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ARF 3182-7  
(Quarterly No. 6)

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

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CHEMICAL CONVERSION OF WASTE HEAT  
TO ELECTRICAL ENERGY

28 May 1962

Prepared under Navy, Bureau of Naval Weapons

Contract NOw 60-0760-c

Report No. ARF 3812-7  
(Quarterly No. 6)

1 October through 31 December 1961

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Chicago 16, Illinois

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## ABSTRACT

Chemical and electrochemical reactions are being studied for converting heat to electrical energy. Project achievements include screening of inorganic oxides, halides, and hydrides for suitable chemical systems, selection of several promising systems, and operation of a complete system. Attributes of the chemical conversion method are high conversion efficiencies and power densities and a relatively low weight-to-power ratio. Cited as possible with present technology are conversion efficiencies above 50%, a power density of 15 kw/ft<sup>3</sup>, and weight ratios of 20 lb/kw. None of these are considered limiting values.

Current work is devoted to the production of breadboard models of two systems. One complete system, based on chlorides of antimony, has been operated on a very small scale. Attributes of this system are simplicity of thermal regeneration, an operating temperature range between 300 and 600° K, conversion efficiencies above 15%, and moderate power density.

The higher power densities have been computed for a system based on chlorides of tellurium and copper. Stepwise operation of all phases has been accomplished. An integrated unit did not function properly, indicating need for further engineering. This system has highly favorable galvanic cell characteristics, but regeneration is more difficult than for the antimony chlorides.

Supporting studies reported include thermal decomposition of tellurium tetrachloride (TeCl<sub>4</sub>) and of antimony pentachloride (SbCl<sub>5</sub>), vapor pressure of melts of aluminum chloride (AlCl<sub>3</sub>) with cupric chloride (CuCl<sub>2</sub>) and with cuprous chloride (CuCl), and corrosion studies in SbCl<sub>5</sub>.

Recommendations for continuing work center on production of an operating system of several hundred watts capacity and on the required supporting studies. Progress with the development is concluded to be very promising.

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# CHEMICAL CONVERSION OF WASTE HEAT TO ELECTRICAL ENERGY

## I. INTRODUCTION

At the initiation of the present contract, converting heat to electrical energy by means of chemical and electrochemical reactions appeared to afford advantages not apparent in other conversion methods. During the past eighteen-month period of the contract the project has demonstrated that these advantages exist and can be achieved within the limits of present technology. This, the sixth quarterly progress report, presents a summary of project achievements followed by a more detailed reporting of progress during the quarter, October 1 to December 31, 1961.

Several aspects of the project have been unique. For example, the time schedule of planned achievements required no significant alterations. Thus systems primarily of solids were investigated in the initial six months, systems primarily of liquids in the second six months; the third six-month period was devoted to development of selected systems. Another unique aspect has been the predominance of positive factors, those favoring the chemical conversion methods, encountered throughout the program. These range from such fundamental factors as limiting conversion efficiency to the more practical or economically advantageous factors concerning availability and cost of chemicals. High purity of chemicals is absolutely not a necessity. Present indications are that commercially available chemicals and materials of construction will suffice for all components except the electrolyte. This latter component seems achievable within the range of current manufacturing equipment and techniques with commercial materials.

We believe the project has achieved the primary goal of selecting optimum systems for conversion of heat, preferably at three temperature

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ranges. Completion of a breadboard model to demonstrate technical feasibility was accomplished as early as the fifth quarter (Report No. ARF 3182-6, pages 18-21). However, project personnel are not satisfied with the scale of this system and have pushed the development of the systems picture in Figure 1 and 2. Both systems have been useful in disclosing factors requiring further development and are modified with each experiment as these developments are advanced. Progress is also being made in the development of multicell systems with emphasis jointly placed on power density, power-to-weight ratio, and potential manufacturing techniques.

Insight into future possibilities of chemical conversion of heat to electricity is now possible. It is conservative to state that the chemical conversion method offers equal or greater promise than thermoelectric, thermionic, photoelectric, or magneto hydrodynamic methods of conversion.

## II. SUMMARY OF PROJECT ACHIEVEMENTS

Completed during the project were: (1) a review of simple chemicals for suitable properties, (2) testing of the most promising chemicals both for electrochemical and thermochemical attributes, (3) selection of those chemicals most suitable for further development, and (4) construction of several "bread-board" systems proving feasibility of the method. Progress reports, technical in nature, have reviewed these developments, and one scientific report was prepared, Report No. ARF 3182-5, "Thermochemical and Thermodynamic Data on Selected Compounds for the Chemical Conversion of Waste Heat to Electrical Energy," so that this useful information is available to other agencies of the Department of Defense.

The review of simple chemicals was an extensive enterprise, since the required information is not assembled anywhere in the literature, and

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**Figure 1**  
**TELLURIUM-COPPER CHLORIDE INTEGRATED CONVERSION SYSTEM**

