COMPUTER SIMULATION OF THE ZINC-CHLORIDE BATTERY

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Abstract

The zinc-chloride battery is being developed by Energy Development Associates for utility load-leveling applications. The many simultaneous and interacting processes occurring within the battery make predicting its behavior difficult without a computer simulation model. Such a simulation has been developed to an accuracy of ≥95%. In this paper, the methodology used to develop the computer model is discussed; sample computer outputs are shown; and the model predictions are verified with operational data from a battery.

INTRODUCTION

The zinc-chloride battery is being developed by Energy Development Associates for the utility load-leveling application (1). In this application the battery will accept and store electrical energy at night when demand is low and will return this energy during the demand peaks, thus leveling the utility power output over a 24-hour period. The battery has many components and during operation chemical, electrochemical, flow, and thermal processes are involved. To aid the development of this multi-faceted load-leveling battery, a computer program was to be written which simulates the operation of the battery.

A simulation that was both accurate and useful to the battery program was to be constructed with only three man-months effort. The work included: (1) developing an understanding of the battery system, (2) converting this understanding into quantitative expressions, (3) developing the architecture for the computer program, (4) coding the program, (5) debugging the program, and (6) validating the results by comparison with data from an actual battery. The simulation program was successfully developed within the specified time frame. The purpose of this paper is to outline the approach used with the hope that other people developing simulations might benefit.

The program defines the battery as a set of state variables (pressure, temperature, energy stored, etc.) and the value of these variables is computed to simulate the progression of the battery through a charge-discharge cycle. Before discussing this simulation program in more depth, a description of the operation and components of the battery will be presented. Then a discussion of the program will include its construction, how it is operated on a computer terminal, and results of verifying simulated operation against actual performance of a load-leveling battery.

BATTERY OPERATION

The computer model evolved from a detailed understanding of battery operation. The following is an introduction to the operation and components of the battery.

A schematic of the zinc-chloride battery during charge is presented in Figure 1. From an aqueous zinc chloride electrolyte, zinc is plated on one electrode and gaseous chlorine is evolved on the

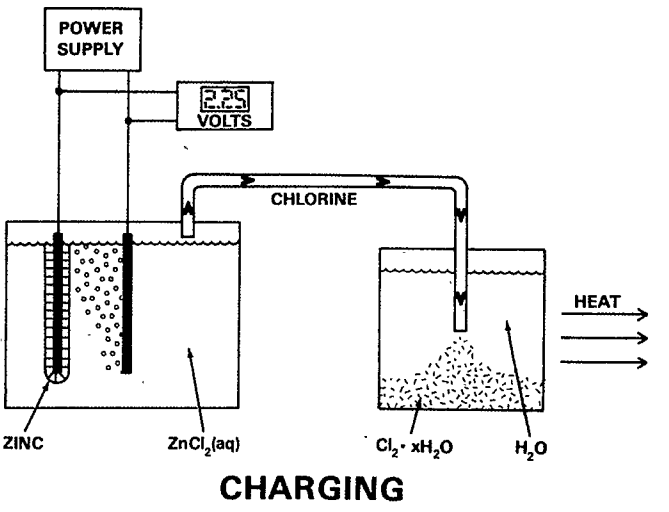

Figure 1. Schematic of a zinc-chloride battery in the charge mode.

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Highland * Chao * Madrigal, Editors

other. The chlorine passes from the gas space above the electrolyte into the store where it reacts with cooled water forming chlorine hydrate, a pale yellow solid.

The reaction is:

$$Cl_2(aq) + xH_2O \rightleftharpoons Cl_2 \cdot xH_2O(s)$$

where the value of x, which is dependent on the experimental conditions, can be as low as 5.7.

To initiate discharge, the chlorine hydrate-water mixture in the store is heated releasing chlorine which passes from the store into the electrolyte adjacent to the chlorine electrode, as shown in Figure 2. Electrochemical reaction of zinc and chlorine occurs forming zinc chloride and releasing electrical energy. Heat is generated in the cell because of thermodynamic, electrochemical, and chemical inefficiencies in the cell reaction. This heat is transferred to the store at the desired rate for decomposing chlorine hydrate and evolving chlorine gas.

