MSAR 61 - 99

Final Report
July 1959 - May 1961
on
Contract DA-36-039-SC-78955
Task No. 3A99-09-022-03
to
U. S. Army Signal Research and Development Laboratory
Fort Monmouth, New Jersey

STUDY OF ENERGY CONVERSION DEVICES

Report No. 7

September 14, 1961

MSA Research Corporation

Subsidiary of Mine Safety Appliances Company

Callery, Pennsylvania

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by

T. A. Ciarlariello
J. B. McDonough
R. E. Shearer

The purpose of this contract is to develop a cyclic or continuous thermally regenerative galvanic cell.

September 14, 1961

MSA RESEARCH CORPORATION
Callery, Pennsylvania

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1. PURPOSE

The research and development work under this contract was undertaken to develop a thermally regenerative electrochemical power system. This system will convert thermal energy to electric power on a continuous or cyclic basis, with the thermal energy being used to dissociate a compound into its elements. The elements (liquid metal and hydrogen in the case of the ionic hydride cell) are separated, cooled, and returned to an electrochemical cell. In the cell, the metal and hydrogen recombine electrochemically to produce electric power and waste heat.

The design objectives are to show a unit with a power capability of 10 watts/lb, a current density of 100 amp/sq ft and an operation voltage of 0. 3 volt per cell.

2. ABSTRACT

Prior experiments at MSAR had shown the feasibility of alkali and alkaline earth metal/molten salt electrolyte/hydrogen gas electrochemical cells. These cells produce metal hydride, heat and electric power. Batch regeneration of a calcium-hydrogen cell had been demonstrated.

During this contract, regenerative cells were built and tested for various periods of time. The major difficulties noted were the plugging of the circulating salt lines, the low dissociation pressure of LiH in dilute solutions, and an electric cell-shorting effect arising after long operation.

Various molten salt electrolytes were tested. Low melting point eutectic salts containing Na, Rb, Cs, K, and Li were found. Fluorides, bromides, and chlorides were found to be the best electrolytes. Borohydrides and iodides were not satisfactory.

Various hydrogen electrodes materials were tested. The best electrodes consisted of mesh electrodes or sintered porous discs. Sintered discs with a dual porosity were also tested. Pd - Ag and Pd diffusion type electrodes were unsatisfactory from a life standpoint. Graphite and platinized graphite electrodes were not satisfactory.

The dissociation of LiH over molten salts was determined, and the Li H content of various cell electrolytes was measured. Volt-ampere data of the various cells were measured.

The feasibility of the electrochemical cell, and of the hydride dissociation has been demonstrated. However, the complete regenerative system has not been reduced to practice.

3. CONFERENCES

On August 13, 1959, Messrs. C. B. Jackson, J. W. Mausteller, R. E. Shearer and R. C. Werner visited the U. S. Army Signal Research and Development Laboratory to discuss the proposed work plan under the subject contract. Messrs. C. Clark, A. Daniel, H. Hunger and J. Lyons represented the Signal Corps. It was agreed that operation of a closed cycle system should be attempted on the basis of the limited available present knowledge, that studies of alternate solvents and anode material should be made, and that studies of single electrode potentials should be considered, especially when lower temperature operation is possible.

On November 13, 1959, a conference was held at MSA Research in Callery, Pennsylvania, to discuss the First Quarterly Progress Report and the program proposed therein. In attendance were Dr. Herbert Hunger, U. S. Signal Research and Development Lab. and as representative of MSA Research: Messrs. C. B. Jackson, J. W. Mausteller, R. E. Shearer and R. C. Werner.

Among the types of data suggested to be of interest in future work were:

1. Distribution coefficients of metal hydrides between the liquid metal and solvent phases.
2. Data obtained from use of a second or reference gas electrode.
3. Catalytic effect of nickel or platinum as gas electrode material.
4. Theoretical emf's as compared with actual.
5. Volt ampere data at equilibrium conditions.
6. Regenerative data with the cell under vacuum rather than an inert atmosphere.

On January 25, 1960, a conference was held at MSA Research Corporation in Callery, Pennsylvania, to review the program under the contract, to discuss the Second Progress Report, and to plan the program for the future. It was agreed that the emphasis would be shifted from basic work to design and operation of closed-cycles systems. In attendance were Dr. Herbert Hunger, U. S. Army Signal Research and Development Laboratories and from MSA Research Corporation: Messrs. C. B. Jackson, J. W. Mausteller, R. E. Shearer and R. C. Werner.

On March 3, 1960, a conference was held at Wright Air Development Division, Dayton, Ohio, so that Signal Corps and Air Force representatives could compare programs of MSA Research and Thompson-Ramo-Wooldridge on regenerative fuel cell work to be sure that there was no duplication of effort. In attendance were: from WADD - Captain E. F. Redden, Messrs. J. Cooper, R. Cooper and R. H. Retz; Signal Corps - Messrs. H. Hunger, D. Linden, and J. Murphy; MSA Research Corporation - Messrs. T. A. Ciarlariello, C. B. Jackson, J. W. Mausteller and R. E. Shearer.

On July 29, 1960, Dr. H. F. Hunger of the U. S. Army Signal Research and Development Laboratory, Fort Monmouth, New Jersey, visited Mr. T. A. Ciarlariello, Dr. J. W. Mausteller, Mr. R. E. Shearer and Dr. R. C. Werner at MSA Research Corporation, Callery, Pennsylvania. At this time it was decided to curtail the support efforts on low melting salts, hydrogen vapor pressure measurement, catalytic electrodes, etc., and devote the remainder of the contract to the testing of a regenerative cell.

On November 10, 1960, Dr. R. C. Werner, Mr. R. E. Shearer, and Mr. T. A. Ciarlariello of MSA Research Corporation met with Dr. H. F. Hunger, Dr. E. G. Baars, and Mr. E. John of the U. S. Army Signal Corps Research and Development Laboratory at Fort Monmouth, New Jersey.

It was decided at this meeting to eliminate the use of inert recycle carrier gas and to operate the regenerative cells under vacuum if necessary.

4. INTRODUCTION

Thermally regenerative electrochemical systems show promise for the direct conversion of heat energy to electric power. In these cells, thermal energy dissociates a compound into the component parts. These parts are then allowed to recombine electrochemically to produce power.

The net result is a thermal energy to electric energy cycle without rotating machinery. Therefore, for smaller sized or portable power plants, direct energy conversion cycle is attractive.

The thermally regenerative cell will have a higher efficiency than a thermoelectric device. This is a consequence of the separation of the heat flow and electric flow paths for the thermally regenerative cell while the thermoelectric approach intertwines the heat and electric flow paths.

The thermally regenerative system should possess the following characteristics:

1. The heat of dissociation should be large. This then decreases the quantity of materials which must be circulated between the regenerator and the cell. Further, for a particular cell temperature and regenerator temperature, a high heat of dissociation must correspond to a large free energy of formation and therefore give a high cell voltage.

2. The free energy of formation per electron involved should be large. This will give a large cell voltage and permit the use of smaller cells.

3. The change in free energy with temperature should be large.

4. The cell reaction should proceed mainly by ionic means. Under these circumstances "chemical" short circuits are not large enough to adversely affect the efficiency of the process. Further, the cell is self-regulating and only consumes reactants when power is being drawn.

5. The reaction products should be easily separated. Preferably, one constituent and only one should be a gas.

6. The dissociation temperature should be high to achieve high carnot cycle efficiencies, while still being compatible with conventional materials of construction.

7. The cell operating temperature should be low so that high thermal efficiencies may be maintained.

The ionic hydride regenerative cell has six of the above seven advantages. The relatively high cell temperature should be lowered. Further research on low melting point halide salts and further research on hydrogen electrode catalysts would result in a lower temperature cell.

Previous work at MSAR, using company funds, had shown the feasibility of the metal hydride cell. In these cells, lithium reacts electrochemically with hydrogen to produce electric power and heat. The LiH is then heated to dissociate the compound to lithium and hydrogen. In this prior work, lithium, calcium and sodium were shown to be satisfactory metals; the molten salt halides in general, and LiCl-LiF in particular, were satisfactory electrolytes; stainless steel or nickel micrometallic filter or mesh were operable hydrogen electrodes; and batch regeneration of calcium hydride was demonstrated.

5. FACTUAL DATA

5.1 Regenerative Fuel Cell

Cell No.I - Operation of Cell No. 1 was undertaken of the system shown in Fig. 1. Not shown are additional external calrod heaters and 3 inch thick Unibestos pipe insulation on all heated cells and pipes. Two 1500 W calrod heaters were wrapped around the cell, and one 1000 W heater around the bottom of the regenerator. One 1000 W calrod was strapped to the top connecting pipe and two similar ones to the bottom connecting pipe. The container material was carbon steel as were the connecting pipe material and electrode cup, which was packed with stainless steel mesh.

The cell was charged with a vacuum dried eutectic mixture of the flouride and chloride of lithium (20 mol% LiF - 80% Li Cl).

Initial operation was conducted with a regenerator at room temperature and only the cell at operating temp. of ~480 C. A small spurious voltage of opposite potential to the hydride emf was observed; but after passage of hydrogen for two hours, a positive emf was obtained and a peak value of 0.55F at one atmosphere pressure was reached. At this point, the voltage dropped to zero and a vacuum developed in the cell. On cooling the cell, it was found that lithium had dropped from the top part of the cell onto the hydrogen electrode and caused a short circuit. It was apparent that lithium was held on the entry tube on charging and spread over the top of the cell. Subsequent charges of lithium were made by inserting the delivery tube further into the cell. On washing out the cell, it was found that the salt phase had cracked during the rapid cooling, permitting flow of lithium under the hydrogen electrode.

The system was recharged in an attempt to run regeneratively. Spurious voltages were observed as high as one volt and required over nine hours to be eliminated with passage of hydrogen and drawing of electrical energy. When the true hydride emf had developed, there was a fluctuation in emf, the speed of which varied with rate of flow of hydrogen. It was further noted that a vacuum developed, unless a minimum flow of hydrogen was maintained, indicating chemical consumption of hydrogen by the lithium. During this operation, a peak of 0.27 F (cell temp. 480° C) was obtained with one atmosphere of pressure. At this point the attempt was made to run regeneratively. With an argon gas purge, the system was closed off and the regenerator temp raised to (~760 C). With argon gas the emf was 0.1 mv. With residual argon and the hydrogen generated by the regenerator, the cell was run for seven days and voltages observed were 5 to 30 mv. No current densities were measured.

At these conditions, two samples of gas were withdrawn from the regenerator while voltage reading of 2.4 and 5.0 mv were being obtained.

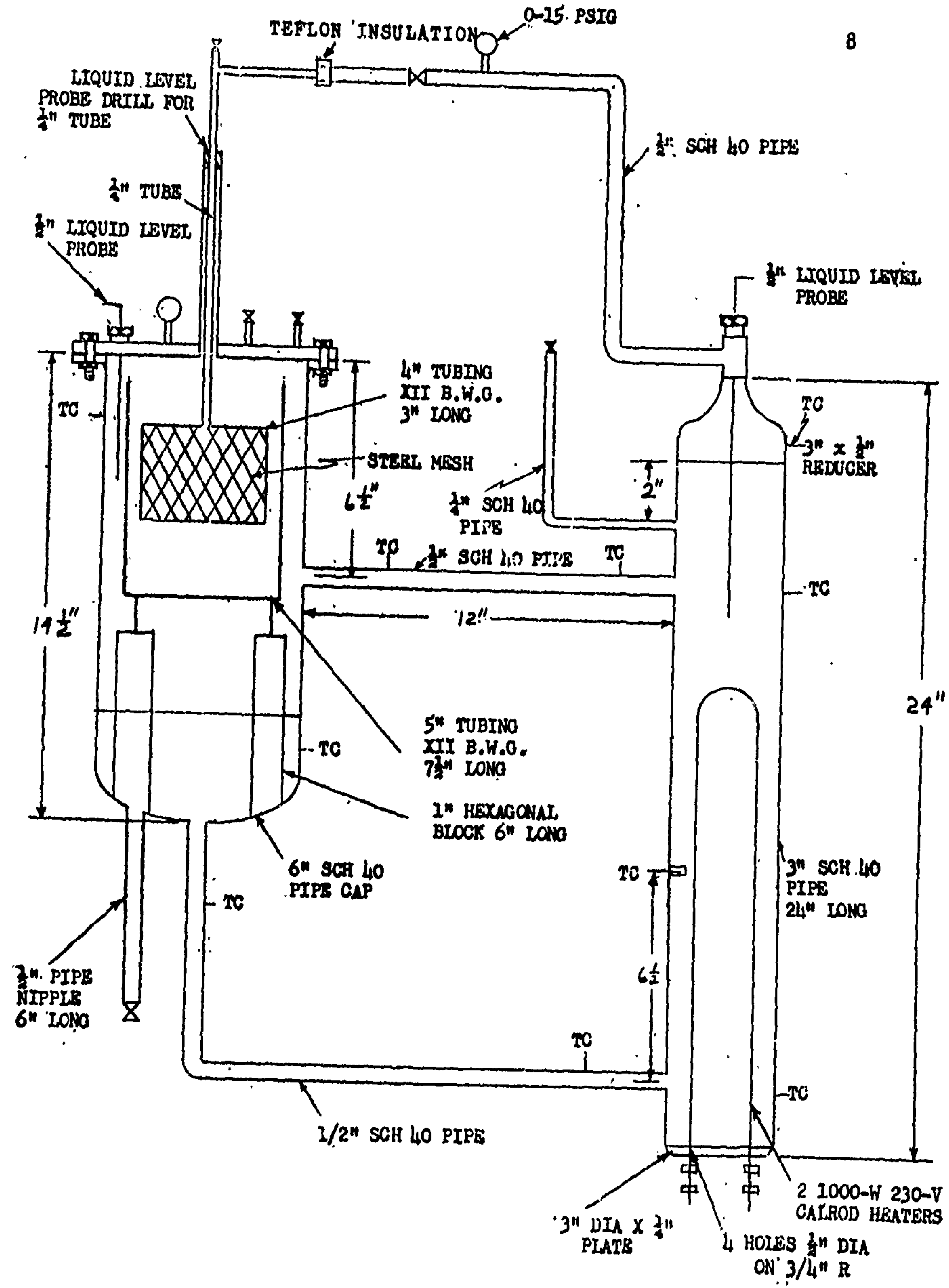

Fig. 1 -Regenerating Fuel Cell

Hydrogen content of the argon cover gas was determined to be 0.008% and 0.009% respectively by use of a Consolidated Engineering Model 21-020 mass spectrometer.

After the above mentioned period of closed cycle operation, a leak developed in a bend in the carbon steel connecting piping. Subsequently the system was shut down.

Cell No. 2 - Cell No. 2 is shown in Fig. 2. Changes in design from Cell No. 1 include use of stainless steel in all high temperature regions, a decrease in size of the larger components, use of a longer weir between the gas electrode and the metal electrode to minimize possibility of passage of liquid metal through cracks in cooled salt, use of a Kanthal heater to obtain regenerator temperatures, sealing the top of the weir to the flange to permit maintenance of an inert atmosphere over the lithium, and use of 1/2 in. stainless connecting pipe instead of 1/4 in. pipe to improve liquid circulation. The metal is lithium and the salt electrolyte is the eutectic LiF - LiCl.

With a hydride content of 1.8 wt % in the solvent, the closed cycle system was put into regenerative operation under an argon gas at one atmosphere pressure. A peak emf of only 5 mv on open-circuit was obtained and fluctuated widely, apparently with variation in circulation rate causing changes in cell and regenerator temperatures, which were nominally 550 C and 890 C respectively. Since analysis had shown higher hydride contents in the solvent in batch-type cells, some LiH was added in bulk to the regenerator. Within 15 minutes, a peak emf of 33 mv was obtained, after which a slow decline set in. At this point, hydride precipitated in the cell, plugging the exit at the hydrogen electrode and forcing hydrogen up through lithium, giving rise to chemical combination. When this was unplugged, the regenerator was cooled down for safe week-end operation. Upon reheating, the salt in the center of the connecting pipes apparently had melted and expanded before that at the ends, with the result that forces building up the expansion caused rupture of the pipe and leaking of the molten salt. This occurred in spite of the fact that the contents of both the cell and regenerator were molten. Upon replacement of the connecting pipe, extra heaters were added where needed to prevent such forces developing.

With the thought that the rate of diffusion of hydrogen through argon from the regenerator to the cell might be slow as compared with diffusion through a vacuum, the system was operated regeneratively under vacuum. A peak emf of 11 mv was obtained with the regenerator at 860 C. Rises and declines in emf were observed with freezing and melting of salt in the pipes connecting the cell and the regenerator, showing the need of analysis of pressure relationships, such as was done for the hydrogen-oxygen cell.[1] Apparently development of a

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[1] Hunger, H., "Investigation of the Hydrogen-Oxygen Fuel Cell," USA SRDL Technical Report 2001, 15 December 1958.

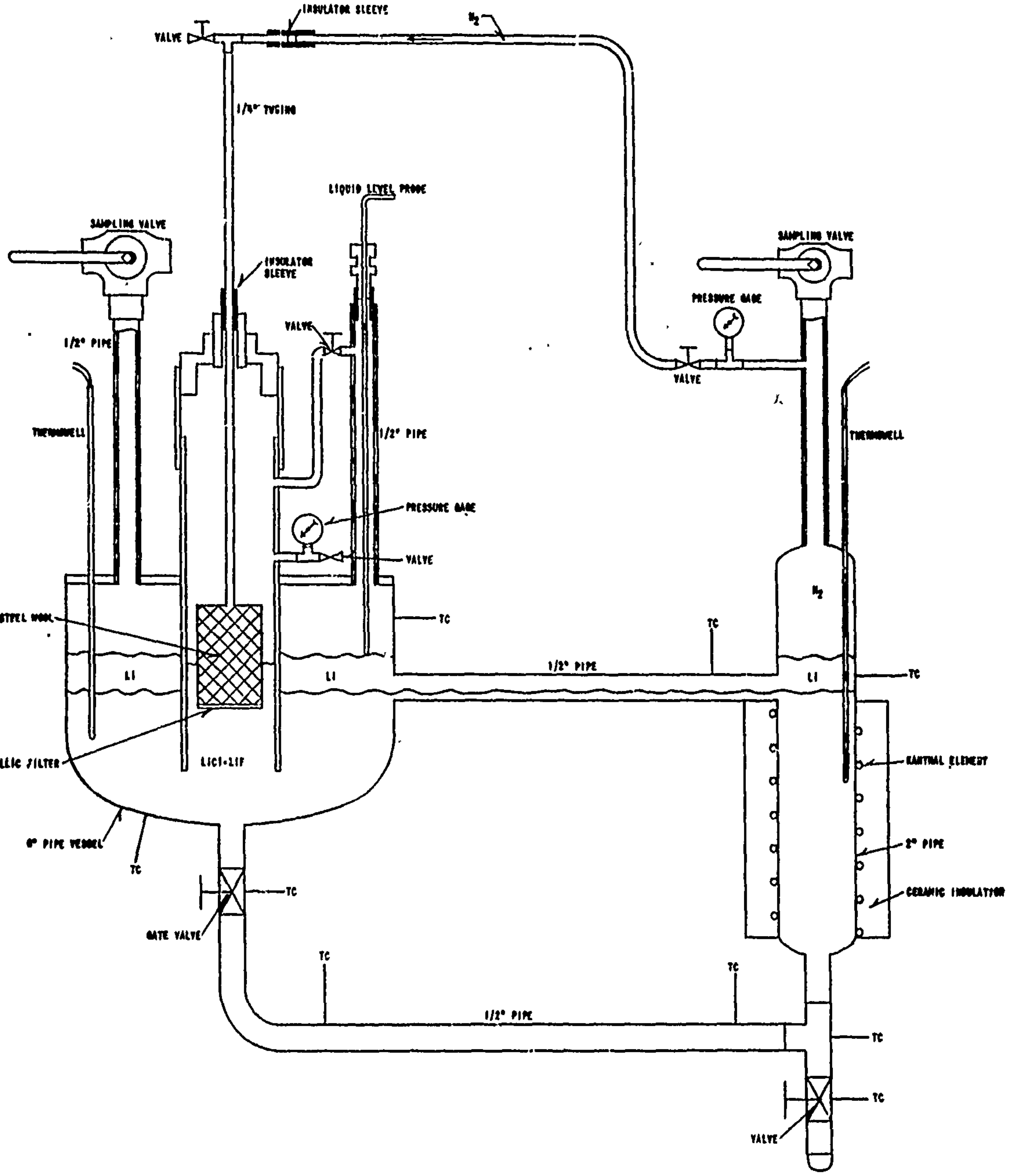

Fig. 2-Regenerative Fuel Cell No. 2

pressure head is needed for hydrogen since diffusion seems inadequate. Higher regeneration temperature likewise is needed; but work was abandoned on the subject in favor of redesign and operation of an improved model.