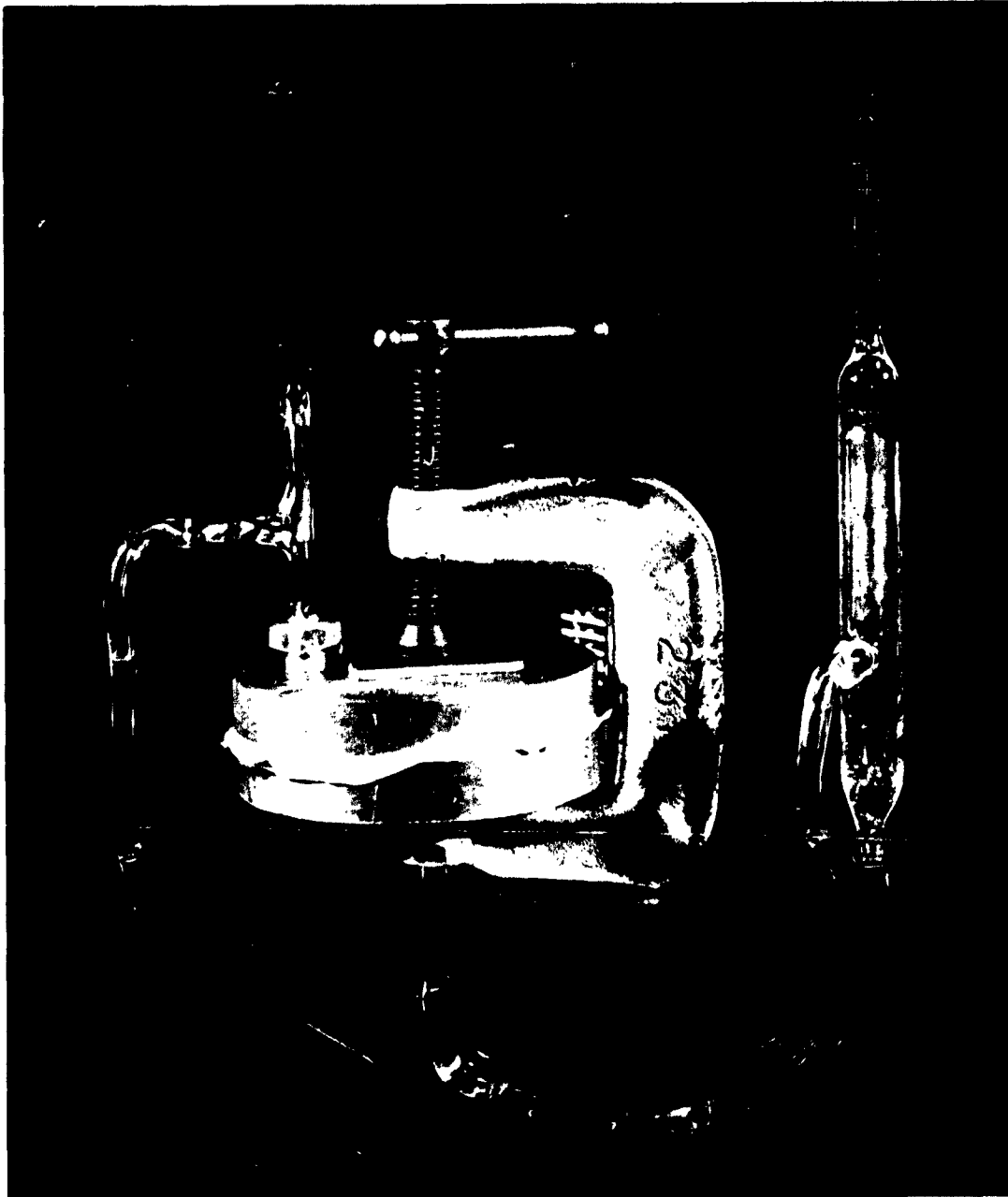
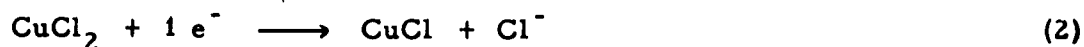
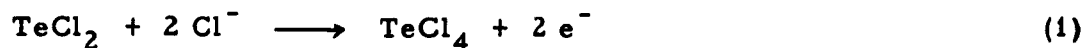


Figure 2

ARSENIC-ANTIMONY CHLORIDE INTEGRATED CONVERSION SYSTEM

only a minor portion of published thermodynamic data has the advantage of experimental origins. Methods adopted allowed selection of several systems that would otherwise be overlooked. The tellurium chloride anode system, Eq (1), is one example of this productivity, and the copper chloride cathode system, Eq (2), is another.



According to previously published data these two systems should operate in reverse. Table 1 contains a list of chemical systems that appear suitable for thermal regeneration.

Since the ultimate product, electrical energy, is obtained from a galvanic cell (battery), the electrochemical properties of the chemicals are of equal importance to their suitability for thermal regeneration. Molten materials, which also have the desirable property of easy transference, are usually better ionic conductors than solids. However, many of the chemicals suitable for thermal regeneration are very poor ionic conductors, even in the molten state. Some examples are the antimony chlorides,  $\text{SbCl}_5$ , and  $\text{SbCl}_3$ ; the higher chlorides of tin, copper, and tellurium,  $\text{SnCl}_4$ ,  $\text{CuCl}_2$ , and  $\text{TeCl}_4$ , respectively; and even aluminum chloride,  $\text{AlCl}_3$ . In this little studied field the project was able to develop techniques to augment the ionic conductivities and also to lower the temperature limit for molten systems. These factors not only allow greater current and power densities, but also permit very significant increases in conversion efficiency.

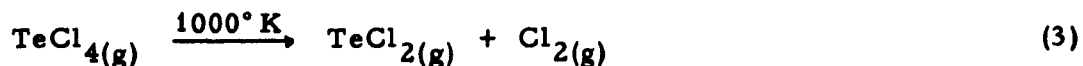
This attention to modification of physical properties by addition of a second or third component also makes possible separation of the products of