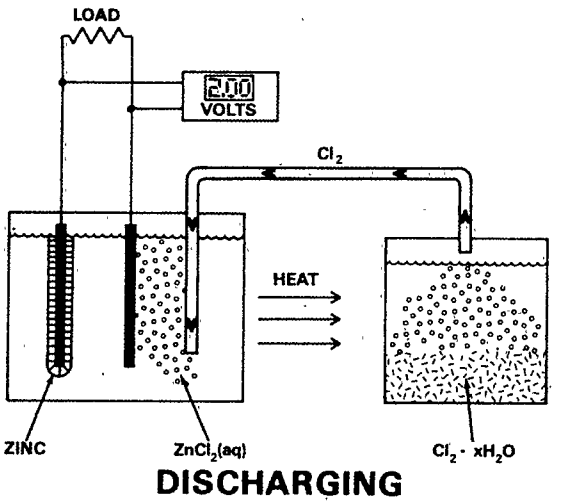


Figure 2. Schematic of a zinc-chloride battery in discharge.

In a practical system means must be provided to achieve the desired flows of chlorine, electrolyte, water, and heat as shown in Figure 3. Pump P1 delivers electrolyte to pockets between pairs of porous chlorine electrodes, the electrolyte passes through the porous-chlorine electrodes into the chamber between the zinc and chlorine electrodes, flows up between the electrodes, and then returns by gravity back into the sump. During charge, chlorine gas is pumped by P2 through line C. Before entering the pump, the chlorine is mixed with chilled water, which passes through line W and comes from the bottom of the store. The chlorine and chilled water are mixed in the gas pump, chlorine hydrate forms, and the chlorine hydrate-water mixture is deposited in the store through line H. The water in line W is chilled by passage through a heat exchanger. Liquid, cooled by means of a refrigeration system, is passed through line R into this heat exchanger.

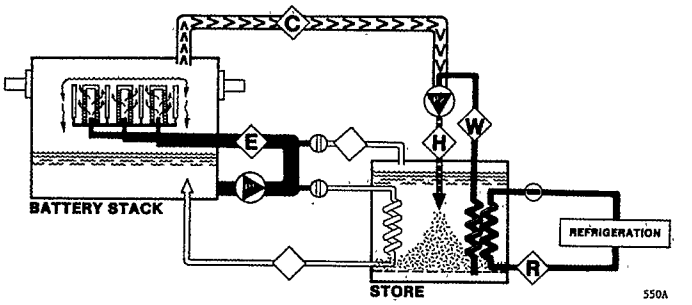


Figure 3. Schematic of a zinc-chloride battery in charge.

Figure 4 shows the battery being discharged. The valve in line D is opened, permitting a stream of warm electrolyte to pass through a heat exchanger in the store. Chlorine is formed by decomposition of chlorine hydrate. On development of the required pressure in the store, the valve in line G is opened and chlorine passes into line E on the high pressure side of the electrolyte pump P1. The chlorine dissolves in the electrolyte, which is then fed to the porous chlorine electrodes. The battery stack can now be discharged. Electrochemical dissolution of zinc occurs at the zinc electrode and reduction of the dissolved chlorine occurs at the chlorine electrode.

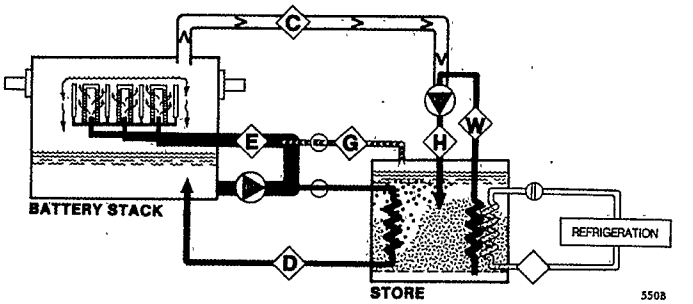


Figure 4. Schematic of a zinc-chloride battery in discharge.