Cell No. 3 - The salt circulation system is shown in Fig. 3. The cell consists of a Sch 40, 3 inch pipe with flat heads. The hydrogen electrode is a 65 micron porous-nickel micrometallic filter cut into a D shaped segment. The liquid metal electrode was similarly shaped and had identical cross section. The lower part of the electrode was designed so that it contained a 1/4 inch Sch 40 salt return line, as shown in Fig. 3.

Liquid metal floats on the salt and is retained by the metal electrode. A barrier plate is inserted between the H_2 and metal electrodes to insure that the hydrogen which bubbles through the hydrogen electrode will not impinge on the metal electrode. The metal hydride formed by the cell reaction dissolves in the molten salt and is carried to the regenerator in solution form. In the 2 in. Sch 40 regenerator, the hydride dissociates to hydrogen and metal; and the salt and metal flow back to the cell. The regenerator is lower than the cell to provide salt circulation by natural convection and to generate hydrogen at sufficient pressure to overcome the pressure drop at the hydrogen electrode.

The system was filled with the eutectic mixture of the chlorides of cesium, rubidium, lithium and sodium. The salt was then circulated, using natural circulation. Next, potassium metal was added to the metal electrode in the cell. The cell was first operated as a batch cell using an external supply of 1 atmosphere hydrogen. The initial open circuit voltage observed was 0.84 volts. On short circuit, the cell initially delivered 1 ampere (232 amp/sq ft) and 10 seconds later the current was 0.15 amperes (34.8 amp/sq ft). As cell operation continued, the cell open-circuit voltage dropped to 0.7 volts. An initial current of 1.4 amps and a steady current of 0.25 amps (58 amp/sq ft) was noted. The cell voltage then dropped to 0.46 volts, and finally to 0.25 volts as the hydride concentration increased. Some difficulty was experienced with hard crusts which insulated the metal electrode. It was necessary to break open these crusts from time to time. The short circuit current was 0.25 amps initially and 0.1 amps steady.

Potassium was then added to the regenerator upper leg to prepare for regenerative operation. Before such regeneration operation, however, two volt-ampere plots were made at 488 C (Fig. 4). These showed open circuit voltage of 0.25 volts and a cell voltage of 0.04 volts at 0.045 amperes. The regenerator temperature was then increased to 750 C for regenerative operation with the result that the cell voltage increased to 0.34 volts. For a current of 0.038 amperes the cell voltage was now 0.13 volts.

The higher cell voltage shows removal of hydride from the cell.

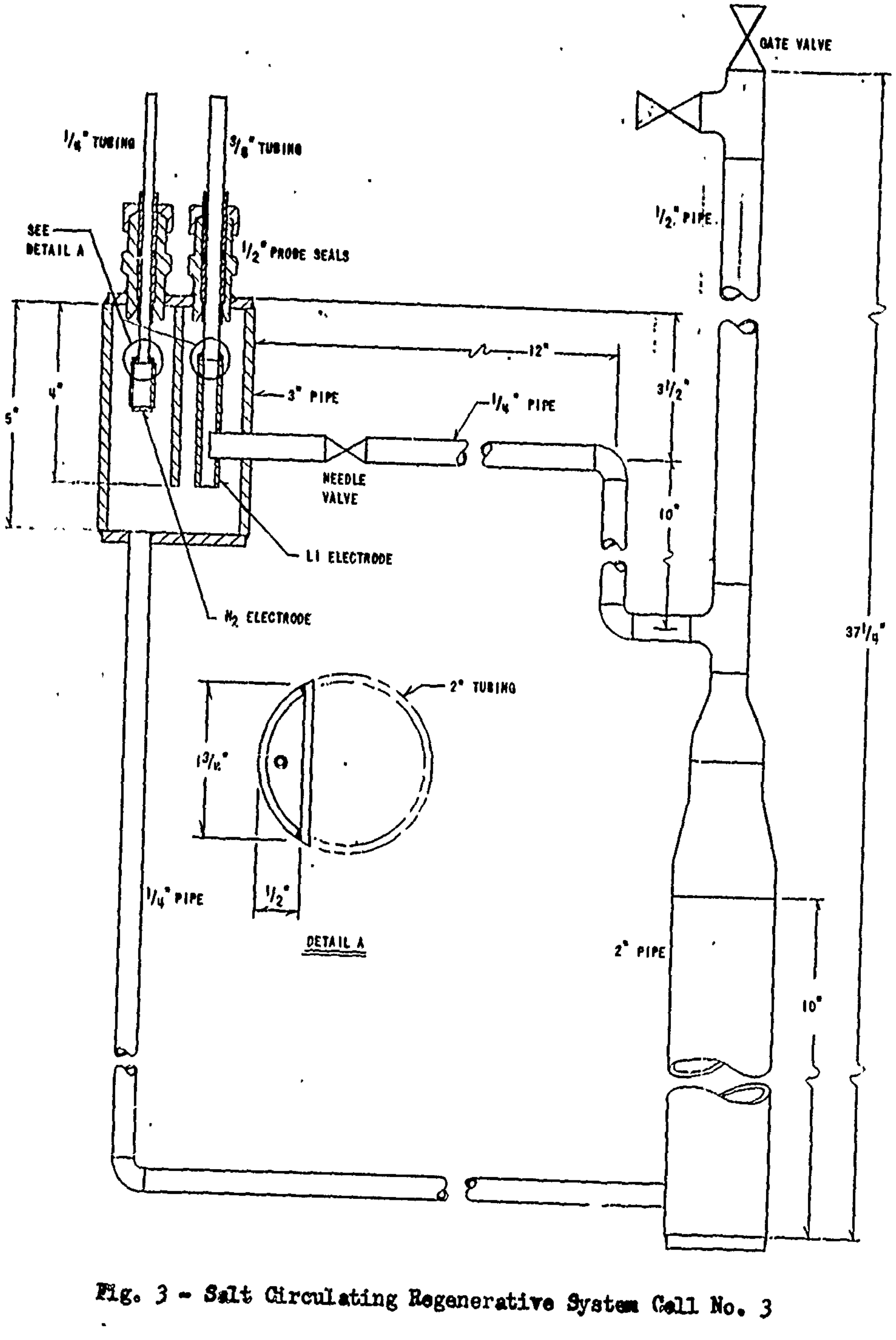

Fig. 3 - Salt Circulating Regenerative System Cell No. 3

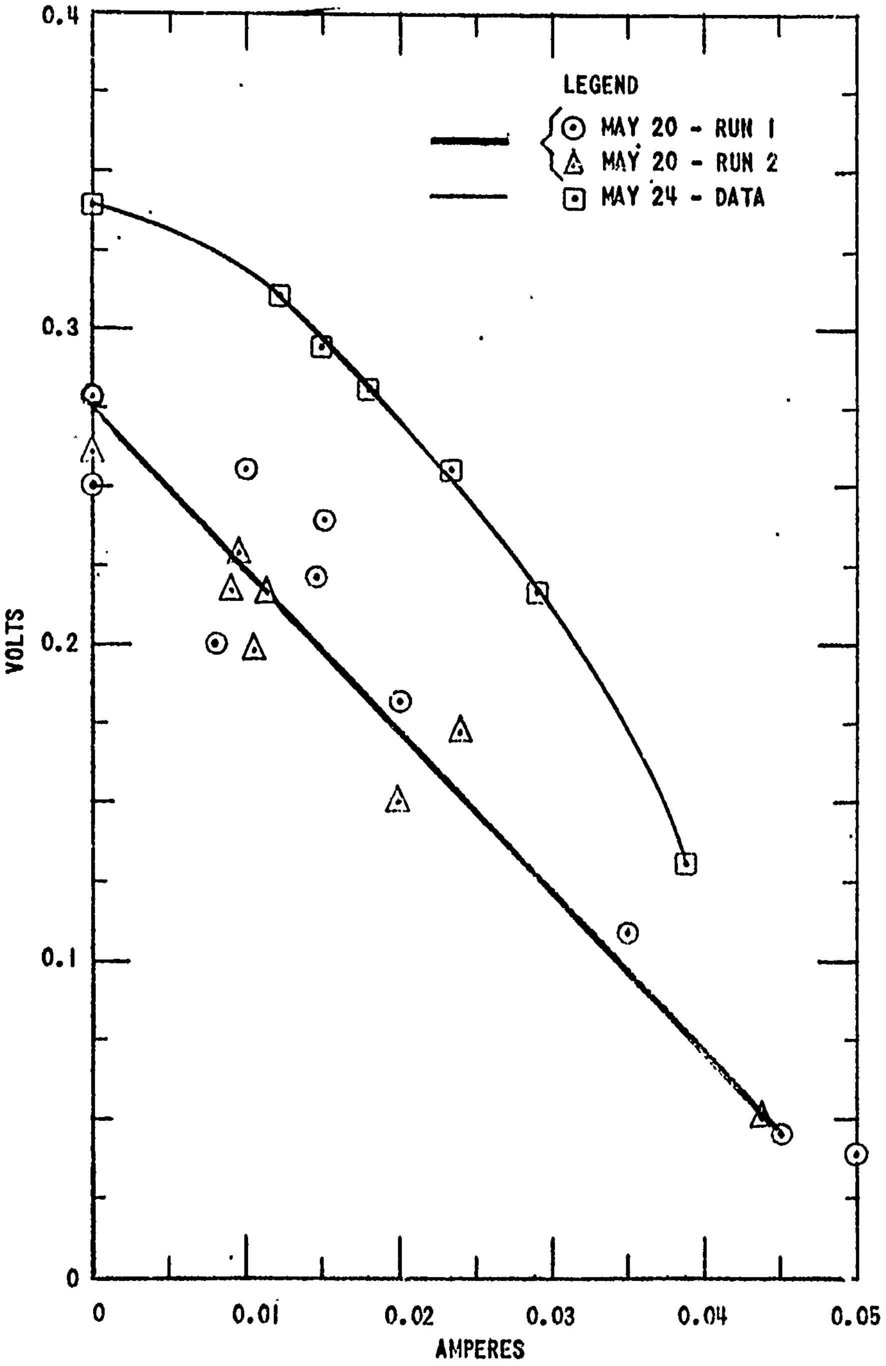

FIG. 4 Volt-Ampere Characteristic of Salt Circulating Hydride Cell

Before a demonstration of regeneration could be performed, the upper salt line plugged. All attempts to restore circulation failed. The unit was then shut down. On washout there was no indication of a plug in the upper line.

Cell No. 4 - Figure 5 shows the metal regeneration system. This was originally constructed as a temperature difference hydride cell but was never tested. A liquid metal circulation loop was added to make it a metal circulation cell. The hydrogen electrode consists of a 1 in. tubing with a micrometallic nickel porous plate mounted at a 45° angle across the bottom of the tubing. The 1 in. tubing is welded to a 1-1/2 in. tubing which serves as a shield to prevent H_2 from impinging on the cell wall and which, in turn, is inserted in one leg of a U-shaped 2 in. pipe. Two 1/4 in. tubes connect with the interior of the 1 in. tubing and the 1-1/2 in. tubing. These 1/4 in. tubes pass through 1/2 in. liquid level prove fittings to insulate the H_2 electrodes from the 2 in. cell wall.

Salt fills the U-shaped 2 in. pipe and liquid metal floats on the salt in one leg. A 25-30 EM pump is used to supply circulation to the regenerator. The hydride is removed from the cell in solution form and decomposed in the regenerator to metal and hydrogen.

The eutectic of potassium bromide and potassium fluoride was used as the electrolyte and potassium metal served as the anode.

An attempt was made to operate the cell on a batch basis with H_2 flow into the 1 in. tubing and out the 1-1/2 in. tubing. However, the salt would continuously be splashed into the vents and freeze because of the close clearances. Since it was not possible to operate the cell for this reason, the unit was shut down and design of a new cell initiated to eliminate the difficulty.

Cell No. 5 - This system is shown in Fig. 6. The cell body consists of a 5 in. long 3 in. Sch 40 pipe with flat heads. The hydrogen and liquid metal electrodes are D shaped with a horizontal cross sectional area of 0.62 sq in. Detail A of Fig. 6 shows a plan view of these electrodes. The electrodes were produced by axially cutting a piece of 2 in. tubing to produce an arc shaped segment with a chord length of 1-3/4 in. and a segment height of 1/2 in. A 1-3/4 in. wide stainless steel plate was welded to the side of the 2 in. tubing and the top of each electrode was capped off with a D shaped stainless steel plate which contained a section of 1/4 in. tubing for the hydrogen electrode and 3/8 in. tubing for the liquid metal electrode. The bottom of the hydrogen electrode was capped off with a D shaped 65 micron nickel porous micrometallic filter plate. The bottom of the metal electrode was left open and a hole was drilled in the lower part of the electrode so that the salt return line could be inserted into the electrode. A barrier plate between the hydrogen and metal electrode prevents impingement of H_2 on the metal electrode.

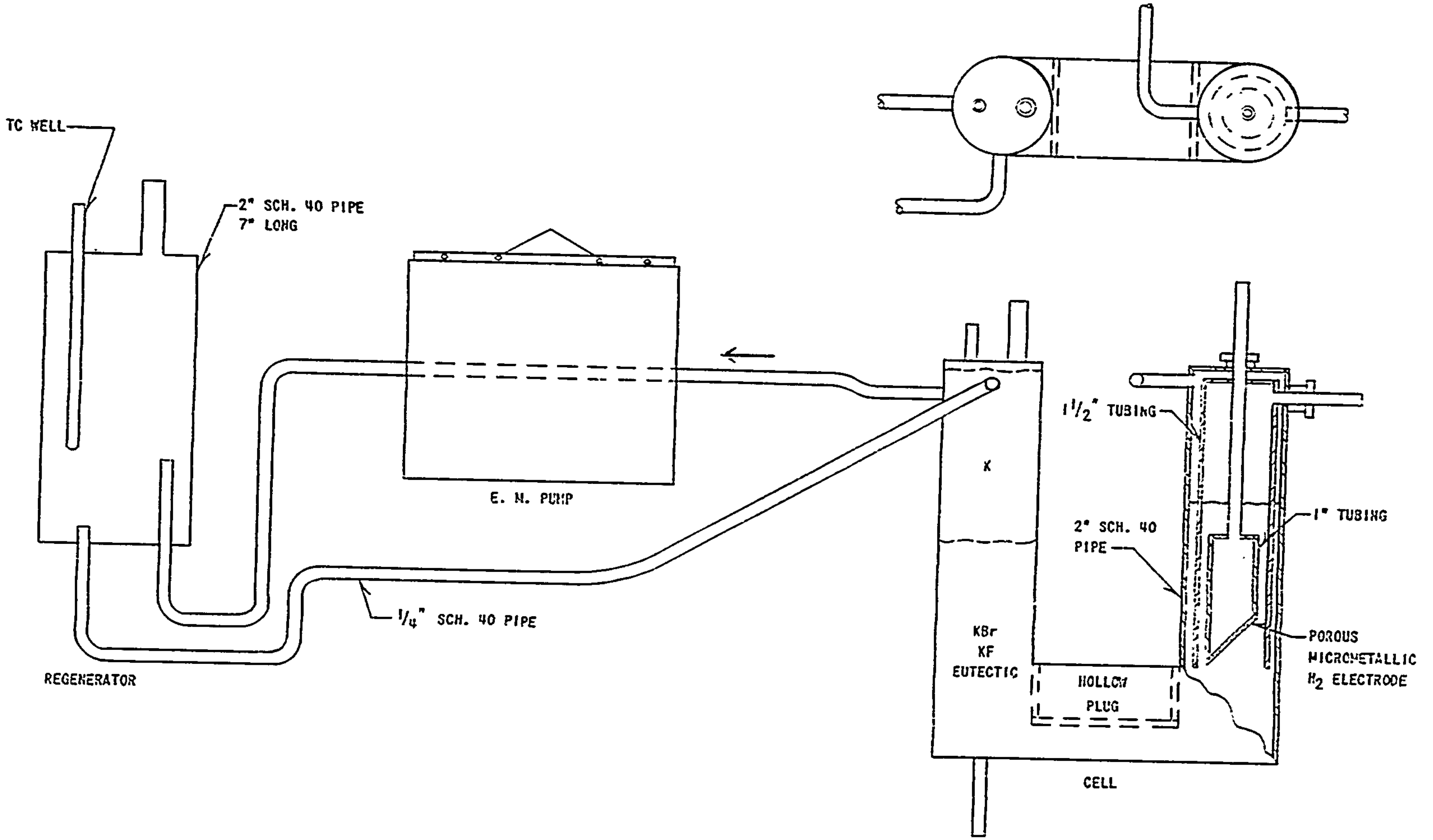

Fig. 5 - Liquid Metal Circulating Regenerative Fuel Cell

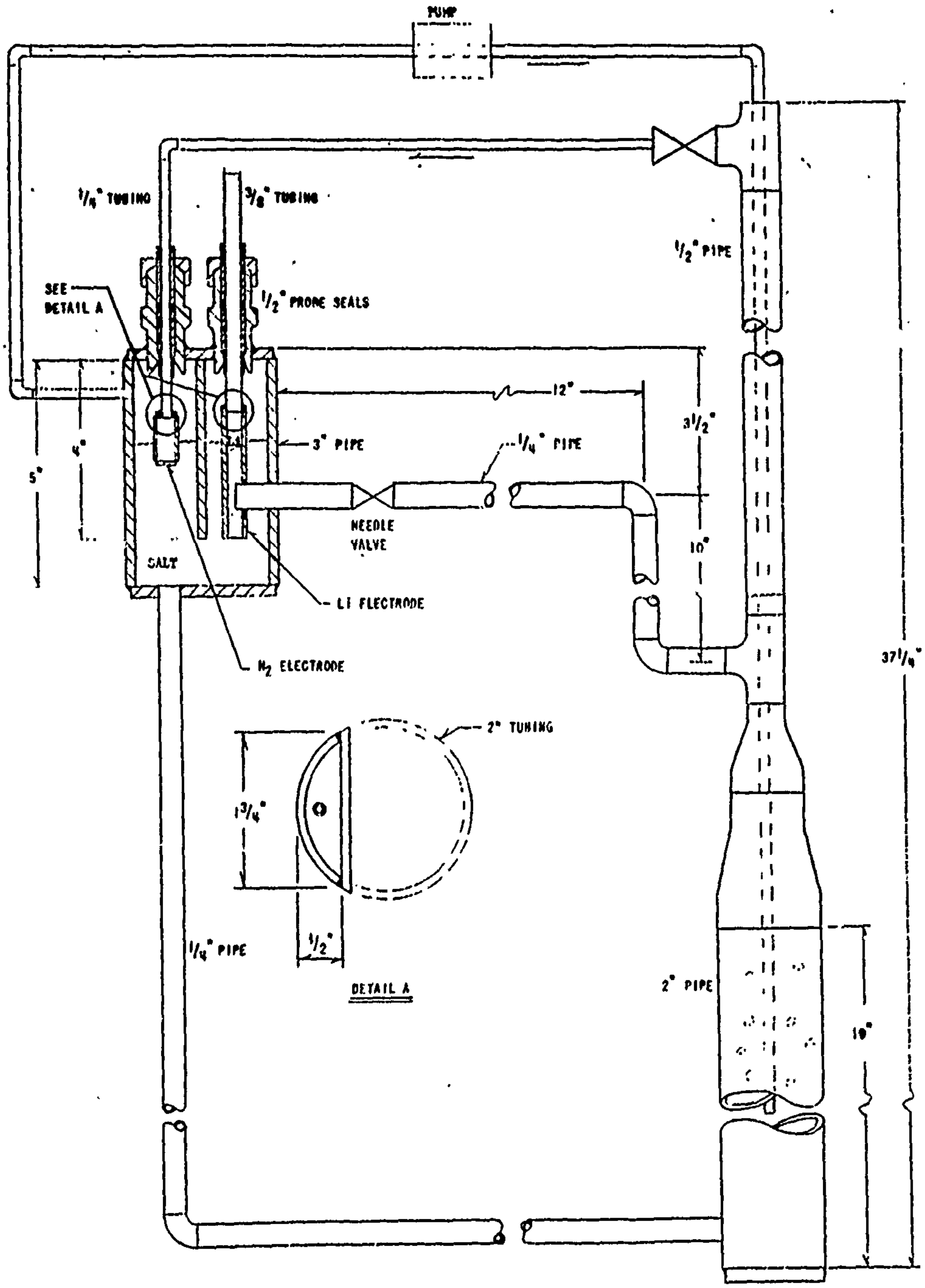

Fig 6 - Regenerative Fuel Cell

The regenerator is a 10 in. long 2 in. Sch 40 pipe and is located lower than the cell to provide natural circulation salt flow and to generate hydrogen at sufficient pressure to overcome pressure drop at the H_2 electrode. The regenerator was heated by an external Kanthal heater. The salt flow rate was controlled by a needle valve in the salt return line.