Table 1

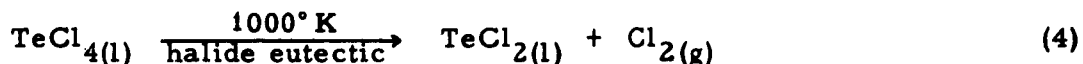
## LOW-MELTING COMPOUNDS WHICH CAN BE THERMALLY REGENERATED

Compound Stable at Low Temperature			Reversal Temperature, °K	Compound Stable at High Temperature		
Name	M. P., °K	B. P., °K		Name	M. P., °K	B. P., °K
SbCl <sub>5</sub>	275	412	640	SbCl <sub>3</sub>	346	495
SbBr <sub>5</sub>	-	(500)	(500)	SbBr <sub>3</sub>	369	552
SbI <sub>5</sub>	351	673	(700)	SbI <sub>3</sub>	439	673
BiCl <sub>4</sub>	497	(645)	(490)	BiCl <sub>3</sub>	503	719
BiBr <sub>3</sub>	490	725	(1700)	BiBr	(350)	(1100)
BiI <sub>3</sub>	sub.	711	(900)	BiI	(500)	(1200)
CuCl <sub>2</sub>	770	(1100)	920	CuCl	694	1638
CuBr <sub>2</sub>	(740)	(1050)	(580)	CuBr	761	1591
CrCl <sub>3</sub>	1218	~1500	1195	CrCl <sub>4</sub>	--	(435)
CrBr <sub>3</sub>	sub.	(1100)	(1100)	CrBr <sub>2</sub>	1115	(1400)
CrI <sub>3</sub>	sub.	(1100)	(600)	CrI <sub>2</sub>	1066	(1100)
GeCl <sub>4</sub>	--	357	(1600)	GeCl <sub>2</sub>	(400)	(975)
GeBr <sub>4</sub>	299	462	(1700)	GeBr <sub>2</sub>	395	(950)
GeI <sub>4</sub>	419	650	(1100)	GeI <sub>2</sub>	(700)	(900)
InCl <sub>3</sub>	sub.	771	(1700)	InCl <sub>2</sub>	508	758
MoF <sub>6</sub>	-	309	(1500)	MoF <sub>5</sub>	(350)	500
MoCl <sub>5</sub>	466	540	(1500)	MoCl <sub>4</sub>	590	700
MoBr <sub>5</sub>	(400)	(600)	(780)	MoBr <sub>4</sub>	(610)	(620)
MoI <sub>4</sub>	(690)	(695)	(650)	MoI <sub>2</sub>	(1000)	(1200)
PCl <sub>5</sub>	433	439	590	PCl <sub>3</sub>	161	348
PBr <sub>5</sub>	sub.	379	390	PBr <sub>3</sub>	233	447
P <sub>2</sub> I <sub>4</sub>	398	(600)	520	PI <sub>3</sub>	334	503
TeCl <sub>4</sub>	496	662	(850)	TeCl <sub>2</sub>	481	599
TeBr <sub>4</sub>	653	693	(400)	TeBr <sub>2</sub>	482	611
SnCl <sub>4</sub>	243	387	(1980)	SnCl <sub>2</sub>	520	896
SnBr <sub>4</sub>	303	480	(1820)	SnBr <sub>2</sub>	505	893
SnI <sub>4</sub>	418	614	(1360)	SnI <sub>2</sub>	593	993
WCl <sub>6</sub>	547	619	(700)	(WCl <sub>5</sub> ) <sub>2</sub>	(g)	-
			(1500)	WCl <sub>4</sub>	sub.	779
WBr <sub>5</sub>	548	605	(560)	WBr <sub>2</sub>	(1000)	(1500)
WI <sub>4</sub>	sub.	690	(530)	WI <sub>2</sub>	(1000)	(1260)
UCl <sub>6</sub>	452	550	600	UCl <sub>5</sub>	560	690
			1840	UCl <sub>4</sub>	863	1060
Sb <sub>2</sub> O <sub>5</sub>	>800	--	900	Sb <sub>2</sub> O <sub>4</sub>	~1400	--
			1000	Sb <sub>2</sub> O <sub>3</sub>	856	929
PbO <sub>2</sub>	>1000	--	515	Pb <sub>3</sub> O <sub>4</sub>	~1000	--
			790	PbO	1745	--
MnO <sub>2</sub>	(1445)	--	665	Mn <sub>2</sub> O <sub>3</sub>	1620	--
			1800	MnO	2058	-
Ag <sub>2</sub> O	~500	--	460	Ag	1234	2475
Tl <sub>2</sub> O <sub>3</sub>	(990)	--	910	Tl <sub>2</sub> O	(573)	773

thermal regeneration. An example here is the promising tellurium chloride system:



where the subscript (g) indicates the physical state, gas. Combining a eutectic halide salt with this system in effect converts the physical states as follows:



where the subscript (l) indicates the liquid state. This development is extremely important to the feasibility of the chemical method of energy conversion.

To summarize, modification of electrical and physical properties by addition of a second or third component has allowed the project to: (1) increase current and power densities, (2) reduce galvanic cell operating temperature, thus increasing conversion efficiency, and (3) separate gaseous products of thermal regeneration in a feasible manner. Several of these techniques are unique to the literature.

The chemical systems that have been selected for development are outlined in Table 2 in order of increasing temperature range. Emphasis was placed on the development of these systems during June and July of 1961. The results are reported in part in Report No. ARF 3182-6 (Quarterly No. 5). Highlights of this report are the galvanic cell studies that ascertained the concentration factors controlling cell emf (and therefore available energy), the exploratory work with large cells, and the operation of several completely integrated systems based primarily on antimony chlorides (system 1 in Table 2). This development work has continued, being concentrated on the

Table 2

**CHEMICAL SYSTEMS FOR THE CONVERSION OF HEAT  
TO ELECTRICAL ENERGY**

System	Approximate Temp. Range, °K	Principle Chemical Component		Allowable Operating Conversion Efficiency, %
		Cathode	Anode	
1	300 - 500	AsCl <sub>5</sub> or SbCl <sub>5</sub>	SbCl <sub>3</sub>	15 - 20
2	450 - 1000	CuCl <sub>2</sub> or SbCl <sub>5</sub>	TeCl <sub>2</sub>	40 - 50
3	450 - 1000	HgCl <sub>2</sub>	Hg	40 - 50
4	450 - 2000	CuCl <sub>2</sub> or SbCl <sub>5</sub>	SnCl <sub>2</sub>	50 - 60

antimony system (No. 1) and the tellurium system (No. 2). Figures 1 and 2 are photographs of integrated systems currently in development. Differences in melting points and vapor pressures between anode and cathode systems have limited the success of the former system. The latter, with modifications, has operated, but not at expected current densities. Note that these systems combine a metal-enclosed galvanic cell with glass-enclosed regeneration systems. The latter material permits visual observation of the processes, considered useful to the development but not necessary from the materials standpoint.

Figure 3 is a photograph of die components for molding a multicell system. Progress with this method of assembly is considered extremely promising. Laminations permitting assembly of 10 cells have been prepared and tested to 87 psi for leakage with carbon tetrachloride,  $\text{CCl}_4$ . Success in the molding operation has led to plans to pot a complete assembly of 10 cells as a farther simplification and to reduce possibilities of leakage. A detailed design study based on this method of assembly for the tellurium chloride-copper chloride system (No. 2) gives the following parameters for the multicell, calculated from experimental data:

Nominal dimensions	12-3/4 in. in diameter, 1 ft in length
Number of cells	160
Output under load (cells in series)	96 volts
Output	15 kw
Total weight	221 lb