A schematic representation of an actual battery is shown in Figure 5. In addition to the pumps and heat exchangers, shown previously, this practical battery system will include: (a) ultraviolet lights for recombination of hydrogen (formed at the zinc electrode) with chlorine, (b) several valves, (c) a heat exchanger in the electrolyte sump which may be employed for cooling purposes during discharge if the temperature increases above a predetermined level, and (d) a filter to permit separation of the chlorine hydrate from the water entering flow line W. Table 1 defines the symbols found in Figure 5.

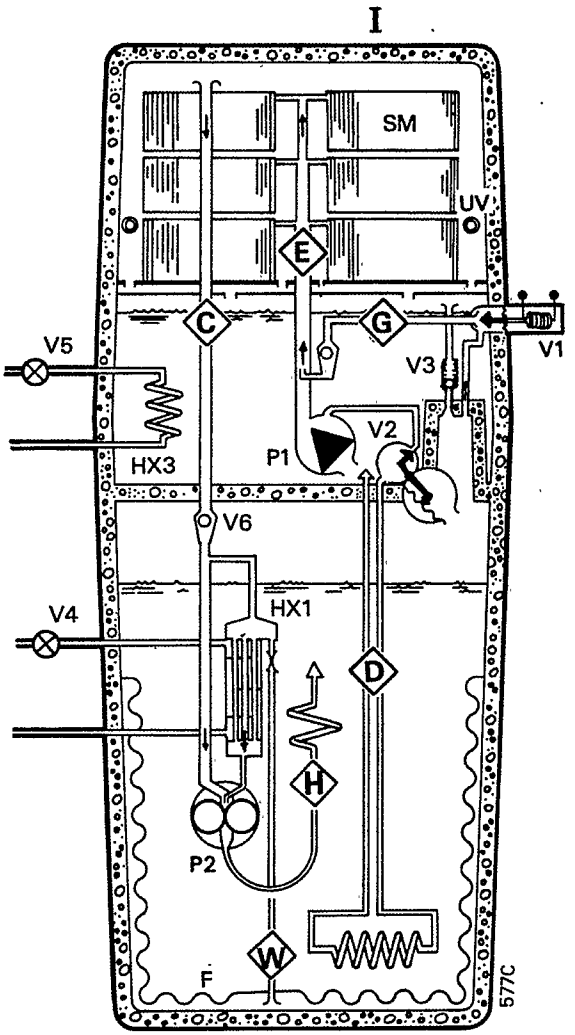


Figure 5. Load-Leveling Battery Schematic

Table 1

SYMBOLS FOUND IN FIGURE 5 AND THEIR DEFINITIONS

Symbols	Description
C	Gas flow line from stack to store, which allows chlorine gas evolved during charge to be pumped to the store where it combines with chilled water to form hydrate.
D	Electrolyte flow line through HX2 which allows warm electrolyte to heat up hydrate during discharge causing the hydrate to disassociate releasing chlorine gas.
E	Electrolyte flow line to submodules.
F	Filter to separate hydrate from the water flowing into line W.
G	Gas flow line from store to electrodes which makes chlorine gas available during discharge for the electrochemical reaction.
H	Flow line from P2 to the store liquid where hydrate is formed during charge.
HX1	Heat exchanger which during charge chills the water used to form hydrate.
HX2	Heat exchanger which uses warm electrolyte to heat hydrate in the store during discharge causing the hydrate to disassociate and, thus, releasing chlorine gas.
HX3	Heat exchanger used to cool sump.
I	Thermal and electrical insulation around battery module and between stack and store.
P1	Electrolyte pump which pumps battery electrolyte from the sump to the electrodes.
SM	Submodule which is a unit containing battery electrodes and associated electrolyte flow channels. There are six submodules in a battery.
UV	Ultraviolet lamp which causes evolved hydrogen to combine with the chlorine gas to form HCl. The lamp in Figure 5 is represented by a pair of concentric circles.
V1	Solenoid valve which opens during discharge to allow chlorine gas to flow from the store to the electrodes.