The salt electrolyte for this system consisted of the four chloride eutectics of cesium, rubidium, lithium and sodium chlorides. The liquid metal used was lithium.

The cell was operated first on a batch basis with H_2 flow through the gas electrode, and open circuit voltage of 0.35 volts was observed. The current flow versus output voltage was determined.

Table 1, data of 7/7/60, gives the cell voltage versus current output for a cell at 480° C. At this particular time, the cell did show a spurious voltage. With argon flow, the cell voltage was 0.23 volts open circuit and 0.04 amp at 0.08 volts. However, the spurious voltage does not have a high current flow and the effect on the H_2 performance is negligible. The current flow with hydrogen was 56 amp/sq ft.

The cell was then shorted to eliminate the spurious voltage. Next the cell regenerator was operated at 705° C for a short time. Table 1, data of 7/12/60, shows the cell performance with a 600° C cell temperature. The open circuit voltage was higher and the current density was larger.

Next a dip tube was added to the regenerator of the cell. The regenerator was heated to 880° C and argon was passed through the dip tube. The gas evolved was then analyzed and was found to be 12.1% H_2, 0.2% CH_4 and 87.7% argon.

The following day, a third volt ampere plot was made. Table 1, July 13, gives this data for an 425° C cell temperature.

A second sample of gas which had been bubbled through the regenerator was taken. The regenerator was held at 840° C and the gas sample showed 4.8% H_2, 0.1% CH_4, 0.6% N_2 and 94.5% argon.

Four more volt ampere plots were made (see Table 1, July 14 and 15) and then the system was operated under regenerative conditions.

Argon was pumped from the cell vent into the dip tube and allowed to bubble up the regenerator. The argon then flowed through the hydrogen electrode and out the cell vent.

TABLE 1 - CELL NO. 5 PERFORMANCE WITH HYDROGEN

Date	Cell Voltage	Cell Amperage	Cell Temperature °C
7-7-60	0.3	0.012	480
	0.27	0.02	
	0.24	0.031	
	0.27	0.05	
	0.16	0.15	
	0.09	0.24	
7-12-60	0.48	0.048	600
	0.40	0.1	
	0.37	0.13	
	0.34	0.2	
	0.28	0.23	
	0.20	0.3	
	0.13	0.32	
7-13-60	0.5		425
	0.275	0.012	
	0.25	0.014	
	0.23	0.0155	
	0.205	0.017	
	0.175	0.02	
	0.135	0.025	
	0.08	0.026	
	0.045	0.028	
7-14-60	0.23	0.01	440
	0.17	0.012	
	0.1	0.015	
	0.03	0.017	
7-14-60	0.37	0.015	480
	0.34	0.0182	
	0.31	0.021	
	0.275	0.024	
	0.255	0.026	
	0.23	0.0285	
	0.14	0.038	
	0.065	0.044	
7-15-60	0.34	0.014	440
	0.16	0.018	
	0.10	0.020	
	0.075	0.023	
	0.04	0.023	
7-15-60	0.55	0.023	440
	0.45	0.037	
	0.42	0.05	
	0.23	0.08	
	0.04	0.10	

Lithium hydride at regenerator temperatures will have a dissociation pressure of less than 1 atmosphere and the partial pressure of H_2 in the regenerator must be low.

The low partial pressure of hydrogen in the regenerator presents operating problems. There are two methods which can be used to circulate hydrogen from the regenerator to the cell: Vacuum operation and recirculation operation.

In the vacuum system, the cover gas consists of pure hydrogen at a pressure corresponding to the vapor pressure in the regenerator. In the recirculation operation, argon at 1 atmosphere pressure is pumped through the regenerator. The argon strips hydrogen from the hydride as it bubbles up the regenerator. The argon leaves the regenerator with a hydrogen partial pressure equal to the dissociation pressure of the hydride in the regenerator. The argon-hydrogen gas then passes through the cell hydrogen electrode where part of the hydrogen is consumed electrochemically, thereby producing electric power. The argon passes out through the cell vent and is then pumped through the regenerator.

The use of an inert carrier gas has the following disadvantages:

1. The system requires a gas pump.
2. The pressure drop in the gas electrode and the regenerator represent inefficiencies.
3. The inert gas carrier increases the polarization loss in the cell by separating part of the hydrogen from the metal and salt. This gives a lower current density.

The decision was made to use recirculating argon on tactical grounds. It was felt that the performance with argon would be satisfactory and, when a more sophisticated cell would be built for vacuum operation, the results would be better. The gas circulation would establish a minimum performance level.

It was felt that the following considerations justified the circulating gas approach:

1. The system can operate at pressures larger than 1 atmosphere. This will allow all leaks to be outward rather than inward. There will be less contamination of the cell with oxygen.

2. The presently used liquid level seals will not allow vacuum operation. A vacuum tight seal will not give the operating flexibility of the present seals.

3. Hydrogen, electrolyte, and metals samples can be removed readily from a system at 1 atmosphere pressure. Vacuum operation will necessitate either no samples or cumbersome sample techniques.

4. The salt level control becomes more difficult with vacuum operation. There is a possibility of flooding of the micrometallic electrode. Therefore, strong dependence must be placed on the surface tension and small pores to keep the electrolyte level in the electrode at the correct level. The regenerator must supply hydrogen gas at sufficient pressure to prevent flooding. For the presently used electrodes, this is about 1/2 psi across the micrometallic filter. If hydrogen does bubble through the micrometallic filter, it will bubble up in the cell and displace electrolyte from the cell. The cell will cease operating when the electrolyte no longer contacts the electrode.

5. In vacuum operation, the gas will dead end at the hydrogen electrode. Any inert gas, even if present in vanishingly small concentrations, will be carried to the hydrogen electrode and vapor blanket the electrode. This will insulate the electrode and the hydrogen must then diffuse through the inert gas barrier. This accumulation of inert gas will then limit the long duration regenerative operation.

6. In vacuum operation, the hydrogen will be produced only at the gas liquid interface in the regenerator. The hydrostatic pressure of the liquid and the low dissociation pressure of the hydride will prevent dissociation below the surface of the liquid. The vertical tube regenerator would then have a low performance. A horizontal regenerator would have a large surface area and give good performance.

The cell was operated under regenerative conditions during the day shift for two days. During the day, the regenerator temperature was held at 815° C with a cell temperature of 425° C. The cell was shut off from all external hydrogen sources, and the gas circulation pump was used to recycle the inert carrier gas from the regenerator to the cell. During the night, the gas pump was shut off, the regenerator temperature was lowered to 535° C, and the cell was held at 425° C with salt still circulating by natural convection. During the day shift regenerative operation, three volt ampere plots were made. Table 2 gives the data obtained.

At this time, two glass sample tubes were inserted in the gas lines, It had been planned to collect gas samples of the argon-helium mixture entering the dip tube and the mixture entering the hydrogen electrode. These samples would have been conclusive proof as to whether or not true regenerative operation had been achieved. However, before the samples could be taken, the natural circulation of electrolyte stopped.

The cell was then washed out. On disassembly, it was found that the nickel micrometallic electrode had disintegrated completely. A black deposit of fine metallic particles was noted in the cell. The stainless steel walls and the welds of the H_2 electrode showed no attack. Separation of the nickel from the stainless was complete. This loss of electrode surface would account for the sudden decrease in current density noticed between July 12 and 13, 1960.

Cell No. 6 - Following the shut down of the fifth salt recirculating cell, the sixth salt recirculation cell was started up.

This unit was similar to the previously tested salt circulation system. Fig. 7 shows the unit. The hydrogen electrode was a circular 1 in. diameter stainless steel micrometallic filter and the metal electrode was an inverted stainless steel cup which contained the liquid lithium. The electrode area is 0.79 sq in. The salt return line from the regenerator discharged into the bottom of the liquid metal electrode so that the metal carried from the regenerator would float into the metal electrode.

The unit was charged with the four chlorides eutectic. Spurious voltage was 0.06 volts with argon with no lithium present. Next, lithium was added to the metal electrode.

A series of volt ampere plots were then made with the cell running on hydrogen. Table 3, data of 8/30/60, gives the results. The open circuit voltage was 1.1 volts and 0.27 amp could be obtained at 0.27 volts with the cell at 480° C. There was a spurious voltage effect present that would allow 0.06 amperes flow at 0.24 volts across the cell. However, the major current contribution of the data obtained 8/30/60 was due to the hydrogen electrode.

The cell was short circuited electrically overnight with argon bubbling through the electrode. In the morning, it was found that the lithium had dissolved in the salt. Therefore, 1.3 gm of lithium was added. Two volt ampere plots were then made using external hydrogen. Table 3, data of 8/31/60, shows these results. Next, the cell was operated for 1-1/2 hr with a cell voltage of 0.18 volt and a cell current of 0.1 amp.

TABLE 2 - CELL NO. 5 PERFORMANCE

	Cell	Cell	Temperature, °C	
Date	Voltage	Amperage	Cell	Regenerator
7-18-60	0.35	0.037	455	815
	0.30	0.05		
	0.20	0.08		
	0.11	0.09		
	0.05	0.10		
7-18-60	0.385	0.00	425	815
	0.30	0.012		
	0.28	0.016		
	0.265	0.018		
	0.25	0.019		
	0.24	0.021		
	0.22	0.022		
	0.205	0.024		
	0.19	0.025		
	0.165	0.027		
	0.11	0.037		
	0.07	0.039		
7-19-60	0.47	0.00	435	815
	0.20	0.008		
	0.16	0.01		
	0.10	0.015		
	0.04	0.019		
	0.16	0.0065		

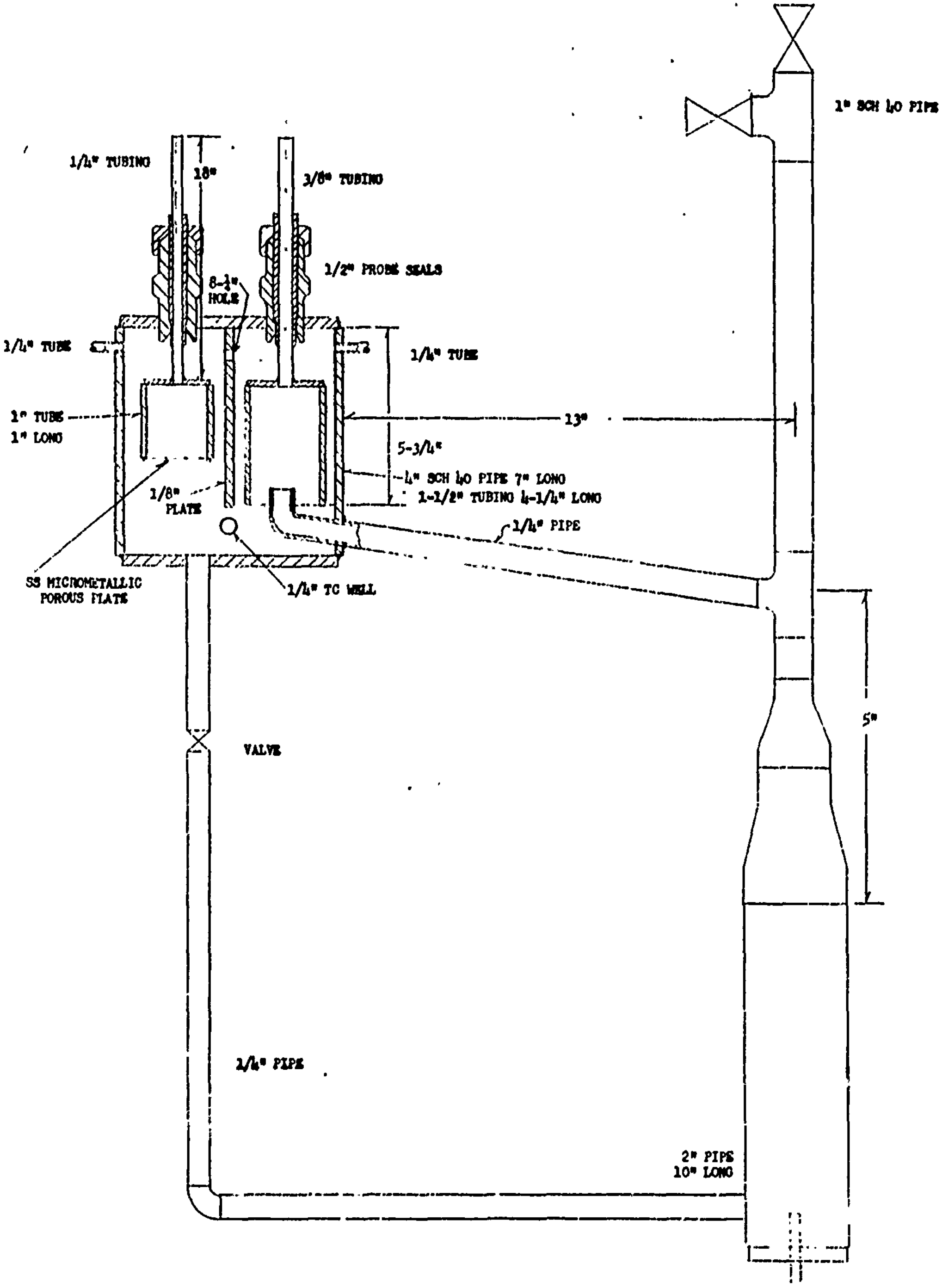

Fig. 7 Regenerative Fuel Cell No. 6

D-64-B-467-A241

TABLE 3 - CELL NO. 6 PERFORMANCE WITH HYDROGEN

Date	Cell Voltage	Cell Amperage	Cell Temperature ° C
8-30-60	1.1	0.0	480
	0.94	0.04	
	0.83	0.045	
	0.78	0.05	
	0.72	0.07	
	0.61	0.1	
	0.55	0.145	
	0.47	0.16	
	0.37	0.185	
	0.27	0.27	
8-30-60	1.05	0.0	425
	0.4	0.19	
	0.41	0.16	
	0.45	0.145	
	0.47	0.135	
	0.31	0.2	
	0.24	0.19	
	0.19	0.21	
8-30-60	0.5	0.14	425
	0.44	0.145	
	0.38	0.155	
	0.3	0.165	
	0.25	0.176	
	0.21	0.18	
	0.18	0.19	
8-30-60	1.0	0.0	425
	0.59	0.155	
	0.49	0.18	
	0.4	0.19	
	0.31	0.2	
	0.27	0.205	
	0.2	0.21	
8-31-60	1.0	0.0	440
	0.59	0.18	
	0.5	0.19	
	0.45	0.21	
	0.38	0.25	
	0.3	0.28	
	0.25	0.30	

TABLE 3 - CELL NO. 6 PERFORMANCE WITH HYDROGEN (Continued)

Date	Cell Voltage	Cell Amperage	Cell Temperature °C
8-31-60	1.3	0.0	425
	0.67	0.21	
	0.55	0.22	
	0.47	0.25	
	0.39	0.27	
	0.25	0.31	
9-8-60	0.16	0.05	465
	0.12	0.07	
	0.09	0.09	
	0.06	0.11	
9-8-60	0.40	0.0	465
	0.3	0.1	
	0.2	0.12	
	0.17	0.14	
	0.14	0.15	
	0.1	0.17	
	0.08	0.21	
9-15-60	0.42	0.0	540
	0.36	0.12	
	0.35	0.17	
	0.32	0.25	
	0.28	0.34	
	0.24	0.49	
	0.17	0.65	

An attempt was made to run regeneratively using circulating argon as an inert carrier. The hydrogen electrode required a large pressure to allow gas circulation. This large pressure was due to surface tension effects on the small diameter pore holes of the micrometallic element. Two pumps were used to circulate the argon; one pumped from the cell vent to the dip tube in the regenerator, and one pumped from the regenerator vent to the cell electrode.

One of the gas pumps developed a leak. A new pump was ordered and gas circulation was attempted with one pump. The remaining pump was repiped such that parallel flow could be achieved in the regenerator and the cell. The argon from the discharge side of the pump divided into two streams. One stream entered the dip tube in the regenerator, while the other stream bubbled through the hydrogen electrode. The hydrogen streams from the regenerator vent and the cell vent then rejoined and entered the suction side of the pump.

After the gas was circulating, with the regenerator at 780° C and cell at 445° C, it was noted that the current was only 0.05 amp. At this time 1.8 gm of lithium was added to the cell. A pressure build-up was noticed immediately after the lithium addition. The excess gas was vented from the system. The gas was combustible and therefore contained hydrogen.

After the lithium addition, the voltage had jumped to 0.83 volt open circuit and 0.2 volt for a 0.33 amp load. The excess pressure was vented through the cell vent and then through the liquid metal electrode. When the metal electrode was vented, the voltage dropped to 0.25 volt.

Next, the lithium electrode was heated to melt the lithium and allow it to drop down into the cell. The open circuit voltage under H_2 then rose to 0.4 volt. Table 3, data of 9/8/60, gives the volt ampere plot.

Next morning, the cell voltage was zero. The lithium electrode was agitated and the voltage with argon was 0.23 volt. However, when H_2 was passed through the cell, the voltage dropped. The gas pump was turned on and the voltage rose to 0.84 volt.

The H_2 electrode was pulled up until only 1/4 inch remained in the salt. The open circuit voltage with recirculating argon then rose to 1.08 volt. Under load, the initial current was 1.2 amp with 0.4 amp at 0.15 volt being held for 5 min and 0.16 amp at 0.08 volt being held for 10 minutes.

The next week, the cell was operated with recirculating argon and a gas sample was taken for analysis. The gas sample taken showed oxygen was present.

A second gas sample was taken while a load of 0.04 amp at 0.15 volt was drawn from the cell. This second sample also showed air. This sample analyzed 33% argon, 58% nitrogen and 8% O_2.

The system leaks were repaired and argon was used to flush out the cover gas. Lithium (1.7 grams) was added to the cell. Table 3, data of 9/15/60, shows the cell performance with hydrogen. After a short period of operation the cell voltage dropped to near zero.

Lithium was then added to the electrode. A pressure build-up was noted but no cell voltage.

Next, a 1-1/2 volt dry cell was hooked up to the cell with the positive terminal connected to the liquid metal electrode and the negative terminal connected to the hydrogen electrode. The battery was left on overnight with the intent to remove the possible oxide from the metal surface.

In the morning, voltage and current could be drawn from the cell; however, this was only temporary, as the cell had behaved as an electric storage battery.

Two grams of lithium were added to the cell. After the addition, there was a large pressure build up in the cell. The pressure rise was large enough to push molten salt out the probe seal around the liquid metal electrode. The salt was then cleaned up from the cell top.

A sample was taken from the metal electrode. It showed no liquid metal was present but only molten salt. The salt was analyzed to determine the chemical composition and the dissolved metal content. The composition was as follows:

Metal Ion	Wt. %
Na	1.7
Rb	33.0
Cs	38.0
Li	[illegible]
Metal Hydride	None
Metal Oxide	None
Metal Hydroxide	None
Dissolved Metal	None

While adding a gram of lithium to the cell it was discovered that the cell had developed a leak. The earlier salt spill had allowed salt, air and heat to corrode the upper salt return line from the outside. The cell was then shut down and washed out. On disassembly, it was found that the H_2 electrode was in good condition. There was no corrosion and very little deposits. The only deposits noted were a few carbon particles.

Cell No. 7 - This salt regenerative cell is shown in Fig. 8. The cell body consists of two 4-1/4 in. long, 2 in. Sch 40 pipe with flat heads. The pipes were joined together with flanges. The flanges were fabricated from a 1/2 in. thick, 12 in. diam. stainless steel plate. The H_2 electrode (upper part of the cell) contained stainless steel mesh which was welded to the pipe for electrical contact. The H_2 electrode was electrically insulated from the liquid metal electrode by an asbestos gasket between the flanges. In addition, the flange bolts were also electrically insulated. The liquid metal electrode was made from a 1 in. Sch 10 stainless steel pipe 4 in. long. The bottom of the metal electrode was left open so that the salt return line could be inserted into the electrode. The regenerator is a 12 in. long, 2 in. Sch 40 stainless steel pipe. Heat is supplied to the regenerator by an external Kanthal heater.

This system was charged with an eutectic mixture (25 lb) of LiCl and LiF. A vacuum (5 in. Hg abs) was pulled on the system to check the frozen salt sealed flange. Vacuum was maintained for approximately 24 hr which indicated a leak-free system.

Sixty (60) gm of Li were charged through the top of the regenerator. The temp of the regenerator was raised to 1650 F and the cell maintained at 1100 F. Natural circulation was observed at these conditions. The salt was circulated continuously for several days to insure transfer of Li from the regenerator to the liquid metal electrode in the cell. Lithium transfer was dependent on the solubility difference (Li in salt) between the regenerator and the cell. When H_2 was added, low voltage (0.05v) was observed. Hydrogen was added intermittently for one week and the voltage ranged between 0.02 and 0.05 volts. It was anticipated that the low voltage was probably due to the inability of the system to deposit free lithium in the cathode.