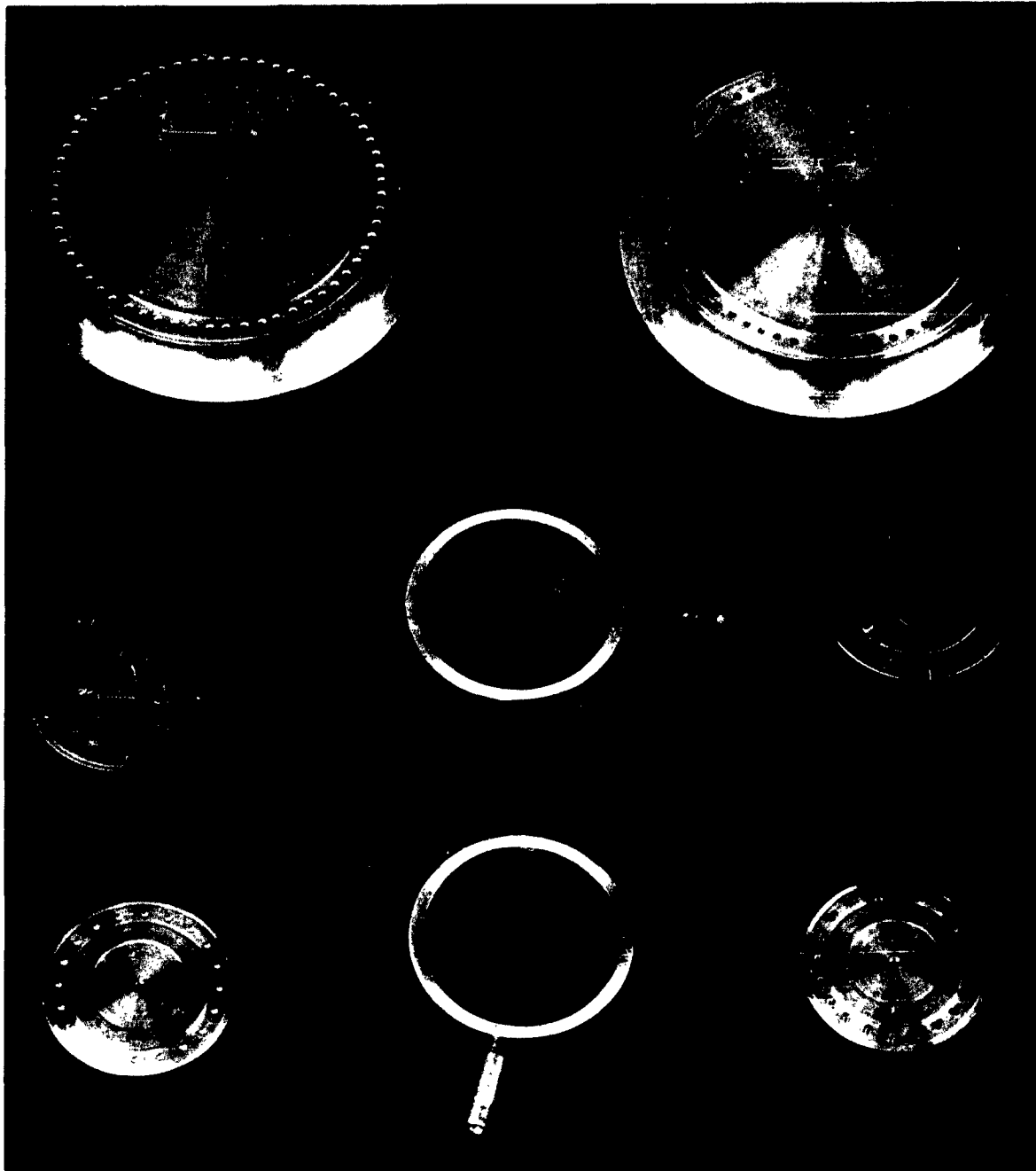


Figure 3

DIE COMPONENTS FOR A MULTICELL SYSTEM

The distribution of weight by components is as follows:

<u>Component</u>	<u>Percent of Cell Weight</u>
Anode liquid	44.2
Cathode liquid	15.0
Electrolyte diaphragm (saturated)	6.1
Insulation liner	3.0
Electrical conductors	16.2
Metal container	15.5

This multicell arrangement requires a heat input of 2200 Btu/min and a single thermal regenerator capable of accepting the  $\text{TeCl}_4$  at the rate of 0.42 gal/min. Present indications are that this unit can be approximately three inches in diameter and three feet in length; however, the actual configuration necessarily depends upon the heat source. A power density of 15 kw/cu ft and a weight-to-power ratio of less than 20 lb/kw are predicted for this integrated system.

Several recent advances associated with material studies for the large galvanic cells are responsible for the progress with the multicell system. Tantalum, gold, Monel, and some other metals have been found useful as electrodes for various anode and cathode liquids. Nickel, early thought promising for the antimony systems, develops an impervious layer. A specially prepared Teflon diaphragm is showing promise as the electrolyte support, and the moldable Teflon 100 appears useful as an insulating material or as a potting material, when loaded with glass fiber. A number of metals have also been tested for construction of the regenerators; nickel and tantalum show promise.

### III. EXPERIMENTAL PROGRAM

The experimental program during the present report period was concerned almost exclusively with the breadboard models of the tellurium-

copper chloride and the arsenic-antimony chloride systems shown in Figures 1 and 2, respectively. Design and construction of these systems required a number of support programs, each of which is described with the parent system.

#### A. Tellurium-Copper Chloride System

The tellurium-copper chloride system was selected for final development because of favorable galvanic cell performance and regeneration characteristics, and probable high conversion efficiency. Since previously published data for chlorides of tellurium and copper are not reliable and could not be used in breadboard model design, an attempt was made in this program to determine data on both systems. In the case of tellurium chlorides, thermochemical data were sought as a means of accurately computing probable operating efficiencies. With the copper chlorides, vapor pressure data were needed for the system in aluminum chloride melts. Finally, experiments were conducted with scaled-up galvanic cells.

##### 1. Tellurium Chlorides

Report No. ARF 3182-6 described experiments undertaken to study the thermal decomposition of  $\text{TeCl}_4$  and the recovery of  $\text{TeCl}_2$  and  $\text{Cl}_2$ . This work directed toward the determination of a precise equilibrium constant,  $K_p$ , was discontinued in favor of more direct measurements of decomposition temperatures and separations of gaseous species under nonequilibrium conditions.

The basic design of the apparatus used in the dissociation experiments is shown in Figure 4. Experimental procedures include means for determining the amount of  $\text{TeCl}_4$  vapor passed through the dissociating chamber (by the difference in the weight of the test tube containing the sample of  $\text{TeCl}_4$  before and after each run), collecting the  $\text{TeCl}_2$  solid deposits for chemical analysis,

