$ .

When a well annealed glass sample is heated, using a probe under known constant pressure against the sample as in the Du Pont 941 Thermo-mechanical Analyzer, a typical curve will be like in Figure II.

FIGURE II

TYPICAL THERMAL EXPANSION OF GLASS



As can be readily interpreted, Tg is an inherent property of the glass, while Mg is merely where the thermal expansion rate of the glass equals the deformation rate of the glass under the given compressive load.

For our purposes, we chose a heating rate of 10°C/min. a sample of ca 7 mm high, and a load of ~2.5 g/mm<sup>2</sup>. The Mg as measured under these conditions is then roughly the desired curing temperature.

Initial search for tube sheet composition was based on the "target" expansion coefficient of T305, which was measured as ~135 x 10<sup>-7</sup>/°C. Also, as explained earlier, the solder glass should have its Tg >300°C and Mg < 430°C.

The initially scanned candidates included:

	<u>"α"* x 10<sup>7</sup>/°C</u>	<u>Tg</u>	<u>Mg</u>
T310 B <sub>2</sub> O <sub>3</sub> · KF	~200	<300	352
T311 B <sub>2</sub> O <sub>3</sub> · 0.9 KF	~180	~300	358
T312 B <sub>2</sub> O <sub>3</sub> · 0.1 K <sub>2</sub> O · 0.25 KF	137	340	400
T313 18 B <sub>2</sub> O <sub>3</sub> · K <sub>2</sub> O · KF	119	~290	362

---

\*These α values may not be reliable.

It appeared that T312 had all the required thermo-mechanical properties sought. A large batch of it was made, and the routine of making it into an extrudable paste was carried out. In doing so, we ran into an unexpected difficulty of not being able to obtain the necessary "fines" by the normal milling process (see following paragraphs).

In the meantime, it was found that tube sheet systems containing high F<sup>-</sup> and B<sub>2</sub>O<sub>3</sub> content are not stable as a melt. Indeed large amounts of BF<sub>3</sub> can be generated and collected over a equimolar melt of NaF and B<sub>2</sub>O<sub>3</sub>. This had been suspected as contributing to the failure of the fibers in the Na/S at the fiber tube sheet interface. Hence, in the related Na/S work, we had turned our attention to simple sodium borates as the tube sheet glass.

Measurements were carried out to determine the expansion coefficients for various K<sub>2</sub>O/B<sub>2</sub>O<sub>3</sub> systems and we found the following:

	$\alpha^* \times 10^{-7} \text{ } ^\circ\text{C}$	$T_g$	$M_g$
T314 (0.97 B <sub>2</sub> O <sub>3</sub> · 0.03 K <sub>2</sub> O)	135	300°C	350°C
T320 (0.94 B <sub>2</sub> O <sub>3</sub> · 0.06 K <sub>2</sub> O)	110	314°C	384°C
T321 (0.945 B <sub>2</sub> O <sub>3</sub> · 0.055 K <sub>2</sub> O)	116	308°C	375°C

They all have the same grinding problem as T321, and T314 was chosen as the solder glass for T305 fibers.

The solder glass must be ground and made into a high solids extrudable paste so it can be applied and shaped into a tube sheet holding all the fibers. To make this paste with a high solid content, the glass particle must be properly sized for good packing. The solder glass cullet is broken up, ground and sieved. The 200-325 mesh portion is spheroidized by feeding it through a CO + O<sub>2</sub> flame. Since the high B<sub>2</sub>O<sub>3</sub> glasses are water sensitive, a hydrocarbon flame cannot be used. The -325 mesh portion is ball-milled to a much finer powder. Equal weights of the spheres and the powder are suspended in cumene to give the paste.

A great deal of trouble was encountered in trying to ball mill the T314 to the proper fineness. "Proper fineness" is defined by its ability to be suspended and extruded in a small amount of cumene. Dry ball milling for up to 18 days did not give even marginal performance. Attempts to wet grind in toluene, isooctane, or hexane were not successful. An investigation of particle sizes using electron microscopy indicated that after a few (2-5) days, the rate of impact fusion of the glass particles equalled the rate of spallation. Ball milling at -17°C or with a surface active agent (hexadecylamine) did not help.

We finally discovered that the glass could be milled to near proper size by ball milling at 90°C in the presence of 1-1/2% hexadecylamine for seven days. Apparently, at 90°C, the vapor pressure of the amine is high enough so that freshly broken glass surfaces are covered with a surface layer of the amine. This helps prevent re-agglomeration.

This marginally usable T314 solder glass paste thus prepared was used to make the first T305 fiber bundles. A new unforeseen problem developed - the curing temperature of this tube sheet is so low (360°C) that we cannot achieve the necessary removal of fugitive organics (mainly a glue used to initially hold the fibers in a parallel array) thereby causing undue mechanical stresses\*

In the meantime, with the same grinding techniques, we found T312, T320 and T321 could be made into satisfactory tube sheet pastes.