Cell No. 7 was modified in an attempt to transfer Li to the cathode by gravity. The modified cell is shown in Fig. 9.

This system was charged with a eutectic mixture (25 lb) of Li Cl and Li F. Lithium (150 gm) was charged through the top of the regenerator. Spurious voltage was observed to be 0.4 volts. To eliminate the spurious voltage, the cell was shorted overnight.

Before an attempt was made to run regeneratively, the cell was operated on a batch basis. Hydrogen was passed through the cell at approximately 15 in. Hg abs pressure.

The current flow and output voltages observed are tabulated in Table 4.

Attempt was made to run the cell regeneratively. Hydrogen was added until the system pressure was maintained at approximately 80 mm Hg abs. The initial voltage and current values are tabulated in Table 5.

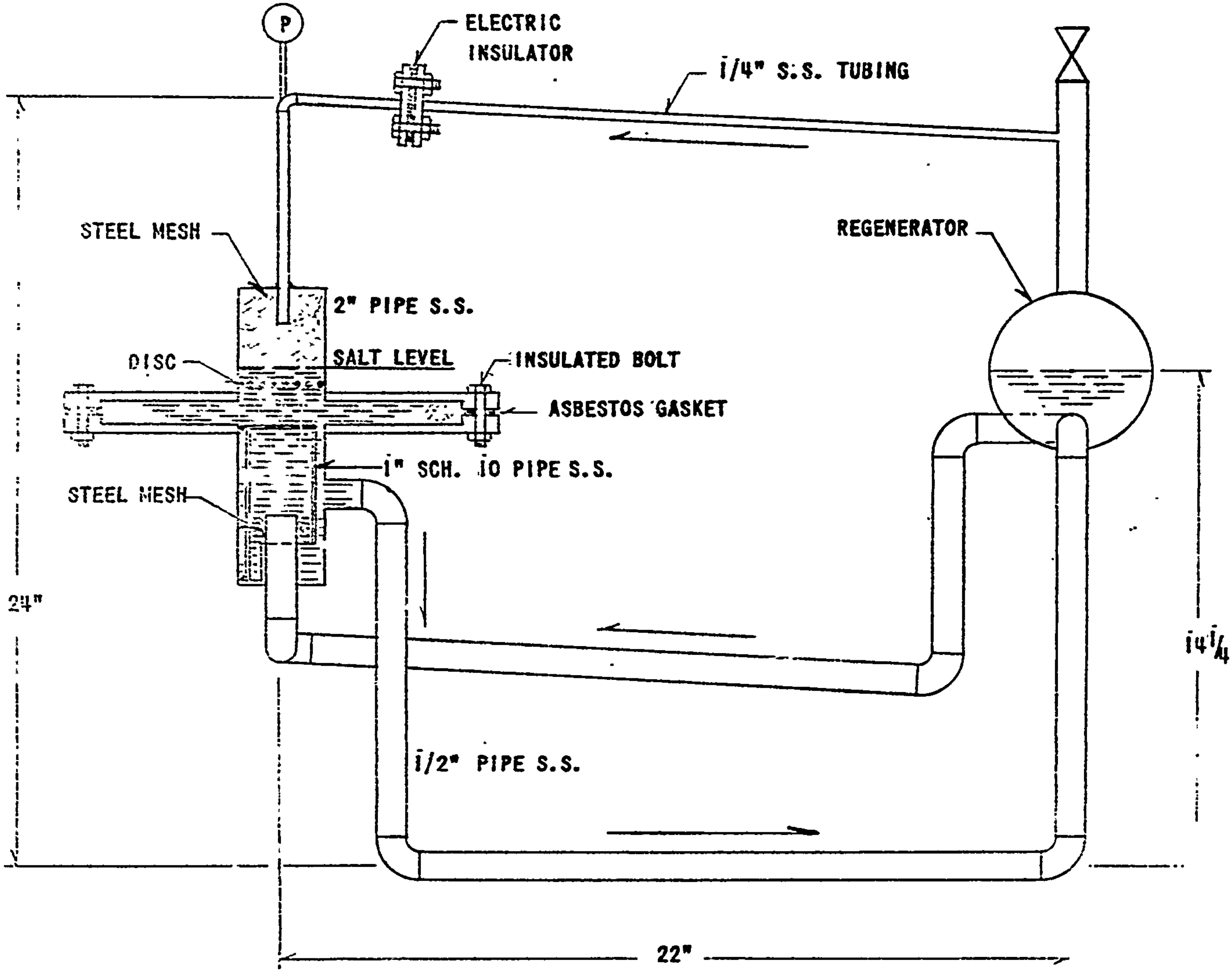

Fig. 8 - Regenerative Hydride Circulating Cell No. 7

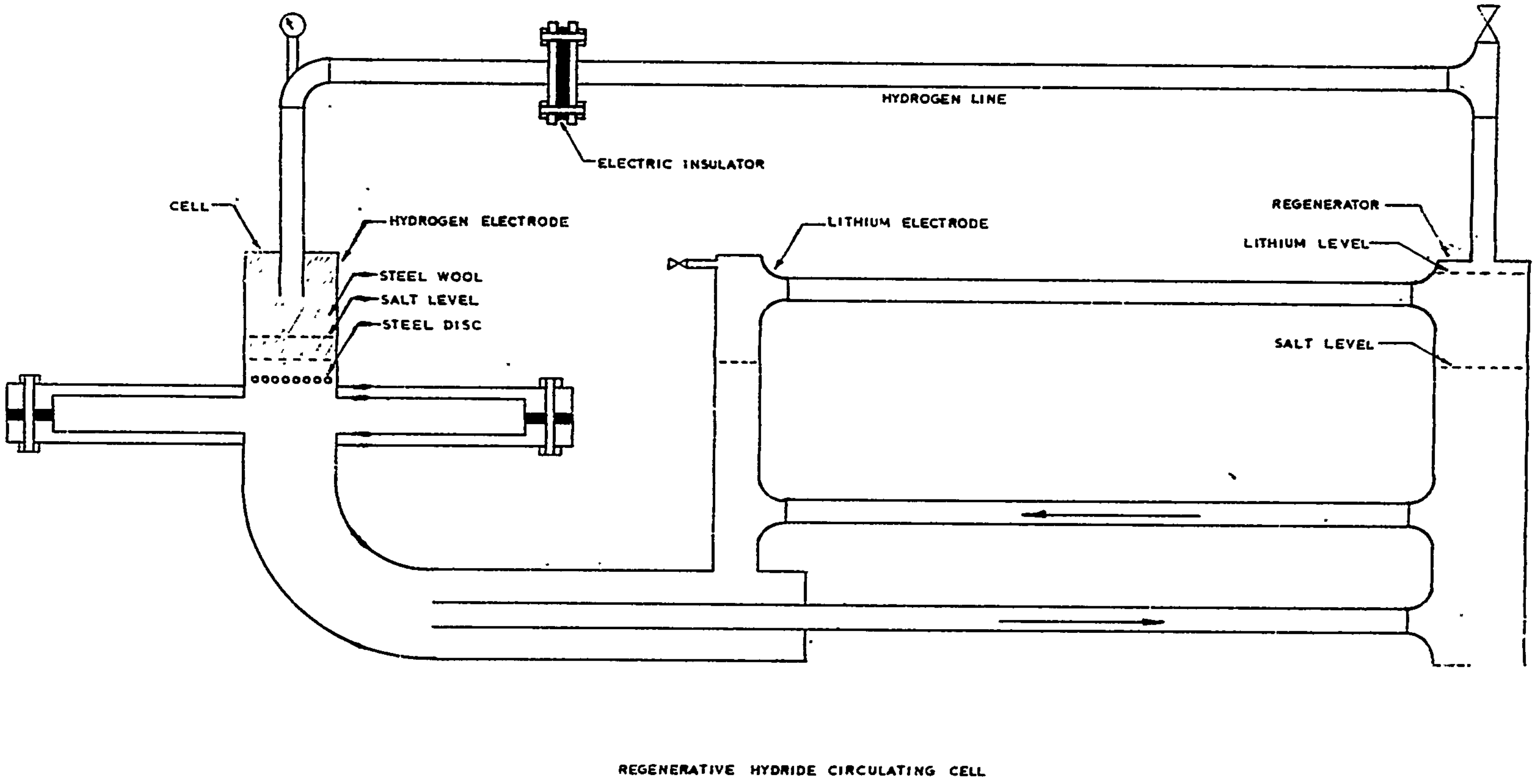

Fig. 9 - Modification of Cell No. 7

TABLE 4 - OBSERVED CURRENT FLOW AND OUTPUT VOLTAGES, CELL NO. 7

Volts	Amps	System Pressure	Cell Temp
0.22	Open	15 in. Hg Vacuum	1100 F
0.20	0.05		
0.185	0.075		
0.175	0.09		
0.160	0.13		
0.170	0.145		
0.20	0.195		
0.11	0.27		
0.10	0.29		

TABLE 5 - INITIAL VOLTAGES AND CURRENT VALUES, CELL NO. 7

Volts	Amps	System Pressure	Cell Temp
0.085	Open	80 mm Hg abs	1260 F
0.082	0.046		
0.079	0.130		
0.075	0.21		

TABLE 6 - OBSERVED CURRENT AND VOLTAGES, CELL NO. 8

Volts	Current (amps)	Pressure	Cell Temp
0.3	Open	1 psig	1240 F
0.26	1.25		
0.20	1.55		

After a period of $\sim$ 4 hrs, the voltage dropped to zero. Due to the low open circuit voltage, and the small change in cell voltage with current, it was concluded that the cell was shorted. The system was cooled down and the salt was allowed to freeze. The resistance was checked with a multi test meter, which showed no direct short. However, it should be stressed that the resistance of the electrolyte was not measured, but that the electron conductivity was being checked. The cell was put back into operation with the addition of more hydrogen. Low open current voltage (0.07 was again observed. The decision was made to terminate this test.

Cell No. 8 - This cell construction is shown in Fig. 10. Cell construction consists of a 3 in. and a 4 in. stainless steel pipe joined together as shown on the sketch. The hydrogen electrode contained stainless steel mesh within a 2 in. stainless steel perforated pipe. The hydrogen electrode is electrically insulated from the liquid metal electrode by a rubber 0-ring gasket between two flanges. The regenerator is a 20 in. long, 3 in. Sch 40 stainless steel pipe.

In this system, the salt circulates by natural circulation from the cell to the regenerator. The heat is supplied to the regenerator by a 2200 w Kanthal heater. LiH decomposes in the regenerator and the hydrogen passes off the top to the hydrogen electrode. Free lithium which floats on top of the salt in the regenerator is transferred to the cell by gravity through a 1/2 in. pipe.

After the system was checked for leaks, it was charged with approximately 13 lb LiF and LiCl eutectic salt. Approximately 175 gms of lithium were charged to the regenerator. No spurious voltage was observed upon the addition of the lithium. Hydrogen was then passed into the cell and vented at the regenerator in an attempt to operate the cell on a batch basis. No voltage was observed on the addition of hydrogen.

Since no voltage was observed, it was concluded that the cell was shorted. The cell was allowed to cool until the salt solidified. A check with a multi test meter showed the cell to be shorted. It was anticipated that when the salt circulated, lithium was carried by the electrolyte to the cell compartment, causing a short. This lithium was probably carried from the regenerator by the electrolyte as a dispersed phase formed when the lithium hydride was dissociated or resulted from the precipitation of lithium when the electrolyte was cooled.

The system was modified (Fig. 11) to improve on the design to eliminate the anticipated problems. (1) The salt lines to the regenerator were moved further apart (9 inches) which insured that only the salt level could flow by natural circulation. (2) The return salt line was increased from 1/2 in. to 1 in. pipe in an attempt to cool the salt before entering the cell.

After the above modifications were made, the system was charged with salt and lithium. Hydrogen was purged through the cell and vented at the

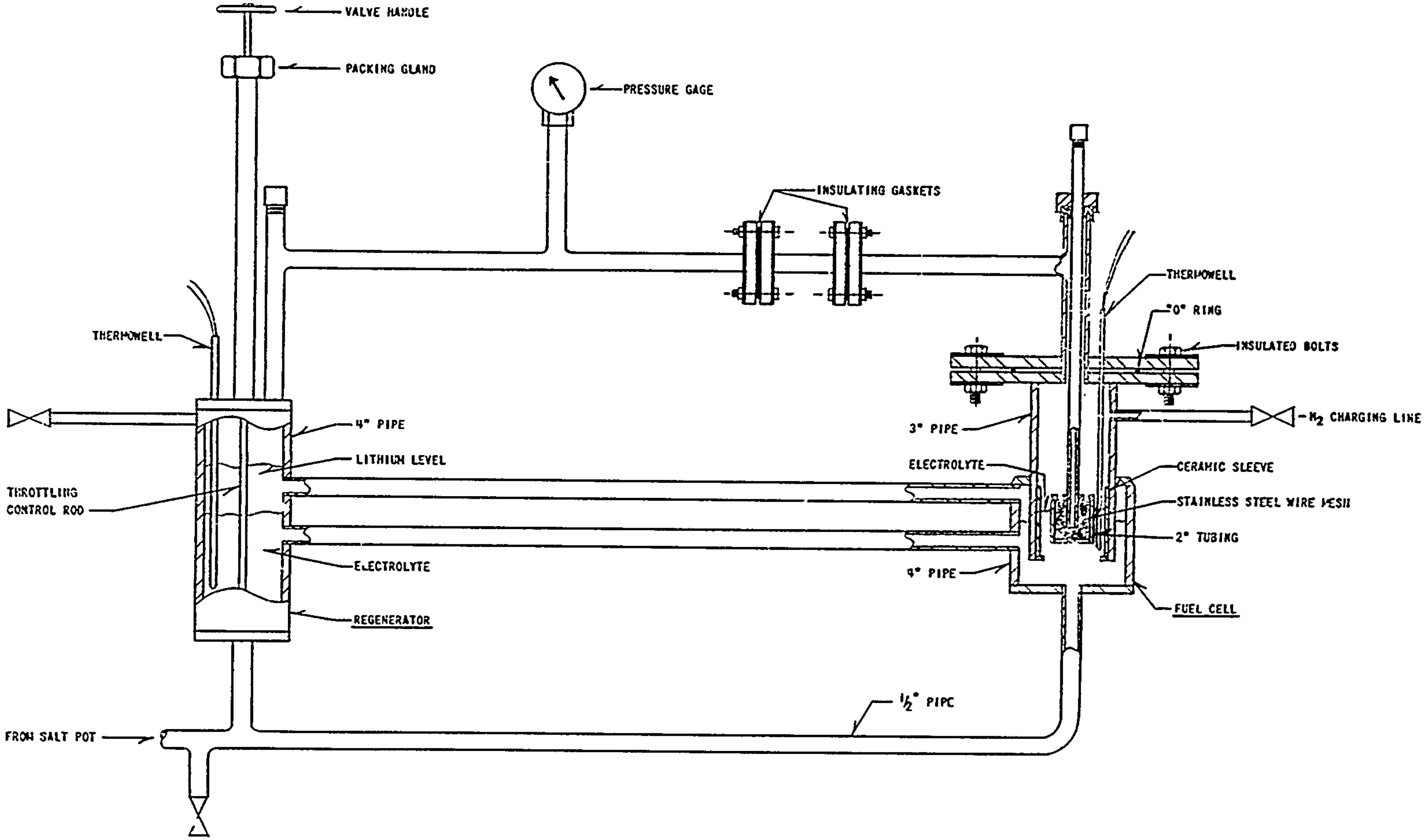

Fig. 10 - Lithium Hydride Regenerative Fuel Cell

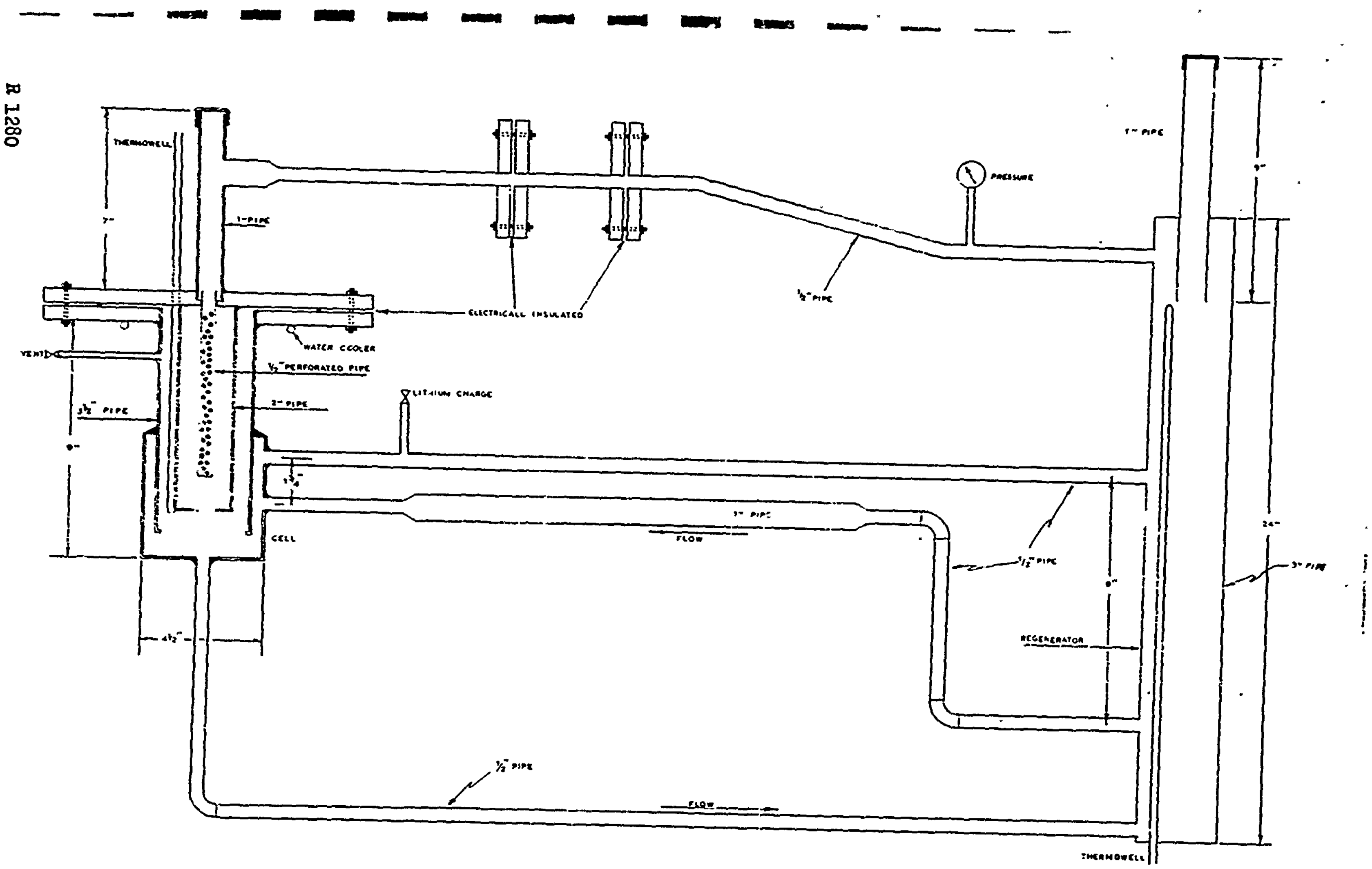

Fig. 11 - Modification of Cell No. 8

regenerator. The current and voltage values observed from this batch operation are listed in Table 6. (Page 30).

After the cell performed on a batch basis, the system was prepared to operate regeneratively. Sufficient hydrogen was added until the system pressure was $\sim$80 mm Hg abs. When the hydrogen was being added, the voltage meter was oscillating between 0 and 0.4 V. Finally the voltage remained at zero, which indicated a short in the cell compartment. A dip tube was inserted through the top of the cell and showed lithium to be present at the hydrogen electrode. The system was shut down, cut apart and drained. Because of insufficient funds, no further work was performed on the system.

The oscillation of the volt meter, when the hydrogen was added, suggested that the pressure drop from H_2 supply to exit was sufficient to allow variations in salt levels which permitted lithium to enter the hydrogen compartment.

5.2 Basis Studies

Basic studies undertaken under the subject contract were directed toward optimizing the parameters briefly studied earlier in MSAR supported work and toward determining conditions which would prevail under regenerative operation. Areas covered included:

a. Screening of various electrolyte compositions.
b. Screening of metal hydrides and other compounds of possible use in closed cycle systems.
c. Studies of electrodes with respect to catalytic effect, stability in various electrolytes, hydrogen gas pressure, and optimin cell performance.
d. Measurement of decomposition pressures of promising hydride-solvent electrolytes.
e. Calculation of theoretical emf of a promising cell formulation.