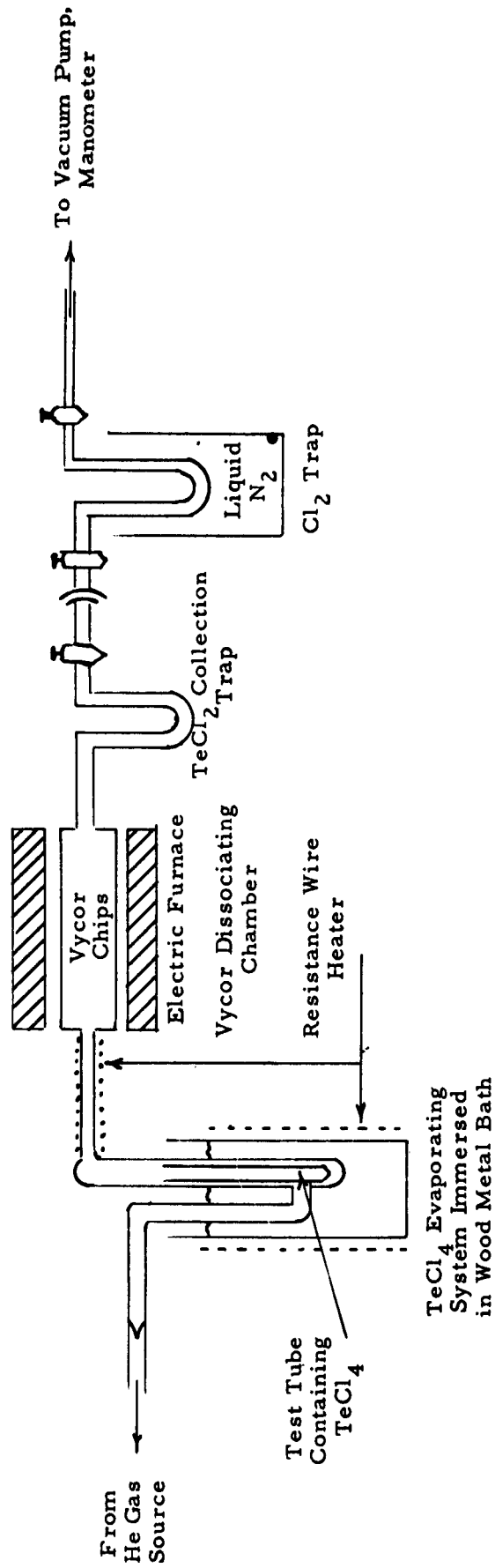


Figure 4

APPARATUS FOR STUDYING DISSOCIATION OF TELLURIUM TETRACHLORIDE

and quantitatively measuring the yield of  $\text{Cl}_2$  trapped in liquid nitrogen as a result of the dissociation process.

The dissociation experiments are summarized in Table 3. The data show that appreciable dissociation of  $\text{TeCl}_4$  vapor occurs under the conditions of both experiments and also indicate that lower decomposition temperatures may be possible. Chemical analyses of the brown-black deposit in the  $\text{TeCl}_2$  collection tube were inconclusive. From total Te and Cl analyses, a formula weight of  $\text{TeCl}_{4.07}$  was obtained for the first experiment in the data.

Table 3

EXPERIMENTAL DATA ON THE DISSOCIATION OF  $\text{TeCl}_{4(g)}$

Experiment No.	Total Pressure, atm	Av. Temp of $\text{TeCl}_4$ Evaporating System, °C	Approx. Dissociation Temp, °C	% of Theoretical* Yield of $\text{Cl}_2$
1	0.02	370	690	52
2	1+	370	705	32

\* Calculated value is based on complete dissociation of  $\text{TeCl}_4$  vapor into  $\text{TeCl}_2$  and  $\text{Cl}_2$  gases. Flow rate of helium gas, 20 cc/min.

2. Vapor Pressure of Copper Chloride-Aluminum Chloride

Design and operation of a breadboard model required knowledge of the total vapor pressure of the cathode system of copper chlorides in aluminum chloride. The apparatus is shown in Figure 5, and data of vapor pressure versus temperature are given in chronological order in Tables 4 and 5. The vapor pressure for the  $\text{CuCl}_2$ - $\text{AlCl}_3$  system does not deviate appreciably from that expected for  $\text{AlCl}_3$  ( $\text{Al}_2\text{Cl}_6$ ) alone. However, the vapor pressure data for the

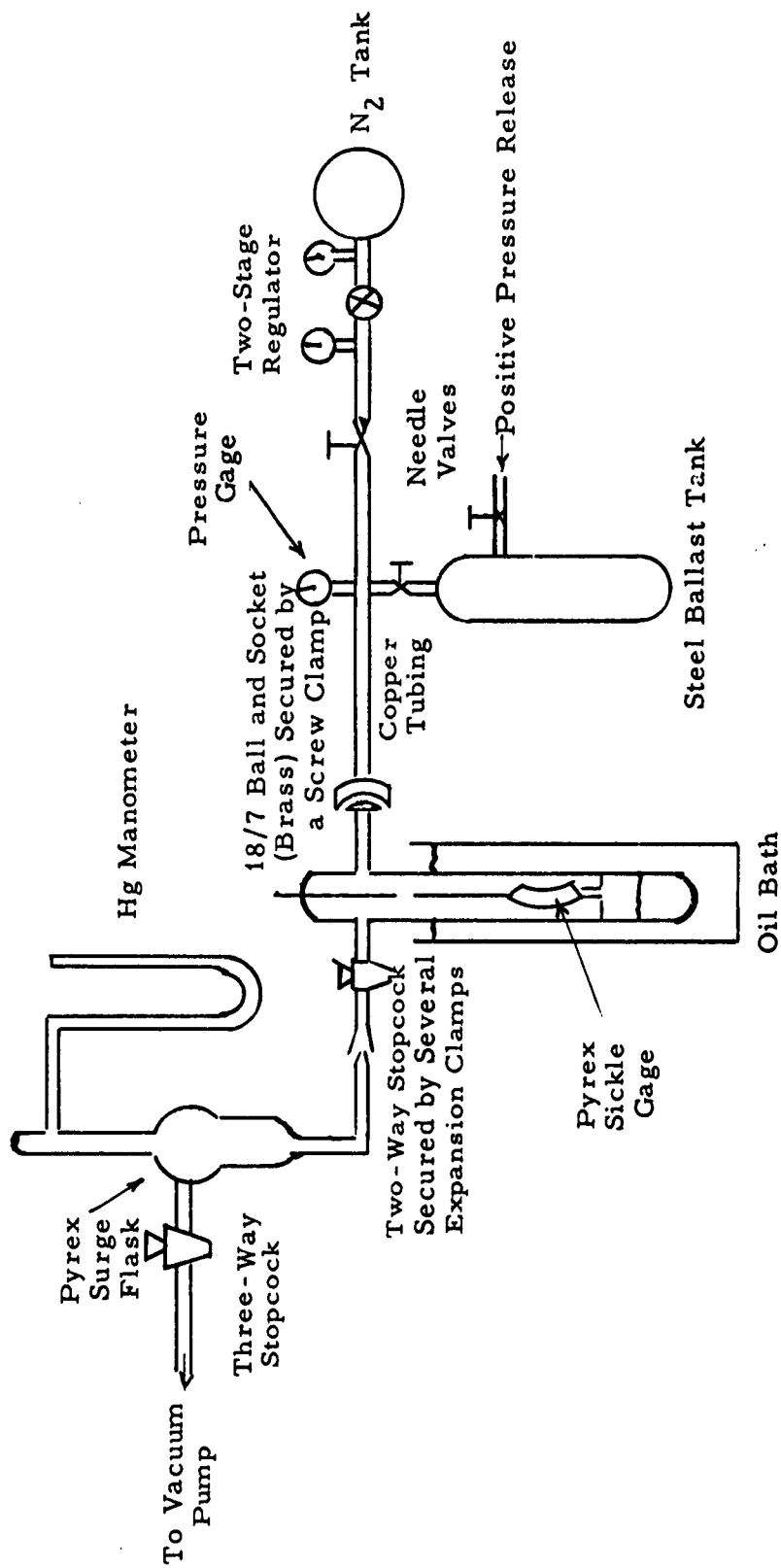


Figure 5

SYSTEM FOR MEASURING POSITIVE ATMOSPHERIC PRESSURES

Table 4

VAPOR PRESSURE OF  $\text{AlCl}_3\text{-CuCl}_2$   
(Mole Fraction  $\text{CuCl}_2 = 0.25$ )