Table 1 (continued)

V2	Pressure-controlled valve that allows electrolyte to flow through HX2 if the store pressure is below a set value.
V3	Relief valve which opens when the difference between store and stack pressure is too great.
V4	Valve to control coolant to HX1.
V5	Valve to control coolant to HX3.
V6	Check valve to eliminate back flow in line C.
V7	Check valve to eliminate back flow in line G.
W	Water flow line from filtered store water to HX1 which supplies the water needed to form hydrate during charge.

MODEL CONSTRUCTION

A time iterative approach, as conceptualized in Table 2, was used to model the battery. The state of the battery is defined at a time t_o by initializing a set of state variables which include pressures, temperatures, moles of chlorine gas, etc. The first iteration of the program calculates the values of the state variables at a time $t_1 = t_o + \Delta t$ using equations that depend on the state variables at time t_o. For the second iteration, the value of the state variables at a time $t_2 = t_1 + \Delta t$ are calculated using the state variables at time t_1, and so on.

Table 2

TIME ITERATIVE APPROACH TO MODELING

	Initial State at Start	First Iteration	i th Iteration
TIME	$t_o = 0$	$t_1 = t_o + \Delta t$	$t_i = t_{i-1} + \Delta t$
STATE VARIABLES	P_o	P_1	P_i
	T_o	T_1	T_i
	VOL_o	VOL_1	VOL_i
	MCL_o	MCL_1	MCL_i
	$MHYD_o$	$MHYD_1$	$MHYD_i$
	Etc.	Etc.	Etc.

To understand how the calculations made during an iteration of the program relate to what is happening in the battery, it is illustrative to examine the flow process in the battery. The two main flow processes are the chlorine flow and the heat flow. Figure 6 shows the flow pattern of chlorine. By keeping track of flow rates into the stack and store, the change in pressure in both these regions can be calculated from iteration to iteration. The heat flow into both the stack and store is shown in Figure 7. From the net heat flow during an iteration, the temperature change in both the stack and store can be calculated.

The success of the modeling depends on how accurately the equations used to calculate the state variables reflect the true behavior of a battery. The beauty of the time-iterative approach is that: (a) it allows the simulation to be developed in terms of easily conceptualized pictures of the battery processes as illustrated in Figures 6 and 7, and (b) any expression discreet or continuous that is programmable can be used to calculate a state variable. Hence the simulation program could be developed rapidly and still produce a credible simulation of the battery. Two inherent

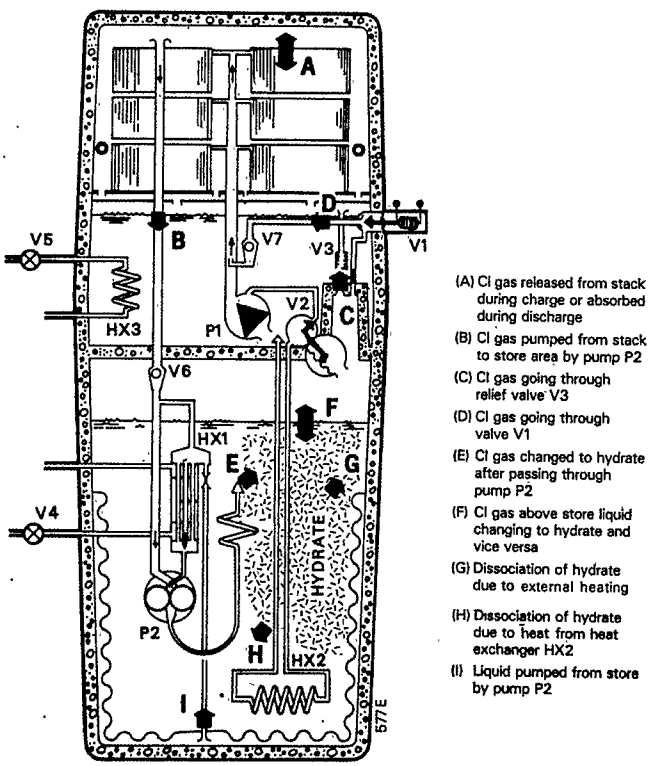


Figure 6. Chlorine and hydrate mass flow in the battery.