These areas will be covered separately below.

5.2.1 Electrolyte Compositions

Since thermodynamic considerations show the advantage of a low temperature cell, lower melting solvents are attractive for improved cell thermal efficiencies. In search for such lower-melting solvents, a program was undertaken with the following goals:

1. Determination of the composition of fused salt eutectics with lower melting points.
2. Determination of the effect of these solvents upon cell voltage and upon the metal electrode from the standpoint of solubility in the electrolyte.

One of the solvent compositions of interest which was studied experimentally was the eutectic of the borohydrides of lithium and potassium, which was reported[1] to have a composition of 54 wt % $LiBH_4$ and 46% KBH_4 and to melt at 102° C. In actual operation, it was found that the melting point was actually 120° C. Cells with a number of formulations were set up as follows:

1. $K/LiBH_4\text{-}KBH_4/H_2$ (stainless steel)
2. $Li/LiBH_4\text{-}KBH_4/H_2$ (stainless steel)
3. $Li/LiBH_4\text{-}KBH_4/H_2$ (nickel)

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[1] Callery Chemical Company - Private communication

4. $M/LiBH_4$-KBH_4/H_2 (Pd-Ag)

5. $Li/LiBH_4$-KBH_4/H_2 (nickel)

The latter cell served a dual purpose in that a nitride cell was screened. However, no galvanic action was observed in this cell when argon cover gas was replaced with a stream of nitrogen, and work was abandoned. In the case of the silver-palladium electrode, it was found to have disintegrated and no galvanic action was observed. Nor were promising results obtained with the other cells; for in Cell 1, a hydrogen voltage of only 0.02 V above the spurious voltage of 0.08 was obtained; in Cell 2, a current density of only 2.9 A/sq ft was obtained at maximum power; and in Cell 3, of only 2 A/sq ft.

Differential thermal analysis[1] was used as a tool in the determination of the melting point and composition of lower melting eutectics of alkali metal halides. The principle is based on temperature differentials between sample and an inert reference as they are heated or cooled. Upon cooling, for example, the rate of cooling of the sample lags behind that of the reference while crystallization is in progress. Completion of crystallization is indicated by increased cooling rate of the sample below the eutectic temperature. The last remaining liquid before the eutectic temperature is reached can be sampled and analyzed by conventional means.

The apparatus used is shown in Fig. 12. It is sealed off to permit vacuum drying of the salts at elevated temperatures and to prevent absorption of moisture from the air. In the first series of tests, sand was used as a reference material. Reproducibility was only fair; but in a number of runs a break was seen in the range of about 395° C to 430° C, as is shown in the typical curves given in Figs. 13 and 14 for the ternary system of the flouride, chloride iodide of lithium. Since this range of melting points was not considered promising, no analysis or further work was done on the system.

For later work on differential thermal analysis, improved procedures were used to sharpen the temperature break and to improve reproducibility. The former was accomplished by eliminating sand reference material to improve thermal conductivity to the reference thermocouple; and the latter by stirring the sample during freezing. This refined apparatus was used on the ternary system of the bromide, fluoride and iodide of potassium. Results are shown in Fig. 15 and indicate a ternary eutectic temperature of 566° C. This was not considered low enough to be of value, and no further work was done on this system.

Information had been obtained[2] that there exists a quaternary eutectic of the chlorides of lithium, sodium, rubidium and cesium melting at 275°.

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[1] Stravrolakis, J. A., Encyclopedia of Chemical Technology, Vol. 13, pp 932-940. Kirk, R. E. and Othmer, D. F., editors.

[2] Catalyst Research Corporation - Private communication.

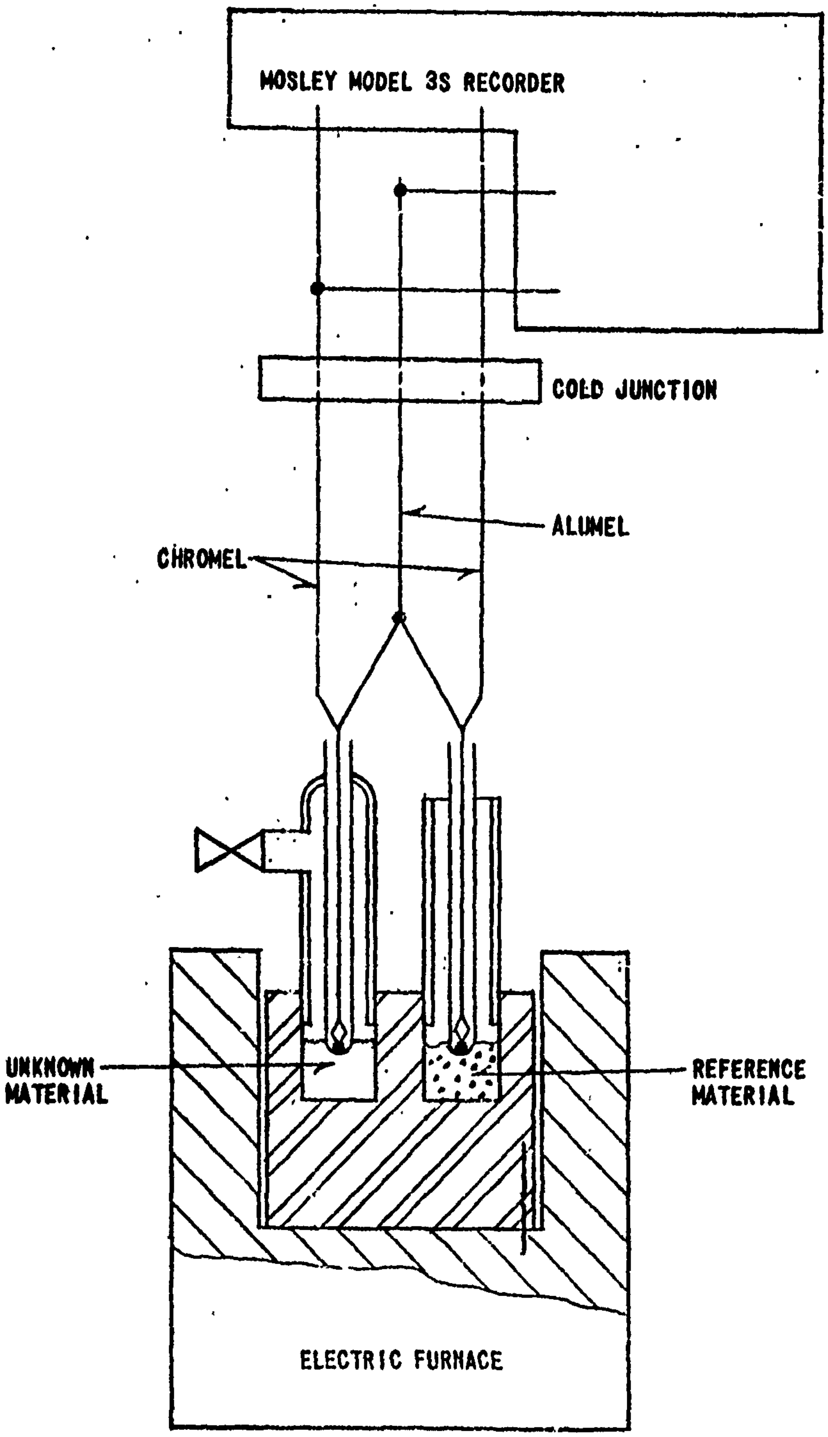

Fig. 12 - Thermal Differential Analysis Arrangement

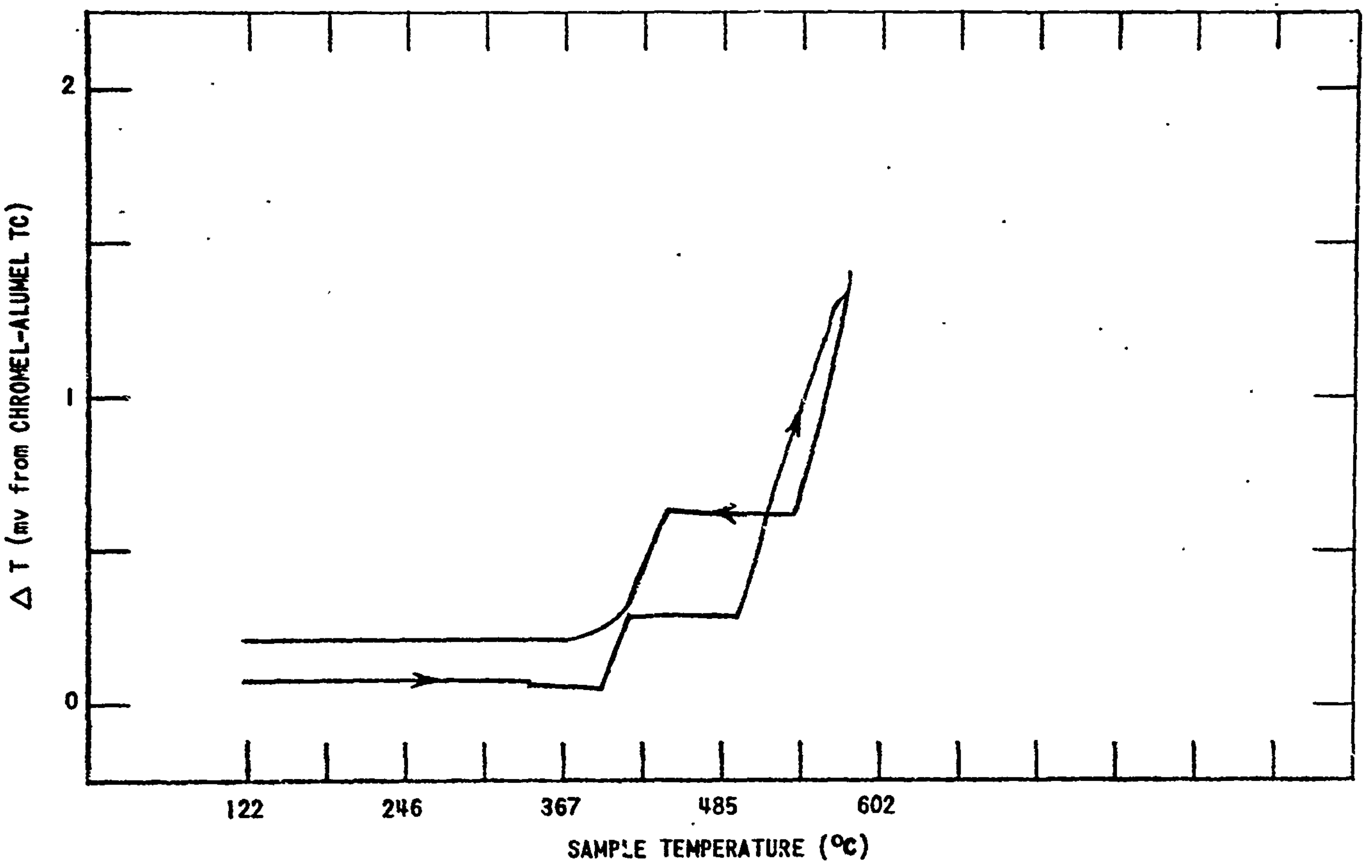

Fig-13 - Sample Temperature vs Temperature Differential Between Reference and Sample of 10 wt% LiI and 90% Eutectic of LiF-LiCl

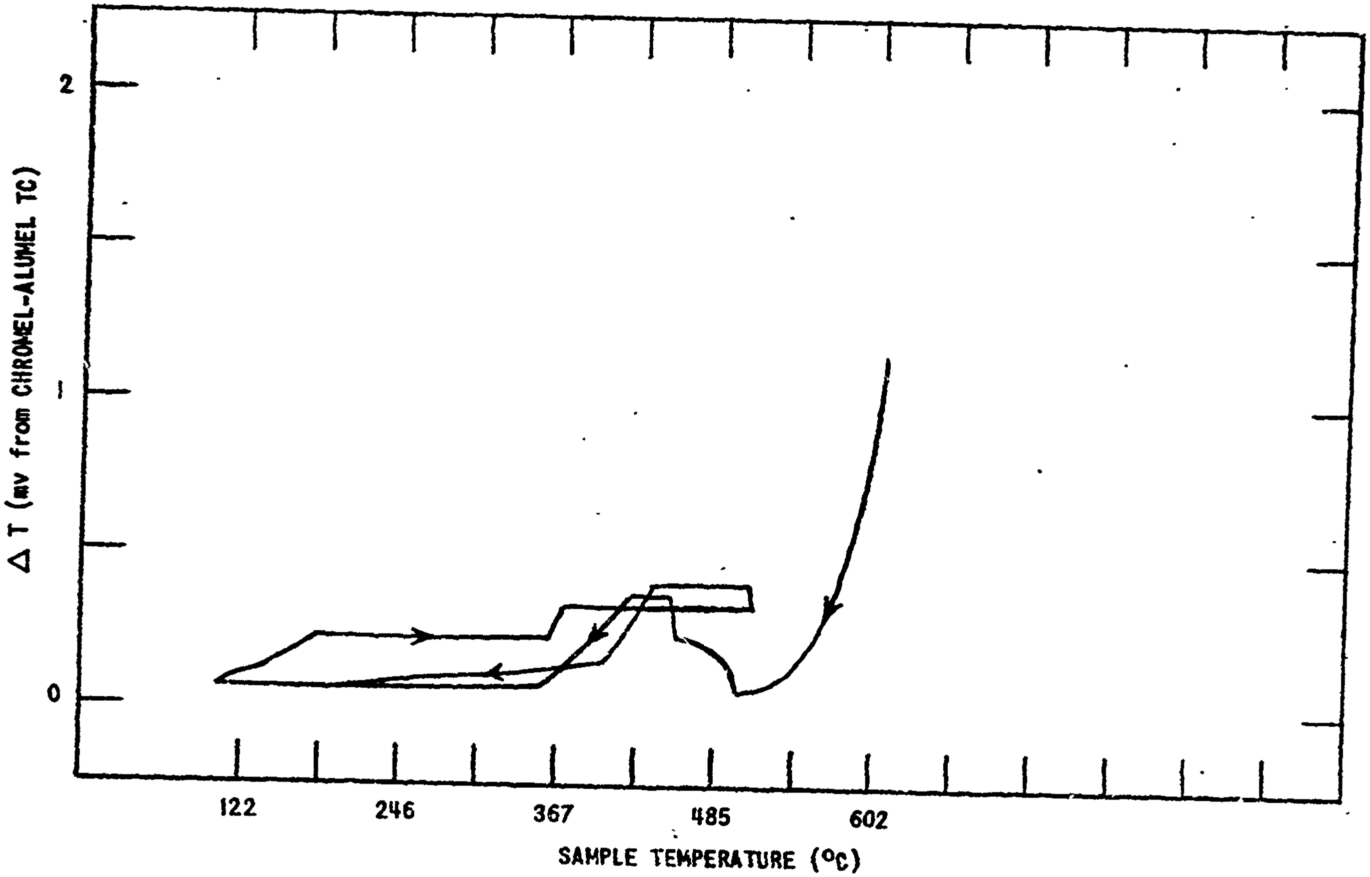

Fig. 14- Sample Temperature vs Temperature Differential Between Reference and Sample of 20 wt.% LiI and 80% Eutectic of LiF-LiCl

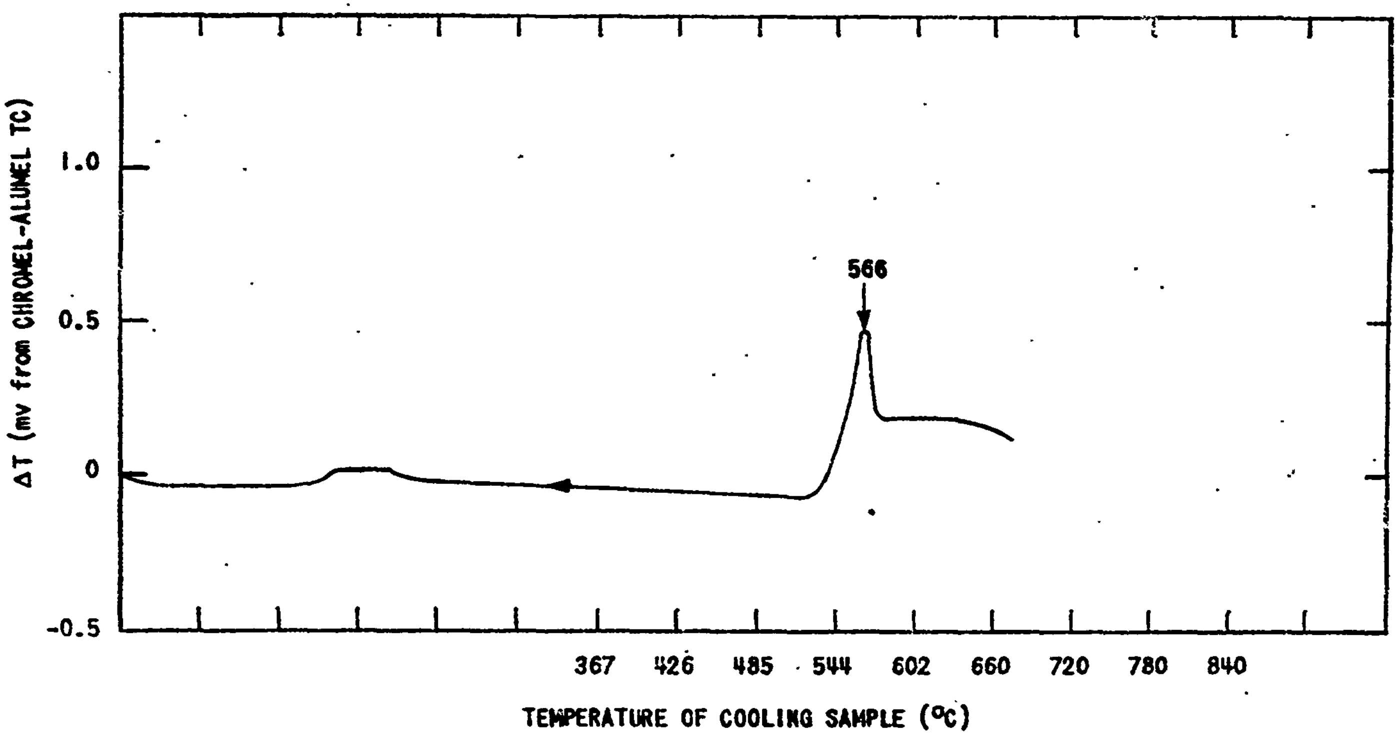

Fig. 15 - Differential Thermal Analysis Curve for the System KI-KBr-KF

Since this is a significant decrease below the eutectics previously used, work was undertaken to determine eutectic composition. This was done by melting a mixture of the chlorides in the following weight ratios: LiCl 58, NaCl 2, RbCl 20, CsCl 20. These were melted down, frozen, ground to a powder and remelted by slowly raising the temperature. The first liquid appearing was vacuum filtered off through an Ace Disc Filter of porosity A. The recrystallized material was analyzed by flame photometry, as is discussed in Appendix I. The composition in weight percentages was found to be as follows: 28.5 LiCl, 3.1 NaCl, 30.5 RbCl, and 38.9 CsCl. When a new mixture was made to duplicate this composition, it was found to melt in the range of 284 to 288° C. This mixture was made with "Trona" RbCl, lot number 6728, assaying 97.38% RbCl and containing 1.82% KCl as a major impurity. The cesium chloride going into the mixture was Trona lot number 6799 assaying 95.95% CsCl and containing 1.67% RbCl as the major impurity.

A mixture of the composition determined above was then used as an electrolyte in a lithium hydride cell. It was necessary to raise the temperature to 340° C to get complete melting of the rather non-homogeneous physical mixture; and initial tests on the cell were made at this temperature. After elimination of the usual spurious emf, hydrogen was passed to the gas electrode which was made of micrometallic stainless steel of porosity "C" and the emf rose to 0.57 v in 10 minutes and held at that value for 20 minutes. Current was then drawn at a density of 1.35 A/sq ft under a potential of 0.46 v for 15 minutes and then at 2.4 A/sq ft under a potential of 0.285 v for an hour. The open circuit emf after this loading was 0.48 v.

While open circuit voltage values were at a reasonable level, current densities are considered unsatisfactory.

Next the solubility of lithium hydride in this quaternary salt solvent was measured. A 700 g. mixture consisting of 28.5 wt % LiCl, 3.1% NaCl, 30.5% RbCl and 38.9% CsCl was melted down, mixed and cooled to room temperature. To this were added 70 g of LiH, and the mixture was heated to 680° C to melt the hydride and to permit it to dissolve. The solution was then cooled to cell operating temperature (316° C), allowing excess LiH to freeze out. A sample of the melt was taken from the bottom of the container.