Temperature, °K	Vapor Pressure, atm
429	0.54
493	2.71
485	2.54
472	2.13
494	2.74
487	2.60

<sup>a</sup>Temperature read to  $\pm 1^\circ$ , pressure to  $\pm 0.5$  psi. Liquid-solid equilibrium mixture observed at about 472 to 475°K. Vapor pressure corrected for residual gas pressure.

Table 5

VAPOR PRESSURE OF  $\text{AlCl}_3\text{-CuCl}$ <sup>a</sup>  
(Mole Fraction  $\text{CuCl} = 0.25$ )

Temperature, °K	Vapor Pressure, atm
457	1.26
475	2.58
488	3.27
495	3.52
486	3.27
479	3.05
464	2.47
475	2.76
478	2.99
486	3.27
464	2.47

<sup>a</sup>Initial mixture began melting in the range of 448 to 453°K. On cooling, solid began forming in the liquid in the range of 453 to 448°K. Vapor pressures corrected for a residual gas pressure of 384.55 mm at 195°K.

CuCl-AlCl<sub>3</sub> system run more than one-half atmosphere higher. Since the melting and boiling points of CuCl (CuCl<sub>2</sub>) are 695 and 1639° K, respectively, the high vapor pressure of the mixture is surprising. It should be noted that the vapor pressures were reproducible when the mixture was returned to a previous temperature.

### 3. Large Cells of Tellurium-Copper Chlorides

The experiments with large cells of tellurium-copper chlorides represent a scaleup by factors of 40 to 120 over the small, all-glass cells (Report No. ARF 3182-4, Figure 1) with which most of the exploratory work was done. In addition to the scaleup, the configurations were changed to increase the effective area per unit volume and thus increase power density. These latter changes were accomplished primarily by reducing the thickness of the electrolyte support and the anode and cathode chambers. The experiments varied in complexity from the operation of a simple cell to the operation of complete systems.

In all cases the experiments met with only qualified success; the predominant problems resulted from differences in melting points and vapor pressures between the anode and cathode systems, primarily during startup. The experiments were successful in emphasizing areas requiring basic study, and this route was selected rather than further cut-and-try experiments.

Data from these large cell experiments are summarized in Table 6. The cells which have a cross section of 16 sq cm are of the type shown in Figure 2, Report No. ARF 3182-6; the cells which have a cross section of 47 sq cm were part of the complete system shown in Figure 1 of this report. Tantalum or gold foils were effective as collectors in the cells.

Table 6

## EVALUATION OF LARGE GALVANIC CELLS OF TELLURIUM-COPPER CHLORIDE

Cell No.	Collectors		Electrolyte Support		Mole Fraction		Electrical Characteristics			
	Material	Area, sq in.	Type	Thickness, in.	Void Volume, %	TeCl <sub>2</sub> in Anode	CuCl <sub>2</sub> in Cathode	E <sub>max</sub> ' volts	I <sub>max</sub> ' ma	R <sub>int</sub> ' ohms
1	Tantalum	16	Teflon <sup>a</sup>	0.005		0.815	0.249	0.71		230
2	Gold	16	TX 10-50 <sup>b</sup>			0.815	0.249	0.76		8.9
3	Tantalum	16	TX 10-50			0.815	0.045	0.44	31	3.2
4	Tantalum	16	TX 10-50			0.815	0.12	0.68	26	14.8
5a	Tantalum	16	Asbestos			0.815	0.12	0.42	4	85
5b	Tantalum	16	Asbestos			0.815	0.12	0.50	15	18.6
5c	Tantalum	16	Asbestos			0.815	0.12	0.25	2	
6	Tantalum	16	Teflon <sup>c</sup>			0.815	0.249	0.57	15	20.8
7a	Tantalum	16	Teflon			0.815	0.249	0.60	15	25.2
7b	Tantalum	16	Teflon			0.815	0.249	0.60	24	11.2
8	Tantalum	16	Teflon	0.008	47	0.815	0.249	0.90	54	4.4
9	Gold	16	Teflon	0.013	67	0.815	0.249	0.62	36	5.0
10		16	Teflon	0.013	67	0.815	0.249	0.62	17	19.4
11		16	Teflon	0.008	72	0.815	0.249	0.62	6	42
12		16	Teflon	0.012	52	0.815	0.249	0.62	14	24.2
13	Tantalum	16	Teflon	0.010	45	0.815	0.249	0.60	23	11.6
14	Tantalum	16	Teflon	0.009	38	0.815	0.249	0.63	33	
15	Tantalum	16	Teflon	0.012	43	0.815	0.249	0.64	35	1.6
16	Tantalum	16	Teflon	0.022	51	0.815	0.249	0.62	4	115
17	Tantalum	16	Teflon	0.015	48	0.815	0.249	0.62	25	10.8
18	Tantalum	16	Teflon	0.008	57	0.070	0.249	0.30	16	1.25
19	Tantalum	47	Teflon	0.021	43	0.575	0.249	0.69	34	6.5
20	Tantalum	47	Teflon	0.021	43	0.575	0.249	0.48	30	3.33
21	Tantalum	47	Teflon	0.021	43	0.575	0.249	0.48	30	0.77

<sup>a</sup>Teflon sheet.<sup>b</sup>Teflon-coated glass fiber mesh.<sup>c</sup>Cells 6 through 21 used specially prepared porous Teflon sheets; water- or acid-soluble components were leached from the sheet after curing.