### Cathode Current Collector

The cathode materials tested here were developed for the Na/S several years ago at Dow. Three different materials were chosen as possible candidates for the K/S system. They are: 1) Al foil coated with commercial Aquadag; 2) Al foil coated with Sprayon graphite; 3) Al foil coated (vapor deposited) with Mo metal. In cases (1) and (2), the Al foil was baked in air @ 300°C for one hour before the application of the graphite (brushed on in one case, and sprayed on in the second) then baked again @ 300°C for one hour. Each of the three samples were sealed into a glass tube with a stainless steel 347 counterelectrode containing  $K_2S_x$  so that both electrodes are immersed in the melt to a known depth. Current was passed through the two electrodes, mimicking cell operation. The current used was 0.2 - 0.5 ma/cm<sup>2</sup>. Samples 1 and 2 had and maintained a surface resistance of ~10 Ω-cm<sup>2</sup>, while sample 3 the surface resistance stayed at ~80 Ω-cm<sup>2</sup>. The samples showed no appreciable change after six months.

### Multi-Fiber Cell Operation

A number of multi-fiber cells were assembled and started during the contract period. Unfortunately, they all failed (< 24 hours) due indirectly to the tube sheet - low curing temperature in the case of T305/T314.

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\*This stress is due to the mismatch of  $\alpha$  between the Al anode foil and the glass fibers. This mismatch will cause a strain on the fibers if the relative position of Al and the glass is fixed at more than one point.

and mismatch of expansion coefficient in the case of T318/T321 and T318/T320. Those cells, in general, contained 50 - 500 fibers. Some of them did last long enough (24 hours) to achieve near theoretical resistance. The failure in all cases is consistent with fiber breakage at the fiber-tube sheet interface, and those cells did not succeed in aiding the evaluation of the machine drawn fibers as operating fibers for cells.

### Cell Design

As called for by the contract, a cell design (Design II) was made on paper, basing it on properties of T305 glass fibers. Such a cell will be technically feasible to achieve with further refinement, mainly in the fiber spinning and winding areas. Another design (Design I) is based on a glass (probably a glass similar to T330 ( $K_2O \cdot 2 B_2O_3 \cdot 1/12 KBr \cdot 0.3 SiO_2$ ) with  $\rho \approx 2 \times 10^5 \Omega\text{-cm}$  @  $300^\circ\text{C}$ ) from which a miniature version ( $\sim 1000 - 5000$  fibers) can be made and studied with present technology. Details for each design are in Appendix C.

#### Design I

Fiber Size:	70 x 50 microns; $\rho = 2 \times 10^5 \Omega\text{-cm}$ @ $300^\circ\text{C}$
Fiber Length:	20 cm working + 0.5 cm above foil
Roll Size:	21 cm (20.5 + 0.5 spacer) long x 9 cm diameter
Amperes:	150 A @ 90% (240 mv. drop due to internal resistance; with 20 mv. drop on fibers)
Spacer Thickness:	87.5 microns
Foil Thickness:	12.5 microns
Tube Sheet Thickness:	0.5 cm $d^* \approx 2.0$
Reaction:	$34 K + 3 "K_2S_{20}" \xrightarrow{\frac{D}{C}} 20 K_2S_3$ with $K_2S_3$ at $d = 2.0$ occupying largest catholyte volume
Total wt.:	= 3.6 Kg
Energy Density:	= 268 watt-hr/Kg total or 248 watt-hr/Kg @ 150 A or @ 90 watts/Kg.

\* d=density

Design II

Fiber Size: 50 x 36 microns;  $\rho = 1.5 \times 10^5 \Omega\text{-cm}$  @ 300°C  
Fiber Length: 20 cm. working + 0.5 cm above foil  
Roll Size: 21 cm (20.5 + 0.5 cm with spacer)  
9 cm Diameter with  $\sim 0.5 \text{ cm}^2$  core  
Amperes: 370 Amp @ 90% (i.e., 240 mv. drop due to internal resistance, including 180 mv. on fiber wall).

Spacer Thickness: 64 microns

Foil Thickness: 6 microns

Tube Sheet Thickness: 0.6 cm @  $d \approx 2.0$

Reaction:  $34 \text{ K} + 3 \text{ "K}_2\text{S}_{20}" \xrightarrow[\text{C}]{\text{D}} 20 \text{ K}_2\text{S}_3$

with  $\text{K}_2\text{S}_3$  @  $d = 2.0$  occupying maximum volume as catholyte, i.e., catholyte volume is maximum at full discharge.

Total wt.: 3.55 Kg

Energy Density: = 300 watt-hr/Kg total or 264 watt-hr/Kg @ 220 watts/Kg.

CONCLUSION

We have found a usable glass in T305. It possesses marginally sufficient ionic conductivity for a reasonable design of desired performance. Its performance as tested with the SFC suggests excellent chemical and electrochemical stability. However, our spinning techniques must be improved before fibers of this glass can be manufactured in the desired quality and quantity. Slight modification of T305 can improve its drawability to where it can be spun satisfactorily with the present technology. Unfortunately, we were unable to give these fibers a final evaluation in multi-fiber assemblies for the lack of a satisfactory tube sheet.

Available cathode materials were studied. They would give desired performance in the actual designs.

Solder glass research was not as successful. We did not get good reliable data until toward the end of the contract. It looks as if T312 or a composite of T321 fines and a higher expansion spheres are possible alternatives.