The sampling of the molten salt was accomplished, using a device consisting of a solid 3/16 in. stainless steel rod and a 1/4 in. tube of similar material. The tube was crimped shut at one end and a slot cut in the wall of the tube about 1/2 in. to 3/4 in. above the crimped end. The rod was inserted inside the tube and pushed down to the crimped end, thus covering the slot, and the tube with the rod inside was lowered into the salt to the desired sampling depth. The rod was raised in the tube to just above the slot to allow the liquid salt to flow inside, then lowered slightly again to cover the slot. The rod and tube were withdrawn from the melt and the end of tube containing the sample, after having been cleaned free of salt on the outside, was sawed off into a flask.

Analysis was made for hydride content by a gas evolution method based on the reaction:

$$LiH + H_2O \longrightarrow LiOH + H_2$$

Hydride content was found to be 0.8%. With this hydride content and an assumed 30% decomposition in the regenerator, a circulation rate of about 210 g. of solution per minute would supply 100 amperes.

The effect of adding bromide ion to the above eutectic was next investigated to determine a salt electrolyte with a lower melting point.

Cooling curves were made using the previously described four chlorides electrolyte with varying amounts of LiBr added.

The four chlorides had a break at 280° to 286° C. Adding 5 mole per cent LiBr gave a break at 278° to 279° C. The salt with 15% LiBr had a break at 269° to 271° C. The salt with 23% LiBr had a break at 263°C.

The results showed successively lower temperatures as the LiBr concentration increased. However, at the break temperature, there was very little liquid present. This showed that the overall composition was quite different from the eutectic composition. It was felt that more bromide ion and less chloride ion would be beneficial. Also, it was decided to use potassium instead of sodium.

Therefore, a mixture of CsCl, RbCl, KBr and LiBr was investigated. The cooling curves of this mixture were not sharp and a visual indication of freezing was used. The equal molar mixture of the salts showed the first solid formed at 500° C with complete solid at 300° C. A mixture with 1 mole each of CsCl, RbCl, KBr and 2.2 moles of LiBr showed the first solid at 350° C, and complete freezing at 270°. Increasing the LiBr content to 2.9 moles gave first solid at 275° C, complete freezing at 240° C. A sample of liquid at 242° C was removed and analyzed. Increasing the LiBr to 5.0 moles gave no improvement.

The liquid removed at 242° C was analyzed and found to be:

	Mole % Cation	Mole % Anion
Li	56	
K	09	
Rb	18	
Cs	17	
Cl		24
Br		76

The eutectic of the chlorides of lithium and potassium (41 mole % LiCl) was considered as a possible advantageous solvent in a lithium hydride cell, having both a relatively low melting point (325° C) and a low lithium ion activity. The question about the stability of lithium metal in a melt containing KCl was judged to be satisfactory, since calculations[1] of standard free energy values showed that of KCl to be -93.3 Kcal/mole and that of LiCl to be -88.8 at 237° C and -81.6 and -80.2 respectively at 737° C.

With a cell operating temperature of 357° C, a peak open circuit voltage of 0.385 v was obtained. Considerable difficulty was encountered in cell operation in that the gas electrode became plugged frequently. It has now been established that this difficulty is encountered most frequently with use of E grade "micrometallic" porous stainless steel and can be minimized with use of the coarser C grade material.

With finding of the relatively poor open-circuit voltage of this cell and of more promising systems elsewhere, work on this particular cell was halted, at least temporarily, so that efforts could be concentrated in more promising areas. With increased current densities since having been obtained by use of Grade D nickel micrometallic gas electrode material as compared with use of Grade C stainless material and with minimizing gas stoppage, it is in order to reactivate this cell with different electrode materials.

The quaternary eutectic of LiI-LiBr-KI-KBr has been reported as melting at 230° C.[2] The composition was reported to be 36% LiI, 29% LiBr, 14% KI and 16% KBr. This adds up to only 95%, so each value was increased by 5% to make a low melting solvent for the lithium hydride cell.

In preparation of this fused salt solvent, it was necessary to prepare lithium iodide in the laboratory. The purity of the resultant salt was questionable as there appeared to be free iodine resulting from the hydrolysis of the salt. This material was combined with reagent grades of the other salts. The resultant mixture melted over the range of 330-350° C. This was placed in a cell with a hydrogen electrode of porous stainless steel; and a lithium electrode was introduced. Ultimately a spurious emf of 0.25 v was obtained with argon passing through the hydrogen electrode. When hydrogen was substituted, the voltage fell off to zero and then reversed in sign with a value of 0.005 v with the hydrogen electrode negative in sign and the metal electrode positive. This suggests that a HI cell had been formed from the reactions: $1/2\ H_2 \longrightarrow H^+ + e$ and $1/2 I_2 + e \longrightarrow I^-$. Presumably the iodine had been liberated by decomposition of the iodide salts at the elevated operation temperature.

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1. Quill, L. L., editor, Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, McGraw-Hill, 1956
2. Callery Chemical Company - Private communication.

With lack of promise of this system, no further work was done.

5.2.2 Screening Compounds of Possible Use in Closed Cycles

While lithium hydride cells and calcium hydride cells had shown promise for closed cycle systems in preliminary work, the possibility existed that decomposition temperatures might prove to be excessive or that decomposition pressures might be inadequate at reasonable decomposition temperatures. To anticipate these possibilities and to determine if superior systems might be found, screening of other compounds of possible use was undertaken. To obtain lower decomposition temperatures, compounds with lower free energies of formation are required.

Potassium hydride is such a compound; and a low melting halide eutectic, that of the chlorides of lithium and potassium, show promise as the solvent. This eutectic has a melting point of 352° C. An unknown factor in this system is solubility of metallic potassium in the solvent. This might prove a serious problem if there is a parallel to the situation in KX-K binary systems, where X is F, Cl Br and I. In these potassium halide systems, there is complete miscibility as close as +47, +48, -7 and +22 degrees, respectively, to the melting points of the salts.[1] An experimental approach was called for, since there appear to be no data on the proposed system in the literature; and this is described below.

Other hydrides of possible use are shown in Table 7 which also includes some physical properties.

Other compounds of possible use appeared to be ionic nitrides, judging from thermodynamic data in Table 8, in which $-\Delta F^{o}$ is the negative of the free energy of formation, E^{o} standard electromotive force and T_d temperature at which nitrogen pressure is one atmosphere.

Work with a nitride cell using a borohydride solvent was described under Electrolyte Compositions above. In addition, another experiment using a sodium anode, a nickel gas electrode and the eutectic of the fluoride and chloride of lithium as solvent, was performed. A maximum open circuit voltage of only 0.06 v and a current density of only 56 A/sq ft at 0.03 v indicated little promise for this system, and work was abandoned.

In order to determine the feasibility of a sodium hydride cell having low sodium ion activity, an assembly was made of a sodium electrode and a hydrogen electrode of Grade C micrometallic stainless steel with the eutectic of the fluoride and chloride of lithium as solvent. After elimination of spurious

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[1] Johnson, J. N. and Bredig, M. A., Miscibility of Metals with Salts in the Molten State, Journal Am. Chem. Soc. 62, pp 604-607, May 1958.

TABLE 7 - REPRESENTATIVE THERMALLY REGENERATIVE IONIC HYDRIDE ELECTROCHEMICAL SYSTEMS

Hydride	Temperature[1] (° C)	E^o from $-\Delta F^o$ at 298° K (volts)	Solvent Composition (mole %)	M. P. (° C)
BaH_2	730	0.70	7 BaF_2 - 93 BaI_2	680
NaH	425	0.36	34.5 NaF - 65.5 NaCl	685
KH	432	0.28	40 KF - 60 KBr	580
SrH_2	840	0.71	11 SrF_2 - 89 $SrCl_2$	740
LiH	850	0.72	89 LiBr - 11 LiF	450
CaH_2	1000	0.78	81 $CaCl_2$ - 19 CaF_2	644

[1] Temperature for dissociation pressure of 1 atmosphere for the pure hydride.

TABLE 8 - REPRESENTATIVE THERMALLY REGENERATIVE IONIC NITRIDE ELECTROCHEMICAL SYSTEMS

Compound	Ba_3N_2	Sr_3N_2	Ca_3N_2	Li_3N	Mg_3N_2	Na_3N	K_3N
$-\Delta F_f^{o}$[2] (Kcal)[1]	73.4	77.0	93.2	37.3	96.2	--	--
E^{o}[2]	0.53	0.56	0.67	0.54	0.69	--	--
Td (°K)[3]	1270	1300	1170	1113	1300	548	628

1. Quill, L. E., ed., <u>The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics</u>, McGraw-Hill 1950.
2. At 29° K.
3. Kirk, R. E. and Othmer, D. F., editors, <u>Encyclopedia of Chemical Technology</u>, Vol. 9, p·347.

voltages, a maximum open circuit voltage of 0.43 v was obtained at 520° C, leveling off to 0.3 v. With the cell in this condition, current was drawn giving a density of 67 A sq/ft at 1/2 open circuit voltage.

Since the above is well below a practical level, a Grade D nickel micrometallic electrode was substituted for the stainless steel one in an effort to increase current density. After elimination of the newly introduced spurious emf, an open-circuit voltage of 0.28 v was obtained at 520° C. At this point a sample of the electrolyte was taken and was found to contain about 2-4% NaH and 3-6% Na. At 0.175 v, current density was found to be 123 A/sq ft, which is greater than that with the stainless steel electrode. After further energy drain from the cell, the open circuit voltage fell to 0.22 v as the hydride content rose to 5% and the sodium content held to this same value.

These values showed only marginal promise of optimizing cell performance to obtain current density of at least 100 A/sq ft at a cell operating voltage above 0.3 v; and no further work was done with these cells.

The feasibility of a potassium hydride cell with the eutectic of the chlorides of lithium and potassium (41 mole % LiCl 59 mole % KCl) melting at 352° C was also studied, and a container made earlier with MSAR funds and shown in Fig. 5 was charged with the above eutectic and a potassium electrode holding 20 ml of liquid potassium. The usual spurious emf was found and persisted for a period of about 50 hours, including 17 hours with a hydrogen atmosphere and 5 hours with the terminals short-circuited through a Model 931 Weston Ammeter to reduce or electrochemically react out metal oxides, probably causing spurious voltages. During this time, the micrometallic filter element on the bottom of the gas electrode had become clogged and was opened only by raising the cell temperature from 370° C to 620° C and the gas pressure raised to a value of the order of 30 psi. Later it was possible to operate at 377° C. After this interval, the emf with argon was down to 0.01 v as measured on a Model 931 Weston Voltmeter. When hydrogen was introduced into the gas electrode, the emf rose to 0.23 v in 12 minutes, then declined to 0.00 v in two hours. It was suspected that the first charge of potassium had been consumed; and a new charge of 22 ml was added. The emf promptly rose to 0.20 v, then to 0.26 v after about 90 minutes when argon was substituted for the hydrogen overnight. Apparently adding the fresh charge of potassium introduced a new spurious emf; for the following morning an emf of 0.21 was measured with argon in the gas electrode. When hydrogen was introduced, the emf started to rise, reaching a value of 0.33 v after six hours. At this point, a load was put on the terminals taking only 55 A/ft^2 of gas electrode area at 0.06 v. On the following morning it was found that the cell had opened up because of excessive temperature arising from a malfunctioning controller. Because of lack of promise with this cell, no further work was done with it.

5.2.3 Electrode Studies

Electrode studies included work with reference electrodes, with double porosity gas electrodes and with possible catalytic materials and measurement of pressure drops across gas electrodes.

In order to evaluate electrode polarization effects and use of double porosity gas electrodes, a cell was assembled with a sodium electrode and two gas electrodes in the eutectic of lithium chloride-lithium fluoride. One gas electrode was of 0.062 in. thick double porosity nickel with 5 and 15 micron pores and with an area of 0.55 sq in., the other of 0.125 in. thick single porosity nickel (65 micron pores) with an area of 0.25 sq in. The sodium electrode area was 0.99 sq in. Cell temperature was held at 540° C. A peak emf of 0.62 v was observed. After the emf had fallen to 0.40 v, current was drawn for 1-1/2 hr from the larger gas electrode under a potential of 0.30 v. Results were as follows:

Time (min)	0	10	65	70	90
Current (amp)	0.52	0.50	0.50	0.48	0.48

After this loading, open circuit potential had fallen to 0.38 v. The polarization voltage or the decrease in voltage from open-circuit potential between the sodium electrode and each of the gas electrodes was now measured with current drawn from the dual porosity electrode. The change in electrode voltage under load was then noted for each electrode. The single porosity electrode showed a small decrease from the open circuit valve even though no current flowed through it.

	Current (amp)	0.31	0.50
	Current density amps/sq ft	81	131
Change in Electrode Voltage	Δ V (dual porosity electrode)	0.05	0.095
	Δ V (single porosity electrode)	0.01	0.03

With an open circuit voltage of 0.32 v, the load was placed on the single porosity electrode with the following results:

Current (amp)	0.50	0.68
Current density amps/sq ft	288	391
Δ V (single porosity)	0.22	0.28
Δ V (dual porosity)	0.03	0.05

Again, the dual porosity electrodes showed a small voltage drop even though no current passed through it.

Additional data were also taken to evaluate the effect upon current density by use of dual porosity material. With approximately equal open circuit voltages in each of the gas electrode circuits, current was drawn from the two electrodes with the results shown in Table 9.

A similar experiment was next run with two 3/4 in. diameter anodes and one 1/2 in. diameter cathode. The hydrogen electrodes were nickel micrometallic filter plates and the electrolyte was LiCl-LiF eutectic salt. Center-to-center distances were 1-1/4 in. between the anodes and 1 in. between each of the anodes and the cathode. Table 10 summarizes the results. In this table, the hydrogen electrode is designated as H, and sodium anodes as A and B.

This shows that the polarization of the gas electrode and the electrolyte determines the cell voltage drop to a large degree. In combination with the earlier results, it is seen that the gas electrode polarization makes the major contribution to overall polarization.

Because of low current densities obtained in a number of cells with lower-melting solvents, the need for catalysts became apparent. Platinum is an excellent catalyst for industrial hydrogenation, but in hydrogen at high temperature, it can disintegrate. Manufacturers' representatives have asserted that this difficulty could be avoided by cooling in an inert atmosphere after use at elevated temperatures. Consequently, a platinum electrode was handled in such a way, but no data were obtained because the electrode disintegrated in short order.

In the hope that a micrometallic nickel base would offer a good support for electroplated platinum, two such bases were plated in a "Platinex III" plating solution in accord with directions of the manufacturer, Sol-Rex Corporation.

One plated electrode was used in a cell with a sodium anode and a LiF-LiCl solvent. The open circuit voltage was 0.49 volt. An equilibrium current density of 330 A/sq ft was obtained from this cell at a potential of 0.17 v compared with 67 and 132 A/sq ft in previous work with stainless and nickel electrodes respectively. Steady-state current density at 0.30 v was 208 A/sq ft. Upon cooling the cell and subsequent inspection of the electrode, it was found that the plated micrometallic element had disintegrated, and it is not known how much platinum, if any, was on the electrode during current measurements.

While there is some indication of beneficial effect upon current density of a platinum catalyst, its mechanical strength under operating conditions is unsatisfactory. Since palladium is a catalytic material comparable to platinum and since a palladium-silver alloy is reported[1] to have good mechanical strength

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[1] Hunter, J. B., U. S. Patent 2773561, Silver Palladium Film for Separation and Purification of Hydrogen.

TABLE 9 - CURRENT OBTAINED USING DUAL AND SINGLE POROSITY MATERIALS

Dual Porosity Electrode on load, area - 0.55 sq in.			Single Porosity Electrode on load, area 0.25 sq in.		
Amps/sq ft	Load Voltage	Open Circuit Voltage	Amps/sq ft	Load Voltage	Open Circuit Voltage
39	0.30	0.332	16	0.30	0.325
114	0.22	0.325	96	0.22	0.316

TABLE 10 - TEST 1 - A-H OPEN, B-H CLOSED

B-H emf	A-H emf	B-H Current Amperes	Cathode Current Density Amps/sq ft
0.42 v	0.42 v	0	0
0.36	0.36	0.30	220
0.26	0.26	0.50	367
0.41	0.41	0	0

TEST 2 - B-H OPEN, A-H CLOSED

A-H emf	B-H emf	A-H Current Amperes	Cathode Current Density Amps/sq ft
0.43 v	0.435 v	0	0
0.375	0.38	0.30	220
0.41	0.41	0	0
0.26	0.26	0.50	367
0.39	0.39	0	0

in high temperature hydrogen, an electrode of this material was made. Because of the high rate of diffusion of hydrogen through films of this alloy and because of possibilities in zero-gravity application, the alloy was used in the film form.

The electrodes were fitted into one cell with the eutectic of the borohydrides of lithium and potassium (mp = 102° C) and into another cell with the eutectic of the chlorides of lithium, sodium, rubidium and cesium. After periods of only several days of attempted operation of these cells without significant results, the cells were opened and were found in both cases to have disintegrated gas electrodes.

Upon recommendation of the manufacturer, another run was made with the Ag-Pd alloy with special precautions to keep oxide content of the electrolyte to a minimum in an effort to avoid the disintegration. Precautions included very careful drying under vacuum just below the melting point of the electrolyte to prevent hydrolysis of the salt upon melting. Again, the electrode disintegrated rapidly in use, and further work was abandoned.

With the thought that silver content of the alloy might be responsible for disintegration, pure palladium was used in the cell with a lithium anode and a solvent of the eutectic of the chloride and fluoride of lithium. This Pd electrode disintegrated in a fashion similar to that of the alloy above.

Attempts were made to use graphite and platinized graphite as gas electrodes; but thermodynamically reversible operation could not be obtained, and in one test the electrode had disintegrated apparently through formation of alkali metal carbides. Evidence of this was obtained through evolution of acetylene upon reaction with water.

To obtain data for optimizing gas electrode structure, the pressure drop resulting from the flow of hydrogen gas and argon gas through a micrometallic filter into molten salt was measured. The micrometallic filter consisted of a 1/8 in. thick, 3/4 in. diameter, Grade D nickel micrometallic immersed 1-3/16 in. into a LiCl-KCl eutectic melt at 380° C. The pressure difference across the micrometallic filter was measured with a mercury manometer, and the hydrogen flow was measured by a low flow rate rotameter. Figs. 16 and 17 show the pressure drop results graphically.

The pressure drop can be considered to be the sum of three pressure drops. One pressure drop consists of the hydrostatic head exerted by 1-3/16 in. of molten salt. The second pressure drop consists of the pressure required to overcome the molten salt-solid nickel surface tension. The third pressure drop is the pressure drop of the hydrogen flowing through the micrometallic filter element.