A number of electrolyte supports or diaphragms were tested for separating the anode and cathode liquids. The Teflon sheet used in cell 1 was of standard porosity and afforded very low conductivities. The TX 10-50 filter sheets used in cells 2, 3, and 4 were of Teflon-coated glass fiber mesh. Although these sheets afforded better conductivity, they also allowed convective mixing through the macro-sized openings. Cells 5a, 5b, and 5c employed an asbestos sheet confined between stainless steel mesh. The stainless was attacked. Cells 6 through 21 employed porous Teflon sheets. The porosity was obtained by leaching water- or acid-soluble components from the sheet after curing. For cells 6, 7, and 8, diaphragm thickness and per cent void volume were not determined. These values are given in inches and per cent, respectively, for all other cells.

The experiments with the large cells clearly demonstrated the need for further testing and development of electrolyte supports or other separators for the anode and cathode liquids. The preparations of porous Teflon appear very promising but require modification to reduce convective flow. Several commercial materials are also of interest.

#### B. Antimony-Arsenic Chloride System

Earlier reports described the operation of several small, complete cells based on the antimony chlorides or on the antimony-arsenic chlorides. These cells were constructed of glass, and the configuration together with the relatively poor ionic characteristics of the cathode liquids permitted only very small currents.

During the period of this report a larger system, Figure 2, was constructed and operated with limited success. Nickel was used as the primary material of construction for the cell and the collector. This material was

selected following a series of static and dynamic tests on the stability of various materials in  $\text{SbCl}_5$  and in  $\text{SbCl}_5$ - $\text{SbCl}_3$  mixtures.

Table 7 gives data on the specimens which were temperature cycled in  $\text{SbCl}_5$ . With the exception of gold, which dissolved, all intact samples gained weight, probably due to the formation of chlorides with a low solubility in  $\text{SbCl}_5$ . Changes in the  $\text{SbCl}_5$  were quite apparent with all the materials except nickel, tantalum, and Nichrome. Nickel gave the least evidence of attack by the  $\text{SbCl}_5$ . Surprisingly, gold was readily attacked. The graphite disintegrated but otherwise was probably not attacked.

Table 7

EFFECT OF  $\text{SbCl}_5$  ON VARIOUS MATERIALS  
CYCLED BETWEEN 300 AND 420°K

<u>Substance</u>	<u>Gain in Weight, %</u>	<u>Visual Estimate</u>
Nickel	0.2	Unaffected
Tantalum	0.2	Unaffected
Nichrome	0.2	Slightly affected
Hastelloy N	0.2	Slightly affected
Stainless Steel No. 304	0.3	Slightly affected
Brass	0.7	Susceptible
Silver Solder	0.7	Susceptible
Iron	1.3	Susceptible
Copper	4.6	Susceptible
Silver	4.6	Susceptible
Beryllium - Copper	7.5	Susceptible
Gold	--	Grossly affected
Aluminum	--	Grossly affected
Soft Solder	--	Grossly affected
Graphite	--	Grossly affected

In other experiments, polyethylene and Viton were destroyed very rapidly; whereas Teflon, either tetrafluoroethylene or fluoroethylenepropylene, was inert.

A diagram of the small, dynamic corrosion test loops is given in Figure 6. These devices, constructed of Pyrex glass, not only served for the corrosion test but also furnished much information on the regeneration characteristics of the  $\text{SbCl}_5$ - $\text{SbCl}_3$  system. A Monel specimen, when tested for a period of 53 days, gave no significant evidence of corrosion, although it extended into the vapor phase and into the liquid phase over a temperature differential of more than  $200^\circ\text{C}$ . Data on the relationship of temperature to  $\text{SbCl}_5$ - $\text{SbCl}_3$  ratio are given in Table 8. The observed temperatures, which were found to be low, have been corrected by standardization of the thermocouple. Note that when liquid chlorine was present the pressure in the system was at approximately 8 atmospheres. The data satisfy present needs but require considerable improvement for future applications.

Table 8

RELATIONSHIP OF  $\text{SbCl}_5$  TO  $\text{SbCl}_3$  RATIO TO TEMPERATURE  
AT 8 ATMOSPHERES  $\text{Cl}_2$  PRESSURE

System 1		System 2	
Temperature	$\text{SbCl}_5/\text{SbCl}_3$	Temperature	$\text{SbCl}_5/\text{SbCl}_3$
230	11.3	187	0.067
237	7.6	187	0.067
237	7.16	228	0.4
265	11.3	235	0.53
265	11.3	235	1.04
265	13.7	210	0.014
245	2.5		