APPENDIX A  
General Preparative Methods

1. Glass

Reagents and pretreatments include the following:

- $B_2O_3$  Purified Boric Anhydride powder (J. T. Baker) was surface dried in a vacuum oven over a period of seven days, with temperature raised slowly to 105°C, this gradual raising of temperature is necessary so it does not "cake". It is stored in a polypropylene bottle in a dry box.
- $K_2CO_3$  Potassium Carbonate, Anhydrous (J. T. Baker) was used as commercially available.
- KF Potassium Fluoride, Anhydrous granula (J. T. Baker) was used without further purification.
- $SiO_2$  Supercil, (-325 mesh) was passed through a -80 mesh sieve to remove large agglomerates.
- KBr, Reagent grade crystals were dissolved in hot water, then  
KCl precipitated as a fine powder by adding this solution into large amounts of acetone under stirring. The powder is collected by filtration and dried up to 300°C in air.

Typically, individual reagents are weighed out and combines in a tightly closed glass jar and mixture by tumbling for several minutes. The mixture is then poured into a Pt dish and placed in a 900°C preheated muffle furnace. After essentially complete fusion (~10 minutes) the contents are stirred with a Pt tipped rod, then reheated to 900°C. This stirring and reheating process is repeated three or four times. Then the glass is poured into either a cold graphite or chromium plated copper mold.

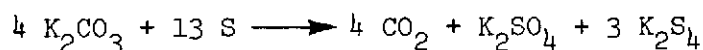


2. S

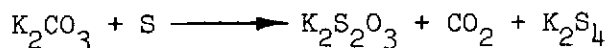
Commercial Reagent Grade flowers of sulfur is melted and then distilled over a two-foot Vycor bed maintained at 800°C in order to react any organic impurity to CS<sub>2</sub> and H<sub>2</sub>S. The distilled sulfur is then purged at 145°C for 4-5 days. The purity of this sulfur is well demonstrated in our Na/S cells.

3. K<sub>2</sub>S<sub>x</sub>

Potassium Carbonate (anhydrous granula from J. T. Baker) is dried by baking in a weighed round bottom flask with a ground glass joint for 24 hours. It is then cooled and weight determined by difference. Sufficient sulfur for the reaction



is added and the mixture is warmed to ~400°C under N<sub>2</sub> and maintained @ ~400°C for 24 hours. The mixture is filtered hot in a N<sub>2</sub> glove box. The filtrate will be of composition near K<sub>2</sub>S<sub>3.5</sub> due to the side reaction.



It is cooled and crushed and stored in a N<sub>2</sub> glove box.

## APPENDIX B

### Assembly of Single Fiber Cells

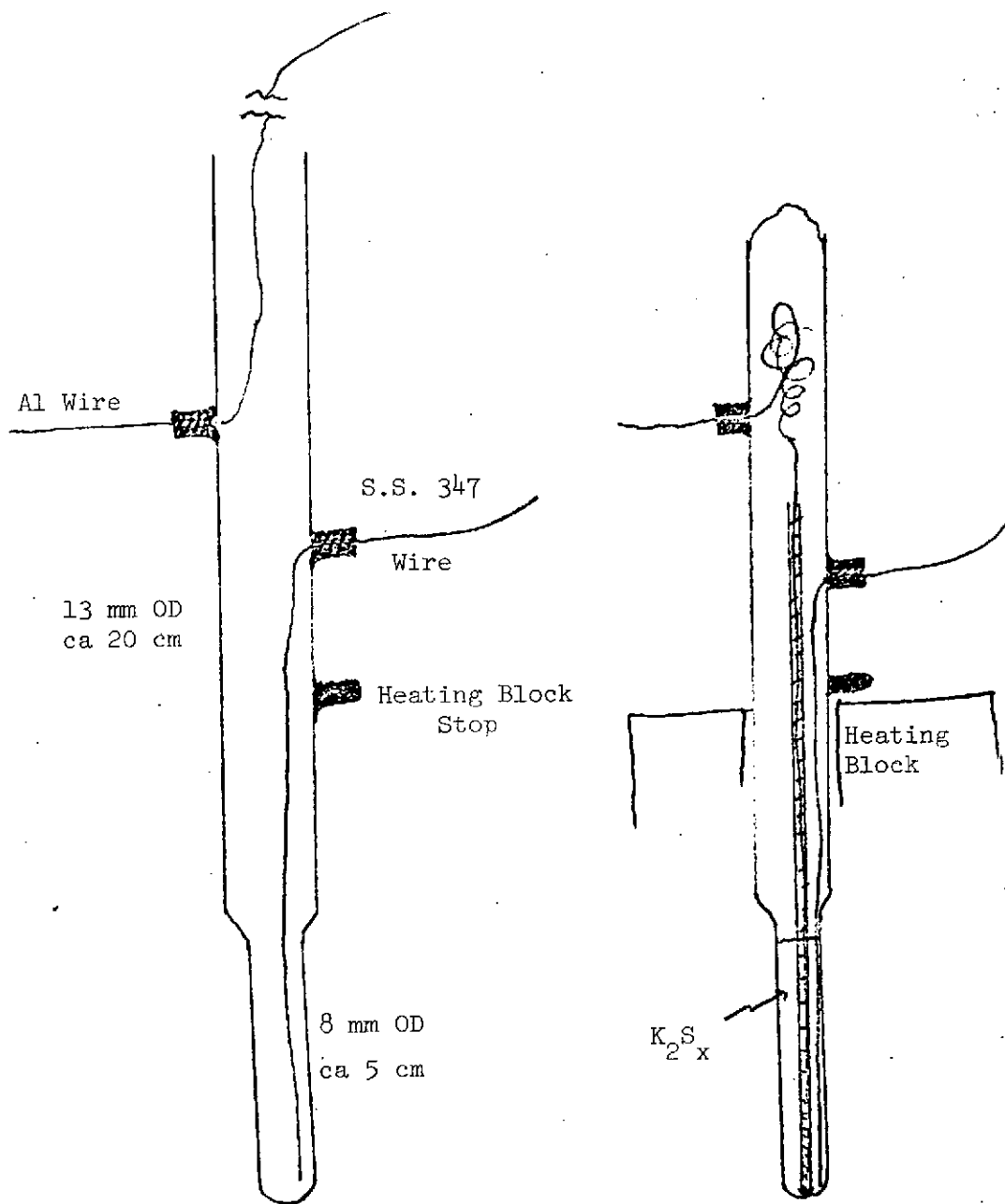
The glass whose fiber is to be tested is made as described in Appendix A. After melting and mixing, the crucible is removed from the oven, and with standard glass-blowing techniques, using a platinum or stainless steel tube, a hollow fiber ca 4 ft. long is manually drawn. Six inch sections are saved from the mid-portion of this fiber, where it is most uniform. The size is generally and preferably 0.4 - 0.8 mm I.D. with a O.D./w.t. ratio of 4 - 10.