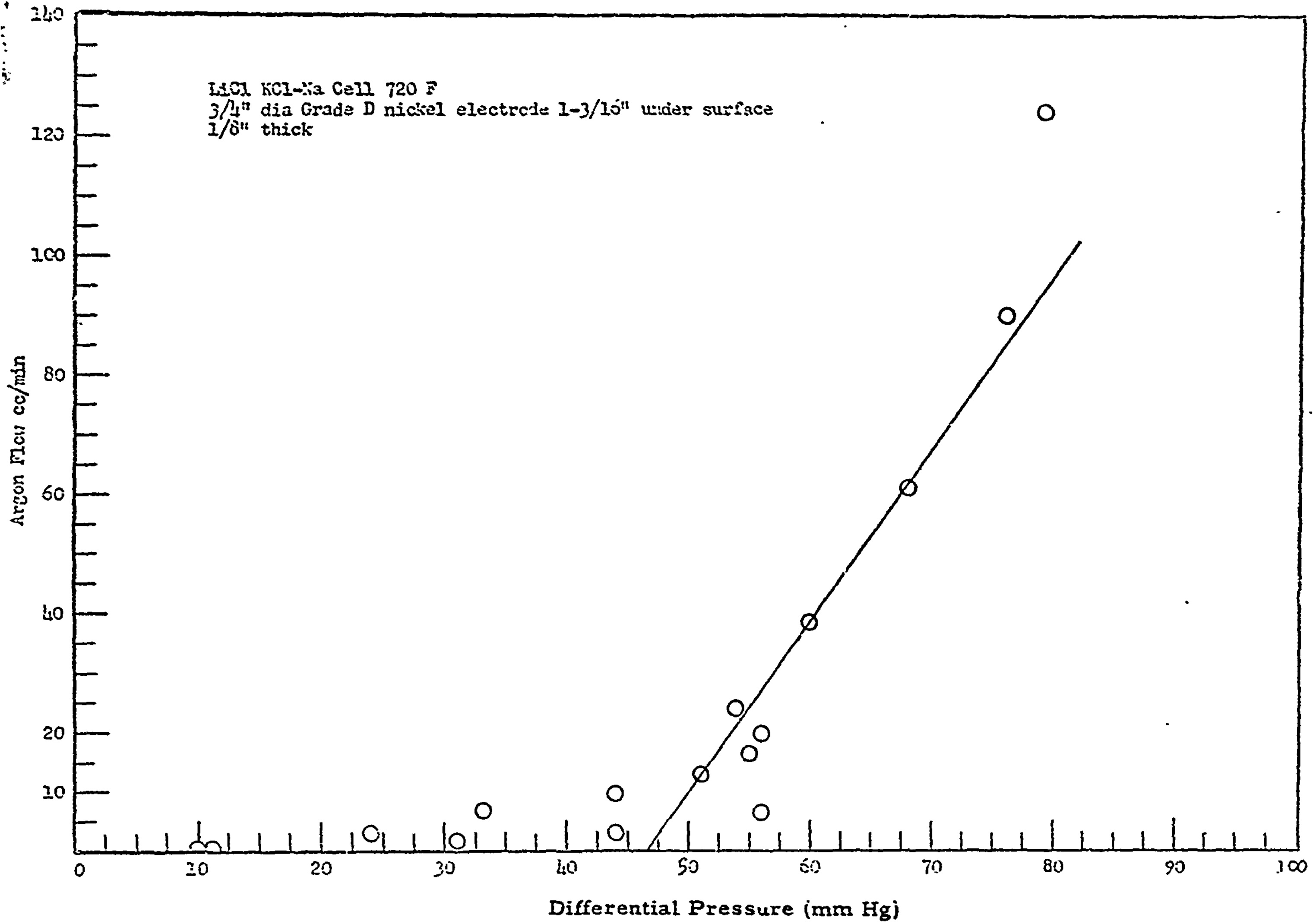

Fig. 16 - Differential Pressure Across Micrometallic Vs Argon Flow

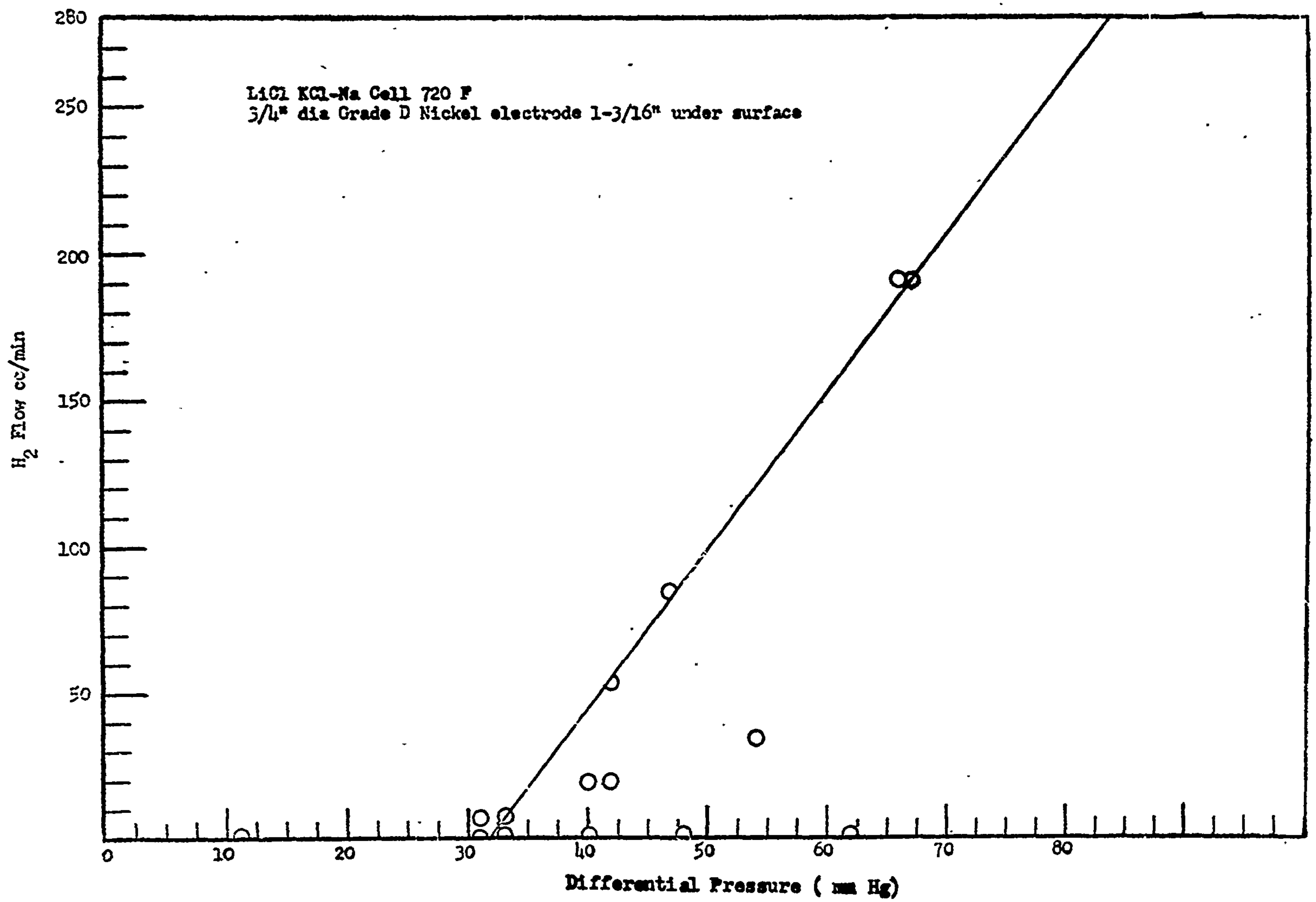

Fig. 17 - Differential Pressure Across Micrometallic Vs Hydrogen Flow

The hydrostatic head of 1-3/16 in. of molten salt is small. This pressure drop is about 4.65 mm of mercury and is small compared to the pressure drops measured in Figs. 16 and 17. The pressure drop due to surface tension is quite important. This pressure arises because the salt tends to wet the nickel and fill the pores of the micrometallic filter. In order for hydrogen to flow through the filter pores, the gas must displace liquid from the pores. The pressure required to do this will depend on the pore diameter and the hydrogen/molten salt/nickel interfacial tensions. Figs. 16 and 17 show that at zero gas flow rate with the electrode immersed in 1-3/16 in. into the melt, a pressure of 46.5 mm Hg was required for argon to displace the salt and 31.5 mm Hg was required for the hydrogen to displace the molten salt. Subtracting 4.65 mm for the hydrostatic head of the molten salt then gives 41.9 mm for the argon pressure and 26.8 mm for the hydrogen pressure.

The pressure drop due to gas flowing through the micrometallic filter can be found by measuring the slope of the lines given in Figs. 16 and 17. Since even at current densities of 450 amperes/sq ft, the gas flow rate is small, this pressure drop is small. The argon pressure drop is 0.58 psi/cu ft/min and the hydrogen pressure drop is 0.31 psi/cu ft/min across a plate with an area of 1 sq ft.

These figures can be compared with the expected pressure drops of 7.1×10^{-4} psi/cu ft/min for hydrogen and 1.98×10^{-3} psi/cu ft/min for argon.[1] The difference between the observed and the expected pressure drops is due to the effects of surface tension. Since higher pressure is required to displace the salt from the smaller pores, at low pressure differences the small pores will be sealed off with liquid and only the largest pores will be open. Comparison of the observed and expected pressure drops yields the percent of the flow area which is available. It can be seen that only 0.228% of the flow area is open for hydrogen and 0.342% for argon flow.

Use of a micrometallic plate with a constant pore size would be highly advantageous. This would give an increased current density and a reduction in the pressure drop. Since the pressure drop is quite small, this reduction would not be important. However, the increased current density would be a very significant advantage. The plate with a uniform pore size would have a significant increase in bubble sites - each pore would be releasing hydrogen bubbles. The increased number of bubbles would then give an increased effective surface area and thereby give an increased current.

Figs. 16 and 17 show some scatter at the low gas flow rates. This scatter can be attributed to a partially plugged micrometallic filter element. It takes a much higher pressure to eject molten salt from a pore after the salt has penetrated into the pore.

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[1] Micro Metallic Corporation PSS Release No. 212.

5.2.4 Dissociation Pressures

In order to determine the hydrogen pressures likely to be developed in the regenerator of a closed cycle system, a bomb was made of 3 in. Type 304 stainless steel pipe with wall thickness of 0.22 in. It was fitted with a mercury manometer and was heated in a Kanthal furnace controlled with a General Electric milli-voltmeter-type temperature controller. Temperatures were measured with a chromel-alumel thermocouple in a thermowell immersed in the melt. The bomb was charged with lithium chloride and lithium fluoride in eutectic proportions (80 wt % of the former) as described below; then with various amounts of lithium hydride, pressures determined at various temperatures.

After introduction of the fluoride and chloride salts, they were vacuum dried overnight at 200° C and a pressure of 1 mm of mercury, then just below the melting point until no more moisture was collected in a trap in the exit line. The salt was then melted under vacuum, then heated to 815° C with pumping overnight. After cooling, a quantity of Class V lithium hydride furnished by Lithium Corporation of America was introduced into the bottom of the bomb. The charge was melted under a cover atmosphere pressure and then hydrogen was bubbled through the melt to insure mixing. This apparently gave rise to dissolving of hydrogen in the melt; for an apparent decomposition pressure of 50 mm was measured at 540° C, compared with a pressure of less then 1 mm for pure hydride at this temperature. The system was then pumped off at 540° C until the hydrogen pressure held at 1 to 2 mm. There had been indications of the possibility of diffusion losses of hydrogen through the stainless steel.[1,2] Reference 1 gives the following values for diffusion of hydrogen under a pressure of 760 mm through 0.020 in. thick Type 304 stainless steel at various temperatures.

Temperature	400	500	600	700	800	900
cc (STP)/cm^2/hr/mm	0.0047	0.019	0.066	0.19	0.44	0.76

Reference 2 gives the rate at 970.9° K through 0.01 in. thick Type 347 stainless steel for various pressures of hydrogen, as follows:

Pressure (cm)	1	4	9	16	25
cc (STP)/cm^2/hr/mm	0.011	0.03	0.049	0.068	0.088

In the case in one run on the 4.2% LiH solution after 5 cycles of heating, evacuating and cooling, pressure at 1065° C fell from 625 mm to 584 mm in 44 min. To

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1. Flint, P. S., "The Diffusion of Hydrogen through Materials of Construction," KAPL-659, December 14, 1951.
2. Randall, D. and Salmon, O. N., "Diffusion Studies of Type 347 Stainless Steel to Hydrogen and Tritium," KAPL-904, March 17, 1953.

minimize these effects of pressure drop with time, readings were taken as soon as apparent equilibrium had set in, generally in 5 to 10 min. after reaching a given temperature. Good reproducibility of results were obtained both upon varying temperature upward or downward and upon successive runs. Fig. 18 shows results of two successive runs together with a curve showing the average of the two runs corrected for vapor pressure of the fused salt solvent. The correction factor was determined as the sum of the products of vapor pressure of each component[1] by its mole fraction. Corrected values for this solution, as well as for the 4.2 wt % solution correspond with products of mole fraction and decomposition pressure of pure hydride up to 850° C.[2] After the second run was made, a sample of the solution was analyzed and was found to contain 0.35% LiH by weight.

A similar set of experiments was run on a solution containing 4.2 wt % LiH. Results are shown in Fig. 19. In this case no hydrogen was introduced into the melt prior to or during mixing, which was done under argon. Mass spectrographic analysis of the gas in the decomposition vessel at room temperature at the end of the experiment revealed only a trace of argon and pure hyrdogen as the only other gas.

Calculations of effect upon emf of the hydride cell were made for hydrogen pressures developed at some attainable regeneration temperatures compared with a pressure of one atmosphere. They show that emf would be lowered by about 0.12 volt for pressure developed from the 0.35 wt % LiH solution at 1100° C and 0.07 v from the 4.2 wt % solution at 1020° C.

Because of the low melting point of the eutectic of the chlorides of lithium, sodium, rubidium and cesium (28, 3 and 39 wt per cent respectively) and of the resulting thermodynamic and material advantages of operating a galvanic cell at lower temperatures, the decomposition pressures of a solution of lithium hydride in this eutectic were determined at a number of temperatures. Results are shown in Fig. 20.

The composition of the melt was made up to be that of a solution saturated with lithium hydride at cell operating temperature, or slightly above the eutectic temperature (284-288° C). After melting and mixing of the components at elevated temperatures, at which some decomposition had occurred, the lithium hydride content was found to be 0.34% by weight, which is within the range of compositions found in cell operation.

The apparatus and procedures were generally the same as those described above. In brief, the salts were vacuum dried at temperatures from 180° C to 315° C over a period of twenty hours. Then followed leak testing,

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[1] Smithells, C. J., Metals Reference Book, p 615, Vol. II, Interscience Publishers, 1955.

[2] Hurd, D. T., Chemistry of the Hydrides, John Wiley and Sons, 1952.