problems limit the accuracy of this time-iterative approach: (1) round off errors, and (2) the inaccuracies associated with calculations of continuous processes using finite time increments. Naturally, as the time increment Δt between iterations is increased, the effects of the first error process would decrease and the effects of the second would increase. Setting Δt equal to one second was found to be the best compromise. This produced a simulation with an accuracy of better than 95% as discussed later.

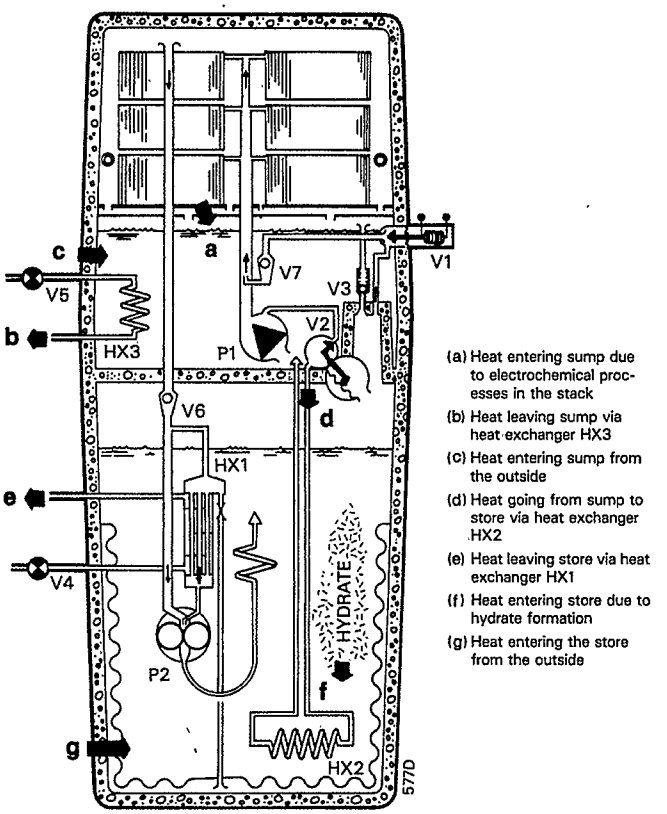


Figure 7. Heat Flow in the Battery

The structure of the program is shown in Figure 8. The vertical column of boxes on the left shows the flow of calculations in the main section of the simulation program. The vertical column of boxes on the right shows the subroutines that are called by the main program.

The sequence of execution for the main program is as follows. First, over 100 variables are given an initial predetermined value. These variables define the initial state of the battery, the mode of control for the battery, and the time variables associated with the modeling. The operator of the program is then allowed to change any of these variables from its predetermined value to a different value. The program then takes the initial variables and calculates additional state variables by calling the subroutines CALVOL, CALCON, and CALCL. Now the iteration progess begins. Each iteration requires the sequence of subroutines shown in Figure 8 to be called so that the value of all the state variables will be calculated. A brief description of each subroutine is also found in Figure 8. The first sequence of iterations is completed when the desired time period of battery operation has been simulated. During the iteration process, selected state variables have been recorded as a function of time. A plot of some of these variables is printed out after the iteration process is completed. Finally, the operator is given the option of continuing the program or ending the run. If the program is continued, iteration will begin using the values of the state variables at the end of the first sequence of iteration, unless the operator chooses to change the value of any of these variables.