One of these 6-inch sections is used for each cell. It is placed in an inert atmosphere box and ca 0.5 cm of it is removed for cell constant measurements (i.e., O.D., w.t.). The end from which this 0.5 cm section is removed is then sealed with a electrically heated Pt wire.

The cell body is largely preassembled. It consists of a two-section pyrex tube with the smaller end sealed approximately 5 cm from the joint. It has two side arms where a stainless steel 347 wire (10 mil O.D. reach to bottom seal) and a 10 mil Al wire (very long, ca 2 ft., for subsequent manipulation) are sealed in with Eccobond epoxy. The interior end of the Al wire is now inserted all the way into the fiber and the fiber is placed open end down into a pyrex boat inside an evacuable glass vessel. A piece of potassium (ca 1 gm) is also placed in the boat and the vessel is evacuated and heated. After the potassium is melted,  $N_2$  is let into the system, and potassium metal is forced up all the way into the fiber.

This fiber is now turned closed end down and placed in the cell body, the long Al wire coiled and stuffed back into it, taking care not to touch the stainless steel cathode lead. A roughly weighed amount of  $K_2S_x$  or  $K_2S_x + S$  is then added, and the cell body is removed from the inert atmosphere box and flame sealed at essentially atmospheric pressure.

The cell is now warmed in a 90°C oven for 1/2 hour to remelt the potassium uniformly, then it is placed in the 300°C holding block and the electrodes properly connected. The sulfide level is measured after it has come to temp. equilibrium for cell constant determination.



Pre-assembled Cell Body

Actual Test Cell

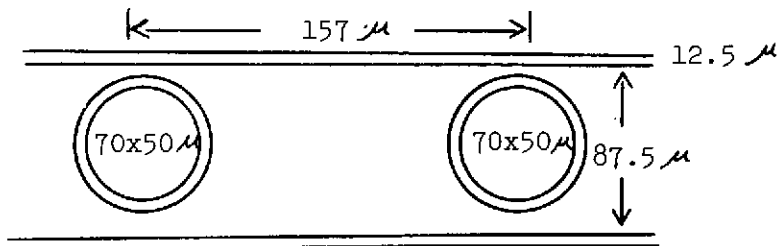
The cell is either held at open circuit, with intermittent resistance measurement, or placed on a fixed schedule charge/discharge, usually at 0.2 - 1 ma cycling each hour. Minute internal resistances changes are regarded as due to air leaks, sulfide wetting/wicking along fiber-outer tube interface, etc., and are recorded but ignored. Large changes resistance, particularly those accompanied by drop in open circuit potential, constitute the criteria of failure.

APPENDIX C

Detailed Cell Design

Design I

Fiber Size	70 x 50 micron; $\rho = 2 \times 10^5 \Omega \cdot \text{cm}$ @ 300°C
Fiber Length	20 cm working + 0.5 cm above foil
Roll Size	21 cm (20.5 + 0.5 spacer) 9 cm Diameter
Amperes	150 A @ 90% (240 mv. drop due to internal resistance; with 200 mv. drop on fibers).
Spacer Thickness	87.5 microns
Foil Thickness	12.5 microns
Tube Sheet Thickness	0.5 cm $d \approx 2.0$
Reaction	$34 \text{ K} + 3 \text{ "K}_2\text{S}_2\text{O"} \xrightleftharpoons[\text{C}]{\text{D}} 20 \text{ K}_2\text{S}_3$ with $\text{K}_2\text{S}_3$ @ $d = 2.0$ occupying largest catholyte volume.
Fibers Needed	Each fiber can provide $\frac{200 \text{ mv } (20 \times \pi \times 6) \text{ cm}}{2 \times 10^5 \Omega \cdot \text{cm}} + 0.377 \text{ mA}$ Hence, number of fibers needed = $\frac{150}{0.377 \times 10^{-3}} = 3.98 \times 10^5$ fiber
Length of Foil	Length of Fiber Band = $\frac{\text{Total Cross-section}}{\text{Thickness/Layer}} = \frac{9^2 \frac{\pi}{4} - 0.6 \text{ cm}^2 \text{ (core)}}{10^{-2}} = \frac{63 \text{ cm}^3}{10^{-2} \text{ cm}} = 6300 \text{ cm}$
Fiber Spacing	$\frac{6300 \text{ cm}}{3.98 \times 10^5} = 157 \text{ microns}$ (center to center)