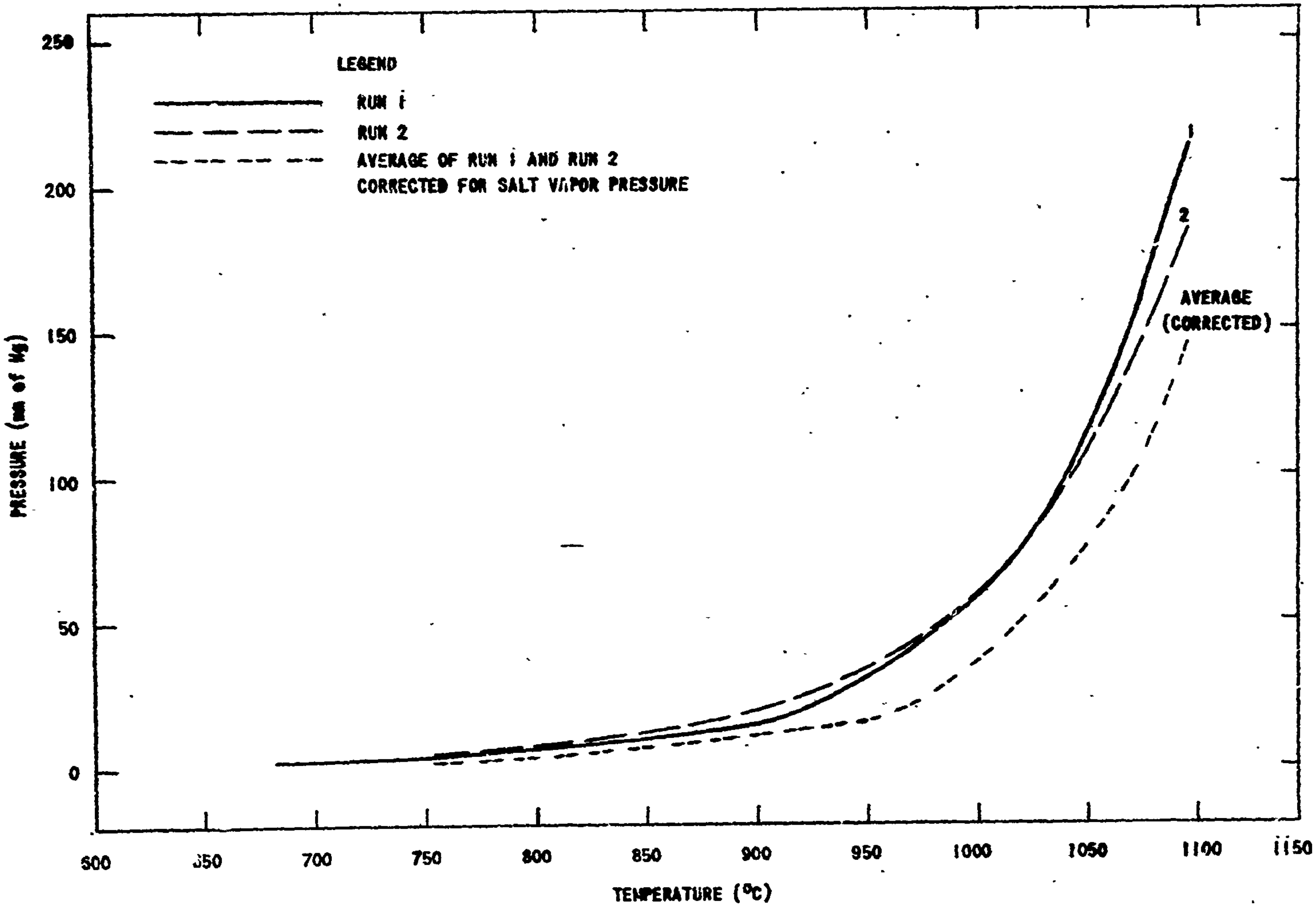

Fig. 18 — Dissociation Pressures of 0.35 wt.% LiH in LiCl-LiF Eutectic

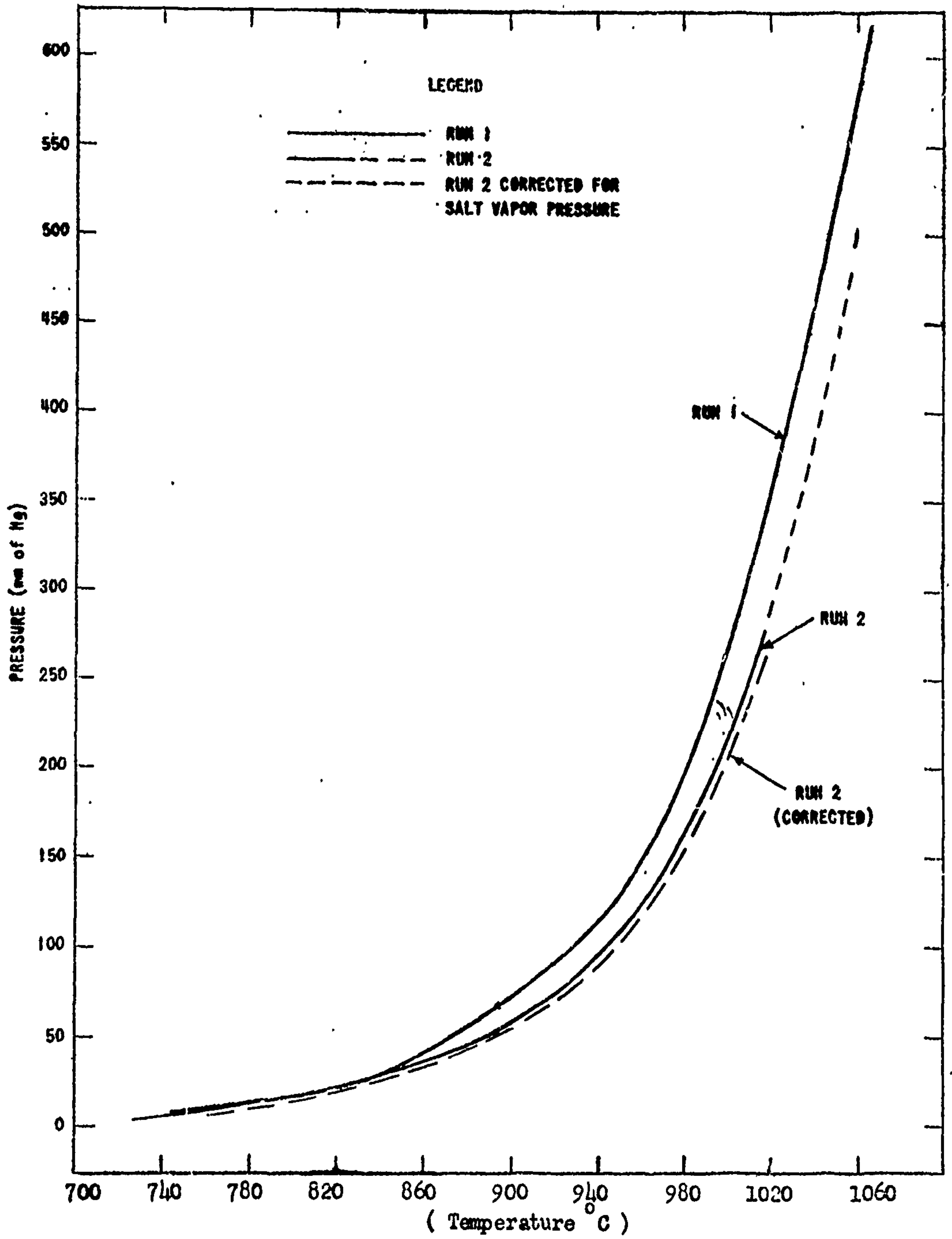

Fig. 19 Dissociation Pressure of 4.2 wt% LiH in LiCl-LiF Eutectic

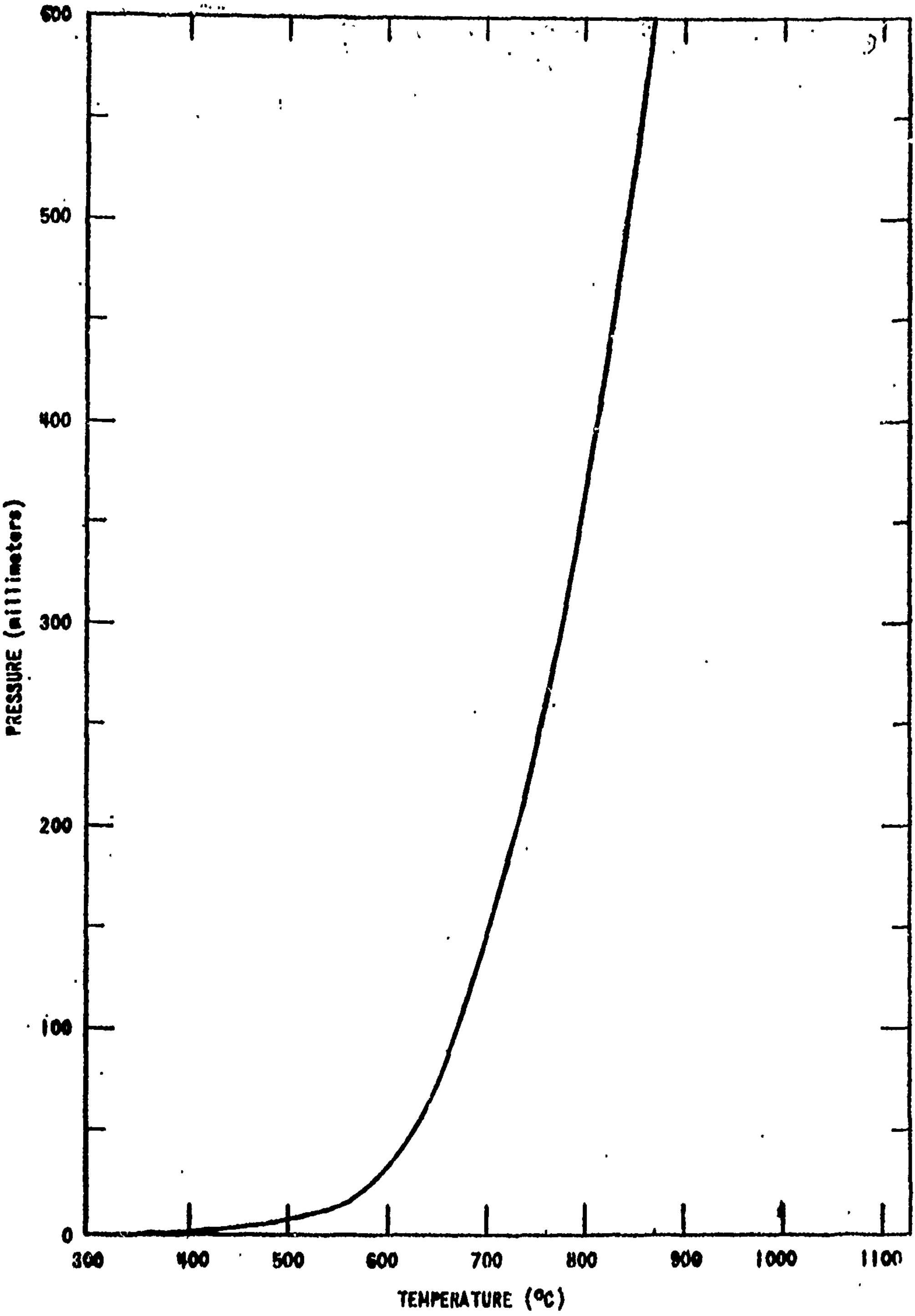

Fig.20-Dissociation Pressures of 6.9 Mole % H^- in a Quaternary Eutectic of Alkali Chlorides

cooling, addition of hydride, reheating and homogenization of the melt. A series of four consecutive pressure-versus-temperature runs were next made and gave reasonably reproducible results, the averages of which are shown in Fig. 20. These results show considerable increase in pressures over those in the LiF-LiCl eutectic given in the Third Progress Report, possibly because of the contribution of the ions other than lithium ions. For example, at 870° C, the decomposition pressure of 4.2 wt % of hydride in LiF-LiCl is 40 mm and that of 0.09 wt % in the quaternary eutectic is 580-600 mm.

The pressures are considerably lower than those reported elsewhere[1]; and several possible explanations can be advanced. One, which is hardly likely, is that differences in solvent composition (80 mole % vs 79 wt % LiCl) may be responsible.

In the results above (Fig. 19), 16 mole % (4.2 wt %) of LiH developed a pressure in the range of 60 to 70 mm at 1630° F while the pressure reported by Fuscoe et al have values of over 240 mm at this temperature for a much more dilute solution (5 mole %). These high values may be a result of the method of addition of hydride to the bomb and may be due to pressures developed by undissolved hydride. Our results are reasonably reproducible; while those of Fuscoe et al are higher at low temperatures than at higher temperatures (70 mm at 1650° C vs 80 mm at 1630° F for 20% dissociation).

Calculations of standard emf for the lithium hydride cell at various temperatures were made on the basis of thermodynamic data to assess reversibility of actual cell operation and to determine feasibility of the LiH cell.

$\Delta F^{o}{}_{T}$ was determined from the relationship:

$$\Delta F^{o}{}_{T} = \Delta H_{T} - T\Delta S^{o}{}_{T}$$

$\Delta H^{o}{}_{T}$ was determined from the relationship:

$$\Delta H^{o}{}_{T} = \Delta H^{o}\,(298) + \int_{298}^{T} \Delta Cp\, dT - \Delta H'\,(Li)$$

where H' (Li) is the heat of fusion of lithium which melts at 180° C. The value for $\int_{298}^{T} \Delta Cp\, dT$ is that of lithium hydride less half that of hydrogen and less that of lithium. The value for that of lithium hydride was determined from the area under the curve of a plot of values obtained from AEC Report Number NYO-8022, entitled "A Survey Report on Lithium

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[1] Fuscoe, J. M., et al, Regenerative Fuel Cell Investigation, WADD Technical Report 60-442.

Hydride: Supplement 1954-59," and written by Charles E. Messer and Thomas R. P. Gibb, Jr. These values are, in cal/mole-deg, 8.2 at 298° K, 11.2 at 500° K, and 13.5 at 800° K. The value H° at 298° K, which is -21.61 Kcal/mole, is that given by NBS Circular 500. Values for hydrogen and lithium were obtained from Thermodynamic Properties of the Elements by Stull and Sinke. These values for the function of lithium above its melting point include the value of the heat of fusion. Interpolations were made between nearest tabulated values in some cases.

ΔS^o_T was obtained from the relationship:

$$\Delta S^o_T = \Delta S^o_{298} - Sm\ (Li) + \int_{298}^{T} \Delta Cp\ d\ln T$$

These values were obtained from the area under the $\frac{Cp}{T}$ vs T curve for LiH, from Circular 500 values of S^o_{298} for ΔS^o_{298}, from Stull and Sinke for entropy changes of Li and H_2.

In calculating actual emf's activity coefficients were assumed to be one in the absence of any reliable data. This may be the source of considerable error, since some dimerization of certain molten salts, as well as covalency, especially of LiF [1, 2] has been reported. Standard states of LiH and Li were assumed to be pure liquid and of H_2, gas at one atmosphere. Liquid LiH was assumed because of its being in solution; and zero free energy change was assumed for the solution process of LiH.

Results of calculations for a number of temperatures are given below:

Temperature (°C)	230	502	688
E^o (V)	0.581	0.364	0.202

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1. Janz, George J., "Construction of Fused Salts," Tech. Note No. 1, ARDC Contract AF 49 (638) - 50.
2. Ibid, Tech. Note 11, August 1959.

6. CONCLUSIONS

Electrolytes

Halides of the alkali and alkaline earth metals are satisfactory electrolytes. Fluorides, chlorides and bromides are satisfactory, with iodides being less satisfactory. A low melting point eutectic of the chlorides of Cs, Rb, Li and Na had a lower open circuit voltage and current density than the LiCl-LiF eutectic. The lower current density at the hydrogen electrode is a disadvantage. The lower cell voltage is probably due to the higher activity of LiH in the salt. Experimental determinations of the partial pressure of hydrogen showed a higher vapor pressure than the LiF-LiCl eutectic. Since the higher activity will also generate a higher H_2 pressure in the regenerator, there will be little difference in voltage between a Cs, Rb eutectic and a lithium eutectic salt.

Metal Electrode

Any of the alkali or alkaline earth metals make satisfactory electrodes. Those existing as liquids at cell temperature permit the ready return of liquid to the electrode. Those metal hydrides with large ratios of hydrogen pressure to metal vapor pressure minimize the distillation of metal from the regenerator.

Hydrogen Electrodes

Both mesh and porous micrometallic electrodes are suitable. Nickel has a higher current density than stainless at the lower cell temperatures. At higher cell temperatures there is little difference - current densities are limited by the diffusion of hydride from the electrode. Platinum, palladium, palladium silver and graphite do not have reasonable lifetimes as electrodes. Apparently, the liquid metal dissolved in the salt attacks these electrodes. Dual porosity electrodes gave slightly higher open circuit voltages, but approximately the same cell voltage drop at equivalent cell currents.

Cell Voltage

Thermodynamic calculations predict an open circuit voltage of 0.25 to 0.35 V will be obtainable on regenerative operation of the cell.

Cell Current

A current density of 200 amps per sq ft of electrode when the cell has a 0.3 volt drop is achievable.

7. RECOMMENDATIONS FOR FUTURE WORK

The hydrogen electrode is the largest source of cell polarization and therefore presents the largest restriction to cell currents. Various catalysts should be examined in an effort to increase current densities, particularly at the lower temperatures. For the non-bubbling micrometallic electrodes, a suitable "wetproofing" coating would be desirable. This would prevent molten salt from entering the pores, would give greater electrode contact, and would decrease the criticalness of the pressure gradient across the electrode.

The phase diagrams for the molten salt-liquid metal-metal hydride systems should be determined. The solubilities of metal in salt and salt in metal should be noted.

The eutectic composition of LiCl, LiF and LiBr system should be determined.

A salt circulating regenerative cell should be constructed to show regenerative operation of the cell. The returning salt line should be cooled to cell temperature to precipitate excess dissolved liquid metal. Sufficient holdup volume should be provided so that the above precipitation step can occur fully. Control of the salt flow rate should be such that an excessive flow of salt through the cell is prevented. Lithium should be the active metal to prevent the distillation of metal from the regenerator.

The hydrogen electrode for the cell should have provisions such that any inert gas which accumulates at the electrode can be removed.

Volt-ampere data should be taken to show the electrical performance of the unit. All streams should be monitored for composition and velocity. Salt and liquid metal compositions in the cell proper and the regenerator should be determined.

8. IDENTIFICATION OF PERSONNEL

Thomas A. Ciarlariello--Technical Advisor

Mr. Ciarlariello received his B. S. degree in Chemical Engineering from the University of Texas in 1951. He graduated from ORSORT in 1957. From 1951 to 1953 he was a Design Engineer for NACA. He was then employed as a Shift Foreman for B. F. Goodrich Chemical Company in 1953. He came to MSA Research Corporation in 1953 and is presently employed as Technical Advisor.

John C. King--Associate Chemist

Mr. King received his B. S. degree in Education at Clarion State Teachers College in 1952. He received a G. E. Science Fellowship at Union College in 1953 and was a Science Teacher from 1953 to 1955. He has been an Associate Chemist with MSA Research Corporation since 1955. He has done much of the assembly work and testing leading to reduction to practice of the thermally regenerative galvanic system.

Dr. J. W. Mausteller--Associate Director-Research

Dr. Mausteller received his B. S. degree in Chemical Engineering from Bucknell in 1944; his M. S. and Ph. D. degrees were obtained from Penn State University in Physical Chemistry in 1949 and 1951 respectively. He was first employed as a Chemist by E. I. duPont De Nemours and Company, 1944 to 1947; then as a Research Assistant in the fluorine labs of Penn State University from 1947 to 1950. In 1950 Dr. Mausteller came to Callery Chemical Company as a Research Chemist and then as an Engineer in 1951. He was a Project Engineer from 1952 to 1955. From 1955 to 1957 he was a supervisor for Mine Safety Appliances Company. From 1957 to 1960 Dr. Mausteller has been Research Manager for MSA Research, and in 1961 he was appointed to Associate Director of Research, Research and Engineering Division, Mine Safety Appliances Company.

John B. McDonough--Test Engineer

Mr. McDonough received his B. S. degree in Science from Pennsylvania State University in 1954. He received a B. S. in Chemical Engineering from the same university in 1955. At the present time he is attending Carnegie Institute of Technology doing graduate study in Chemical Engineering under an MSA scholarship. He was employed by Standard Oil of Indiana from 1955-1956. He was employed by the Allegheny County Sanitary Authority for a period during 1956 and then in November 1956 as a Test Engineer by MSA Research Corporation.

Robert E. Shearer--Research Chemist

Mr. Shearer received his A. B. degree (cum laude) from Marietta College in 1938. He then did graduate work at Johns Hopkins University 1938 to 1939, and at West Virginia University 1939 to 1941. In 1954 he attended the Oak Ridge Institute of Nuclear Studies. He was employed as a Research Chemist and later as Supervisor at Union Switch and Signal from 1941 to 1957. Since 1957 Mr. Shearer has been employed as a Research Chemist by MSA Research Corporation. He is co-inventor with Dr. Werner of the thermally regenerative galvanic system.

Samuel J. Veccharella--Associate Chemist

Mr. Veccharella received his B. S. degree in Chemistry from Grove City College in 1958. During his summer vacations he worked as a technician for Callery Chemical Company; and he attended the Graduate School of Chemistry at the University of Pittsburgh during the academic year 1958-1959. In September 1959 he was employed as an Associate Chemist by MSA Research Corporation.

Dr. R. C. Werner--Associate Director-Engineering

Dr. Werner received his B. S. in Chemical Engineering and Engineering Math from University of Michigan in 1938. He received his M. S. and Ph. D. in Chemical Engineering from the University of Michigan in 1939 and 1943. He was employed by the Blaw Knox Company from 1942 to 1944. Dr. Werner joined Mine Safety Appliances Company in 1944 as the Project Supervisor and later was made Supervisor of Development Engineering. From 1957 to 1960 he was Operations Manager and Associate Director of Research. In 1961 he was appointed to Associate Director-Engineering in Research and Engineering Division, Mine Safety Appliances Company. Dr. Werner is responsible for the original concept of a thermally regenerative galvanic cell and will be monitoring all phases of the contract.

9. DISTRIBUTION OF HOURS

T. A. Ciarlariello, Technical Advisor	466
E. C. King, Project Supervisor	182
J. C. King, Associate Chemist	1,331
J. B. McDonough, Test Engineer	1,478
J. W. Mausteller, Associate Director Research	61
R. E. Shearer, Research Chemist	780
S. J. Veccharella, Associate Chemist	1,474
R. C. Werner, Associate Director Engineering	44
Miscellaneous Salary Hours	595
Hourly Personnel	4,816
TOTAL	11,227

10. APPENDIX

Determination of Alkali Metals in the Chloride Eutectic[1]

The method used to determine the relative quantities of the four alkali metals in the quaternary eutectic of their chlorides is one used by San Antonio Chemicals, Inc., in their analysis of "Alkarb". It is done by the use of a Beckman model DU spectrophotometer. The procedure given below was modified at MSA Research by elimination of the step involving the determination of potassium, which was not present in the eutectic, and by use of a hydrogen-oxygen torch in place of the oxygen-acetylene burner to reduce background.

Procedure

Preparation of Sample - Weigh 0.5000 grams of sample and place in a 400 ml beaker. Add approximately 100 ml of distilled water and several drops of methyl orange indicator. Cover the beaker with a watch glass and acidify with hydrochloric acid. Boil to remove CO_2, cool to room temperature and transfer to a 250 ml volumetric flask. Dilute to the mark and mix thoroughly.

Standard Solutions - Discussion

Standard solutions for flame spectrophotometric comparison are prepared by diluting appropriate volumes of stock solutions which have accurately known concentrations of pure salts of the individual elements. The following stock solutions are used:

potassium stock solution	0.0100 gm	K_2O per ml
rubidium stock solution	0.0100 gm	Rb_2O per ml
cesium stock solution	0.0010 gm	Cs_2O per ml
sodium stock solution	0.0010 gm	Na_2O per ml
lithium stock solution	0.0010 gm	Li_2O per ml

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[1] Private Communications - San Antonio Chemicals Incorporated.

In making up the stock solutions, the following salts and conversion factors are used:

1.584 gm KCl = 1.00 gm K_2O
1.235 gm Rb_2CO_3 = 1.00 gm Rb_2O
1.195 gm $CsCl$ = 1.00 gm Cs_2O
1.886 gm $NaCl$ = 1.00 gm Na_2O
2.473 gm $LiCO$ = 1.00 gm Li_2O

Note: Acidify all carbonates with hydrochloric acid before diluting to volume.

Note: Pure rubidium carbonate can be purchased from DeRewall International Rare Metals Corporation, Philadelphia, Pennsylvania.

In using the flame spectrophotometer for quantitative analysis, the preparation of accurate standard solutions is of prime importance since all results are obtained by comparison of the sample to the standards.

The alkali metals influence each other in their reactions in the spectrophotometer flame. For this reason, all standards must contain all of the alkali metals in very nearly the same concentration as the sample.

Standard Solutions-Preparation

Three standard solutions are required for the determination of each element. These are called "high standard", "low standard", and "middle standard". The middle standard should be near the sample composition with respect to the element to be determined. The high standard must contain more of the element sought than does the sample, and the low standard must have a lower concentration than the sample.

The elements must be determined in the following order: K_2O, Rb_2O, Cs_2O, Na_2O, and Li_2O. Make up the middle K_2O standard by adding together the correct volumes of stock solutions to make a synthetic 0.5000 gm sample of the following typical Alkarb composition.

K_2O	48.0%
Rb_2O	18.0%
Cs_2O	1.5%
Na_2O	1.8%
Li_2O	0.7%

This will require the following volumes of stock solutions, which are diluted to 250 ml and mixed thoroughly in a volumetric flask:

K_2O	stock solution	24.0 ml
Rb_2O	stock solution	9.0 ml
Cs_2O	stock solution	7.5 ml
Na_2O	stock solution	9.0 ml
Li_2O	stock solution	3.5 ml

The high K_2O standard is made up to contain 0.025 gm more K_2O (2.50 ml of K_2O stock solution) than the middle standard, and the low K_2O standard contains 0.025 gm less K_2O than the middle standard. Both high and low standards contain the same quantities of the order alkalies as the middle standard, and are diluted to 250 ml in volumetric flasks.

The K_2O must be determined according to the procedure outlined under "Flame Spectrophotometric Technique" before making the rubidium standards.

In making the three rubidium standards, substitute the determined percent K_2O for the originally assumed value. This practice of substituting the correct value is followed with each succeeding element as it is determined. Thus the standards for the elements in lower concentration (where the effect of inaccurate standards would be greater) will be as precise as possible.

Tabulated below are the differences in percent between the three standards for each of the elements yet to be determined. The tabulated values are based upon 0.5000 gm of sample and all standards are diluted to 250 ml in volumetric flasks.

Composition of Standards

Standard	High Standard (%)	Middle Standard (%)	Low Standard (%)
Rb_2O	21.0	18.0	15.0
Cs_2O	2.0	1.5	1.0
Na_2O	2.3	1.8	1.3
Li_2O	1.2	0.7	0.2

Flame Spectrophotometer Technique

Details of the technique for making flame spectrophotometer comparisons are given below. These apply only to the Beckman Model DU instrument equipped with an oxygen-acetylene burner.

The spectrophotometer should be turned on to "warm up" for 20 minutes before it is used. The exact wave length setting must be located by placing a dilute solution of the element under the capillary of the lighted burner, and slowly rotating the wave length dial until maximum intensity is obtained. Having thus located the correct setting, the wave length dial must not be moved again during subsequent manipulations with the given element.

Measure the radiation intensity of element from the three standards and the sample solution, reading one after the other until five readings have been taken for each of the solutions. Experimental technique and instrument stability should be such that the total variation in the readings, for any one of the solutions, will not exceed one scale division. The average of the five readings for each standard is plotted on graph paper vs the corresponding percent of the element. Draw a smooth curve through the points to form the calibration curve. The average of the sample readings is plotted on the curve and the percent of the element is read from the graph.

It is necessary to plot a new calibration curve for each sample since burner characteristics instrument settings cannot be duplicated from day to day.

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During this contract, regenerative cells were built and tested for various periods of time. The major difficulties noted were the plugging of the circulating salt lines, the low dissociation pressure of LiH in dilute solutions, and an electric cell-shorting effect arising after long operation.

Various molten salt electrolytes were tested. Low melting point eutectic salts containing Na, Rb, Cs, K, and Li were found. Fluorides, bromides, and chlorides were found to be the best electrolytes. Borohydrides and iodides were not satisfactory.

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