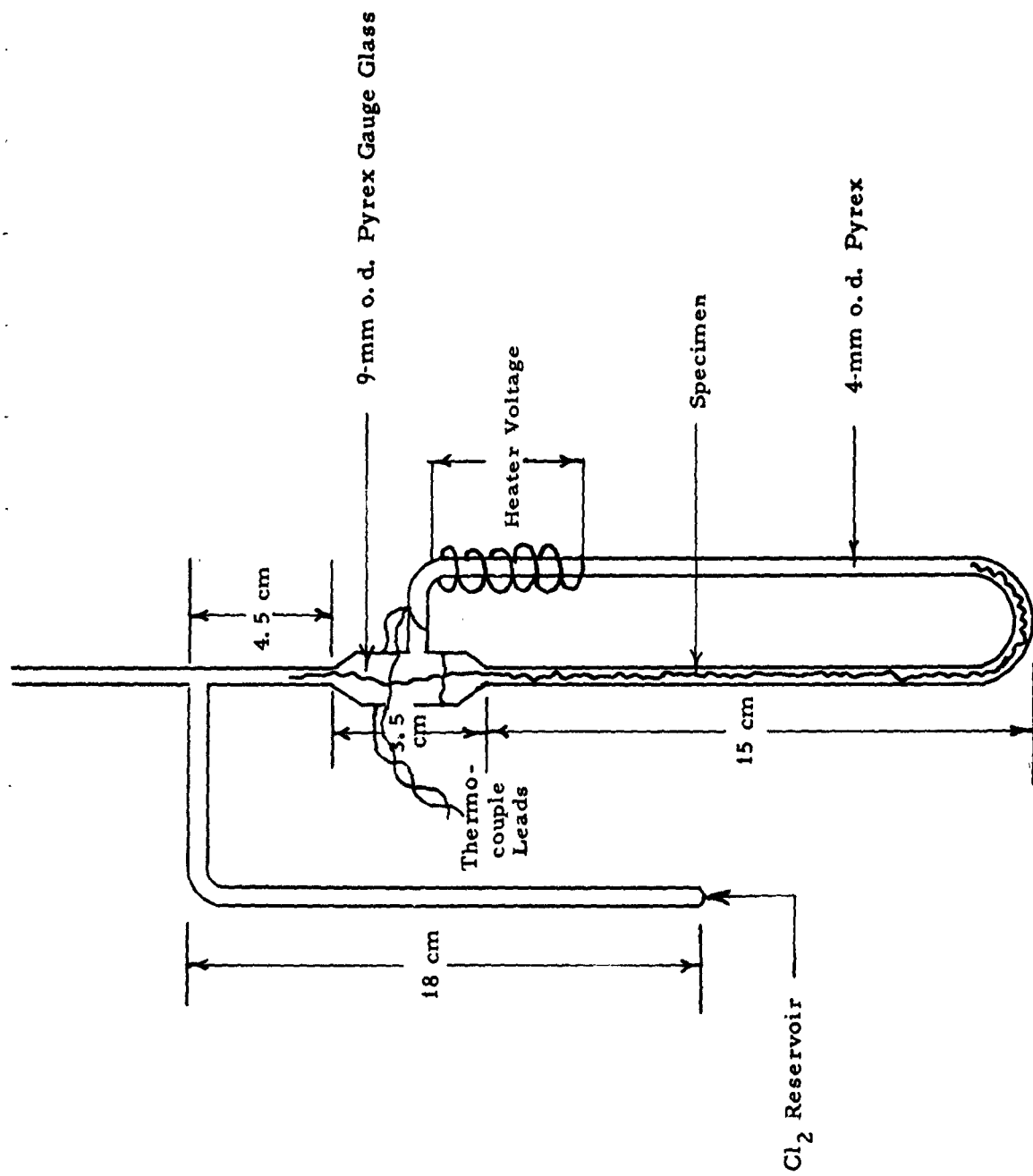


Figure 6

**DYNAMIC CORROSION TEST LOOP**  
 (Note Insulation and Temperature Control Baths)

The very successful operation of the dynamic corrosion test system in the regeneration of  $\text{SbCl}_3$  from  $\text{SbCl}_5$  led to the selection of a similar design for the regeneration of the system of Figure 2. Circulation through the anode chamber was adequate, and it was possible to convert the  $\text{SbCl}_5$  charged to the chamber to  $\text{SbCl}_3$ . However, the design did not provide circulation to the cathode chamber and the single C clamp was insufficient to prevent leakage around the gasket separating the two nickel plates that formed the halves of the cell. The maximum voltage obtained was 0.3 volts; the current was not measured. The design has been modified to overcome the above difficulties.

#### IV. CONCLUSIONS AND RECOMMENDATIONS

Work during the first 18 months of this project has highlighted the technical and economic promises of the chemical method of converting heat to electricity. Technically the project has achieved all of the principal goals and has exceeded some. However, the goal of most interest to project personnel, an intact workable system for delivery to the sponsor, has not been achieved in the scale desired. The reasons for this delay are primarily attributed to the need for additional support work to provide information for chemical engineering design and not to critical difficulties encountered. Provision for obtaining this basic information is included in plans for the continuing development.

Conclusions concerning the ultimate role for chemical conversion of heat to electricity are far more encouraging. Project work has definitely demonstrated the technical feasibility and economic promise. Power density and weight per unit of power projected from experimental results are extremely favorable. Further, estimates of operating efficiencies remain

above those for any other systems except the most modern, extreme-pressure steam plants.

Despite recognition that an operating system of the desired scale has not been achieved, progress with this development has been phenomenal when compared, on an expenditure basis, with that achieved on other energy conversion developments. For example, expenditures for development of thermo-electric conversion have been averaging more than \$7, 000, 000 for several years, although these conversion devices were common to laboratories and industrial plants for many years. Present achievements provide either very low efficiency or high cost, and even with high cost the efficiencies are below 10%. We believe that much of the progress with the chemical conversion method is due to the fundamental advantages of the method itself.

Lines of continuing development recommended here are directed toward producing an operating device of sufficient scale to permit engineering determinations of operating efficiencies for units of various capacities. A unit with a capacity of several hundred watts appears advisable. It is recommended that both systems 1 and 2 of Table 2, the antimony chloride system and the tellurium-copper chlorides system, be included in the development. With the former system emphasis will be given to improving the galvanic cell capacity. This will include studies of additives to increase the ionic conductivity and improved electrolyte membranes. Additives will also require phase studies to ensure knowledge of all possible solid phases that could interfere with system operations.

In the case of the tellurium-copper chlorides system, emphasis must be placed on the regeneration process. This process may also dictate the composition in the galvanic cell or require some compromises in the

composition. Fundamental information on phases and the solubility of  $\text{TeCl}_2$  and  $\text{Cl}_2$  in melts of  $\text{NaCl-KCl}$  or other eutectics will be required, as well as the effect of these eutectics on the decomposition of  $\text{TeCl}_4$ .

Other fundamental information required will be viscosity, density, and heat capacity data to permit design of heat exchange systems. Electrolyte membranes also require development. Ionic solids are of interest, possibly incorporated in a porous media. Early experiments are planned with flow-through mock-ups of possible galvanic cell configurations. The work outlined will require a minimum of two to three quarters of effort.

#### V. RECORDS AND CONTRIBUTING PERSONNEL

Experiments on thermal decomposition of  $\text{TeCl}_4$ , recovery of  $\text{TeCl}_2$  and  $\text{Cl}_2$ , and vapor pressure of  $\text{AlCl}_3\text{-CuCl}_2$  and  $\text{AlCl}_3\text{-CuCl}$  were performed by Dr. J. Keith, Research Chemist, and W. K. Sumida, Assistant Chemist. Analyses of spent anode and cathode materials were by Mr. H. Combs, Associate Chemist. Galvanic cell studies were carried out by Mr. T. M. Rymarz, Associate Engineer, and Mr. S. B. Nicholson, Associate Engineer, assisted by Mr. R. J. Dausman, Technician. Dr. Morton J. Klein, Assistant Director of Chemistry Research, and Mr. Charles K. Hersh, Manager of Propellant Research, are administering the program.

Data for the project are recorded in ARF Logbooks C 10401, C 10402, C 10401, C 10467, C 10472, C 10473, C 10481, C 10568, C 10643, C 10646, C 10825, C 11093, C 11095, C 11200, C 11225, C 11229, C 11440, C 11452,

C 11563, C 11633, C 11663, C 11725, C 11726, C 11842, C 11859, C 12254,  
C 12369, and C 12380.

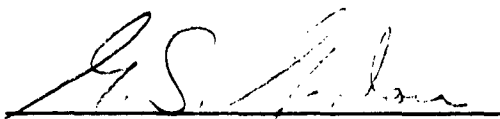
Respectfully submitted,

ARMOUR RESEARCH FOUNDATION  
of Illinois Institute of Technology



C. Roland McCully  
Scientific Advisor  
Chemistry Research

Approved by:



G. S. Gordon  
Director of Chemistry Research

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