Total Volume Inside  
Roll (i.e. foil +  
fiber + catholyte)  
(Spacer part is  
tightly wound Al)

Total Volume of Fiber  
(incl. K)

$$3.98 \times 10^5 \times (70 \times 10^{-4})^2 \times \frac{\pi}{4} \times 20 = 306 \text{ cc}$$

This includes 156 cc of K = 120 gm

$$150 \text{ cc of glass} = 330 \text{ gm}$$

Total Volume of Foil

$$6300 \times 20.5 \times 12.5 \times 10^{-4} = 162 \text{ cc of foil} = 437 \text{ gm}$$

∴ Total Volume for  
Catholyte

$$1282 - (306 + 162) = 814 \text{ cm}^3 \cdot \text{K}_2\text{S}_3$$

$$\approx 1628 \text{ gm K}_2\text{S}_3$$

$$\approx 28.1 \text{ mole S}$$

From simple calculation, we get for each mole of  
S:

$$15.2 \text{ Amp hrs/mole S}$$

$$34.9 \text{ watt hrs/mole S @ trickle discharge}$$

$$32.0 \text{ watt hrs/mole S @ 240 mv drop}$$

Hence, total energy content = 970 watt hrs @ trickle  
discharge or 900 watt hrs @ 240 mv drop or 424 amp hrs  
or ~ 2.83 hr rate @ 150 amps.

Amount of K  
required (outside  
fiber)

$$28.1 \text{ mole S} \times \frac{2 \text{ moles K}}{3 \text{ moles S}} \times \frac{39.1 \text{ gm K}}{\text{mole K}} = 732 \text{ gm}$$

∴ Use 770 gm K

$$\text{@ } d \approx 0.77 \text{ gm/cc @ } 300^\circ\text{C}$$

$$\text{Volume of K in reservoir} = 1000 \text{ cc}$$

$$\text{Volume of reservoir} \approx 1100 \text{ cc}$$

$$\text{Anode cup cross-section (inside)} = 10.0 \text{ cm}$$

$$\text{Hence, height needed} = 14 \text{ cm}$$

Weights	K	$770 + 120 + 10 =$	900 gm
	S	$900 \text{ gm} + 110 \text{ gm}$ (dead) =	1010 gms
	Glass (Fibers)		330 gms
	Tube Sheet	$0.5 \times 10^2 \frac{\pi}{4} \times 2 =$	79 gms
	Al Foil =		437 gms
	Anode Lead	$16 \text{ cm} \times 7 \text{ min}^2 \frac{\pi}{4} \times 2.7$	17 gms
	Ceramic Seal		5 gms
	Anode Cup	Area = $520 \text{ cm}^2$ $t = 0.05 \text{ cm}$	70 gms
	Top	$86 \text{ cm}^2$	} $1260 \text{ cm}^2$ $t = 2 \text{ min.}$ 680 gms
	Top/Side	$520 \text{ cm}^2$	
	Bottom/Side	$590 \text{ cm}^2$	
	Bottom	$64 \text{ cm}^2$	
	Spacer	$0.5 \times 9^2 \times \frac{\pi}{4} \times 2.7$	85 gms
			<hr/> 3613 gms
			7.95 #S
			122 watt hr/lb. trickle discharge
			113 watt hr/lb 150 A
			or @ $\sim 41$ watts/lb.

## Design II

Fiber Size	50 x 35 microns; $\rho = 1.5 \times 10^5 \Omega\text{-cm}$ @ $300^\circ\text{C}$ (O.D./I.D.)
Fiber Length	20 cm working = 0.5 cm above foil
Roll Size	21 cm (20.5 = 0.5 cm with spacer) 9 cm Diameter w. $\sim 0.5 \text{ cm}^2$ core
Amperes	370 Amp @ 90% (i.e. 240 mv drop due to internal resistance, including 180 mv on fiber wall)
Spacer Thickness	64 microns
Foil Thickness	6 microns
Tube Sheet Thickness	0.5 cm @ $d \approx 2.0$
Reaction	$34 \text{ K} = 3 \text{ "K}_2\text{S}_{20}" \xrightleftharpoons[\text{C}]{\text{D}} 20 \text{ K}_2\text{S}_3 \text{ with } \text{K}_2\text{S}_3 @$ $d = 2.0$ occupying maximum volume as catholyte, i.e., catholyte volume is maximum at full discharge.

Fibers Needed

Each fiber can provide

$$\frac{180 \text{ mv} \times \left[ 20 \cdot \pi \cdot \left( \frac{50}{7} - 1 \right) \right]}{1.5 \times 10^7 \text{ -cm}} = 0.463 \text{ ma}$$

$$\text{Hence, need } \frac{370}{0.463 \times 10^{-3}} = 8 \times 10^5 \text{ fibers}$$

Cross-Section of  
Active Bundle Roll

$$\frac{\pi}{4} (9 \text{ cm})^2 - 0.5 \text{ cm}^2 \text{ core} = 63 \text{ cm}^2$$

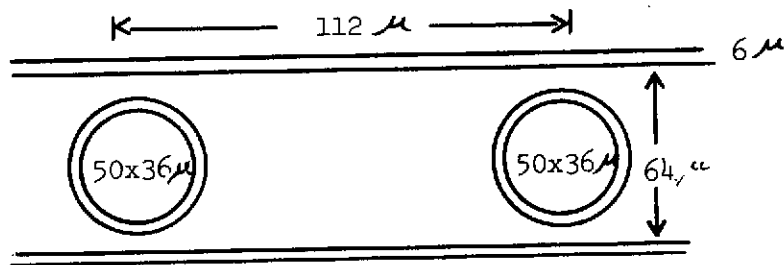
Length of Foil

Length of Fiber Band =

$$\frac{\text{Cross-Section}}{\text{Thickness/Layer}} = \frac{63 \text{ cm}^2}{64 \mu + 6 \mu} = 9000 \text{ cm}$$

Fiber Spacing

$$\frac{9000 \text{ cm}}{8 \times 10^7 \text{ fibers}} = 112 \text{ micron (center to center)}$$



Total Volume in  
active Foil Roll

$$63 \text{ cm}^2 \times 20.5 \text{ cm} = 1290 \text{ cm}^3$$

Total Volume Occupied  
by fibers (glass + K)

$$8 \times 10^5 (50 \times 10^{-4})^2 \frac{\pi}{4} \cdot 20 = 314 \text{ cm}^3$$

This includes: 163 cm<sup>3</sup> K = 126 gms

and 151 cm<sup>3</sup> glass = 332 gms

Total Volume of Foil

$$9000 \times 20.5 \times 6 \times 10^{-4} = 110 \text{ cc of foil} \\ = 297 \text{ gms}$$

Total Volume for  
Catholyte

$$1290 (314 + 110) = 866 \text{ cm}^3 \text{ K}_2\text{S}_3$$

$$= 1732 \text{ gm K}_2\text{S}_3$$

$$= 29.7 \text{ moles S}$$



Hence Total Energy  
Content

$$34.9 \times 29.7 = 1070 \text{ watt hrs @ trickle discharge}$$

$$32.0 \times 29.7 = 950 \text{ watt hrs @ 370 A or}$$

$$15.2 \times 29.7 = 452 \text{ amp-hrs}$$

$$\Rightarrow 1.22 \text{ hrs @ 370 Amps (or 800 watts)}$$

Amount K Require  
(Outside of Fibers)

$$29.7 \times \frac{2}{3} \times 39.1 = 774 \text{ gm}$$

Use 1080 cc or  $\sim$  800 gm K

$$V \text{ of reservoir} = 1150 \text{ cc}$$

Anode cup x section = 10.0 cm Diameter

Hence, height needed = 14.7 cm

Voltage Drops @ 370A

Anode Lead (1 cm <sup>2</sup> )	26 mv
K Column ( $\Sigma = 8.2 \text{ cm}^2$ )	13 mv
Fiber Wall	180 mv
Foil Surface	10 mv
Foil (as lead) ( $\Sigma = 5.4 \text{ cm}^2$ )	5 mv
	<hr/>
	234 mv

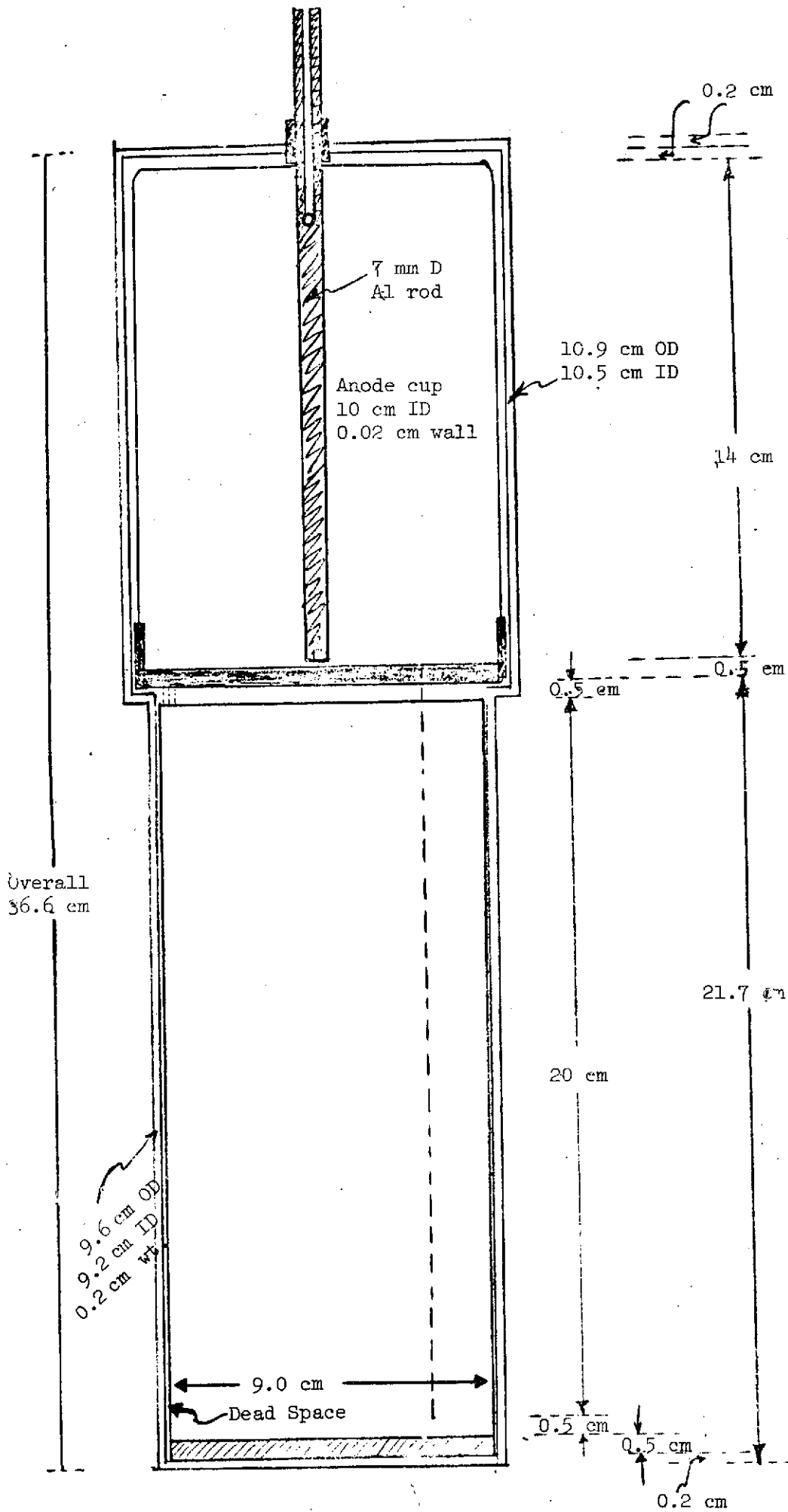
Weights

K =	800 + 126 + 12	938 gms		
S =	950 + 42 (for 1 mm Diam.)	992 gms		
Glass (Fiber)	332	332 gms		
Tube Sheet	@ ave. density $\approx 2.0$	79 gms		
Al Foil	(20.5) cm	297 gms		
Spacer (+ remaining 0.5 Al foil)		85 gms		
Anode Lead	(1 cm <sup>2</sup> cross-section 16 cm long)	43 gms		
Ceramic Seal		5 gms		
Anode Cup	(540 cm <sup>2</sup> x 0.05 cm)	73 gms		
Case:				
Top	86 cm <sup>2</sup>	} 1285 cm <sup>2</sup> x 2 mm	693 gms	
Side/Top	545 cm <sup>2</sup>			
Side/Bottom	590 cm <sup>2</sup>			
Bottom	64 cm <sup>2</sup>			
			<hr/>	= 3537 gms

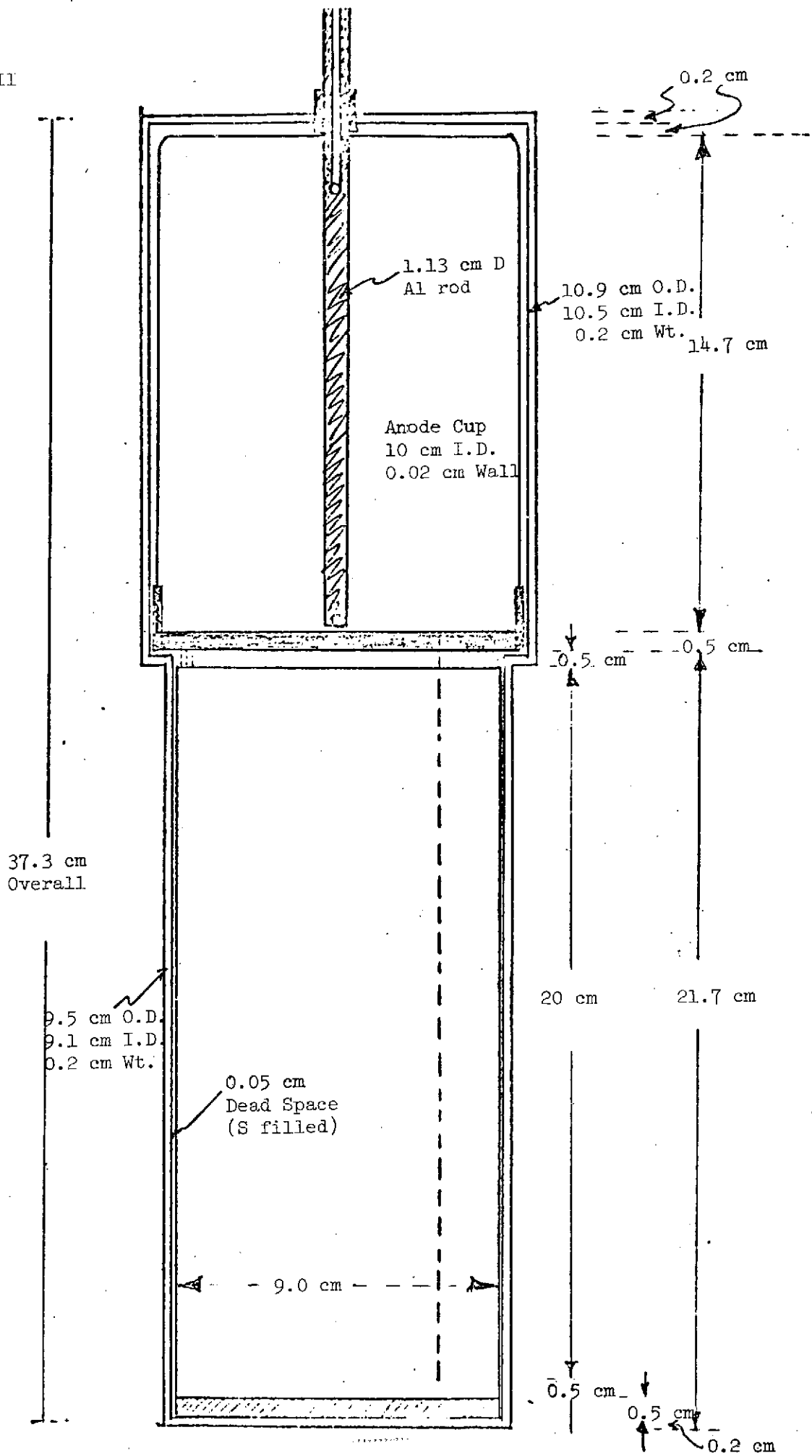
Ave Discharge Rate - 780 watts @ terminal @ 90%  
or 100 wt/lb.

Energy Density - 120 watt-hr/lb. @ 100 Watt/lb.  
or 137 watt-hr/lb. @ trickle  
discharge.

DESIGN I

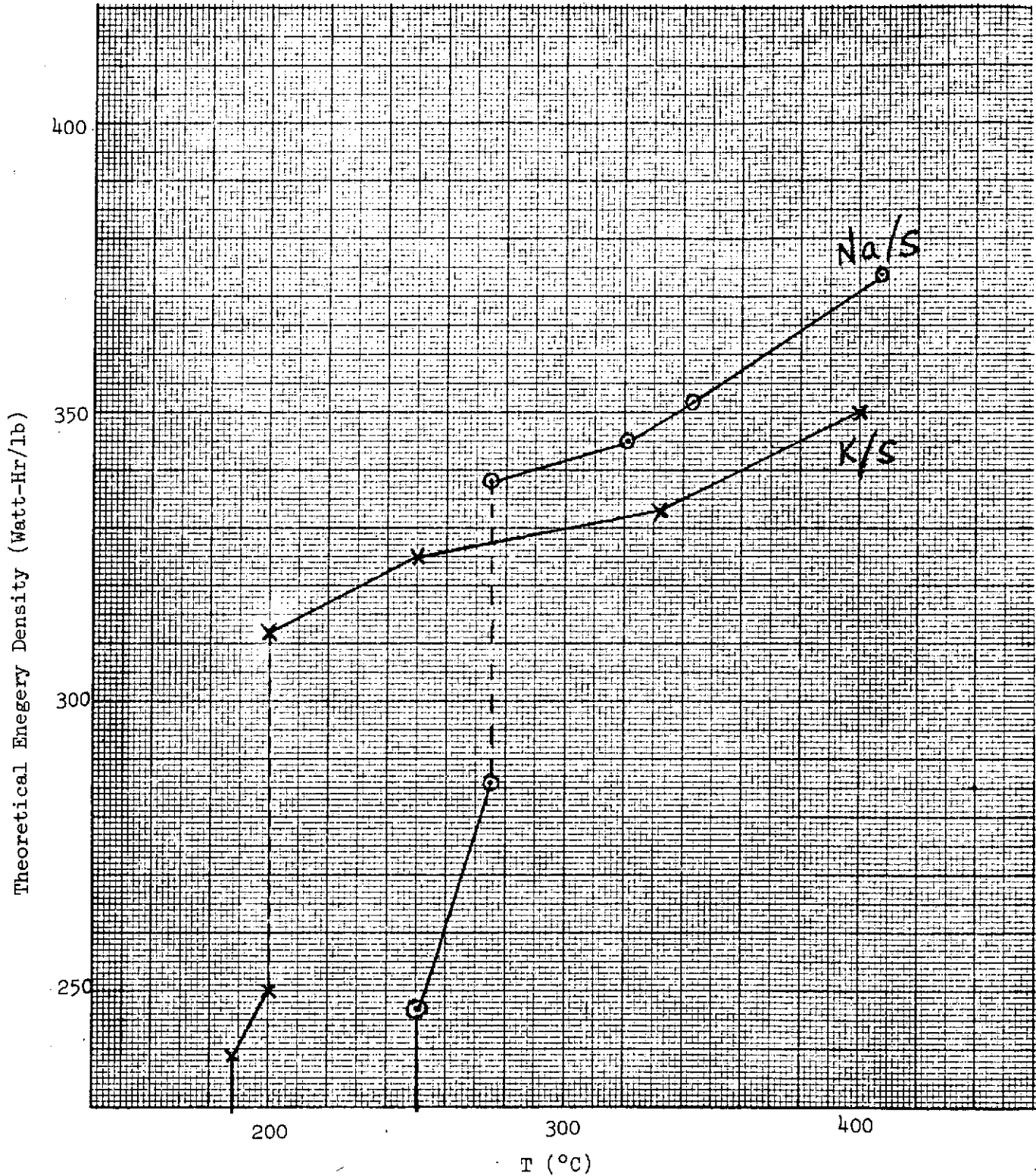


DESIGN II



APPENDIX D

APPENDIX D



Comparison of K/S and Na/S Systems