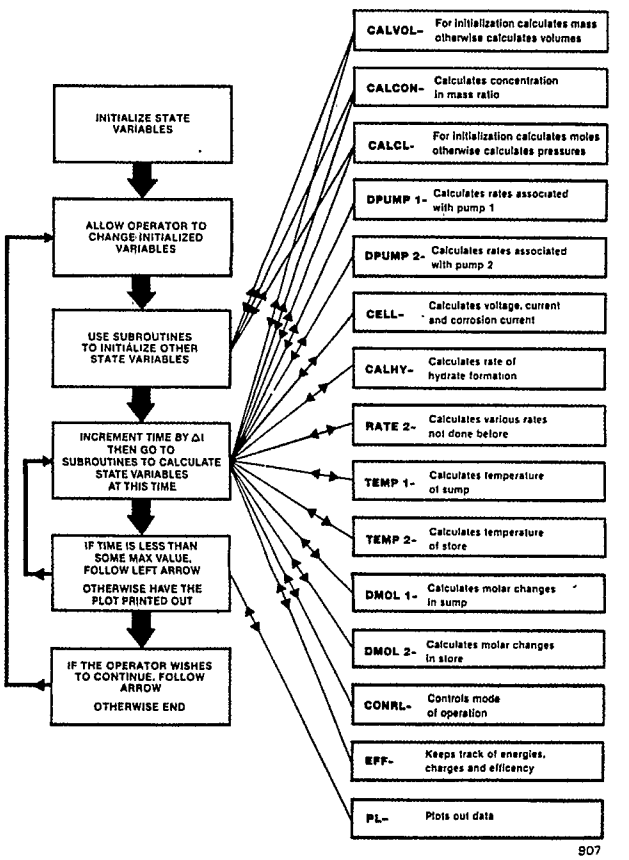


Figure 8. Computer Flow Diagram

MODEL OPERATION

A sample computer terminal session using the simulation is shown in the sequence of Figures 9 and 10, where the lines circled are the operator's input and the other lines are the computer's response. The first line in Figure 9 shows the

input by the operator required to start a run of the simulation program. It tells the computer to run the program stored in the file called LOAD and to place data generated during the run in the file called -DATA. The operator is then given the option of having the initial values of variables used by the program printed out. This he does by typing 1. The variables are then typed out in data sets which are denoted by NUM1, NUM2, etc. On the second page of Figure 9, it can be seen that the operator is given the option of changing values in a data set. First, he chooses to change data set NUM1 by typing 1. In data set NUM1, he changes the value of TT to 40000. This is verified when the computer responds by typing out data set NUM1 with the change that has just been made. The next change made is in data set NUM2 where the sixth value of IT is changed to -1. When the operator has made all the desired changes, the iteration process is started by typing 00 as shown on the bottom of the second page of Figure 9.

After the iteration process is completed, the output shown in Figure 10 is typed by the computer. First, there is a plot that shows the value of selected variables as a function of time. In the plot, time increases in the down direction and the value of the variables increase going to the right. As the plot takes several minutes to type out, many variables are shown on one plot rather than having a separate plot for each variable. In the plot, P stands for the stack pressure; 2 stands for the store pressure; T stands for the stack temperature; @ stands for the store temperature; V stands for the battery voltage; H stands for the moles of hydrate; C stands for the percent of CO_2 gas in the stack; and O stands for the percent of CO_2 gas in the store. The plot with a time scale of sec x 10^4, shows 40,000 seconds of battery running time. A discussion of the plot is included in the next section. Besides the plot, a table is printed of electrical changes, energies, and efficiencies associated with the battery's simulated performance.

The operator is then given the option of continuing the program or not and elects not to by typing 0. The cost of this run, $9.16, which consisted of 40,000 iterations, can be seen at the bottom of Figure 10. During the running of this program, values of selected variables are stored in the computer file -DATA. This file can be accessed after the simulation run has been completed.

Having run the simulation program and retrieved the data from the run, analysis can begin. The next section will compare a simulation with the performance of a battery.

```
RUN LOAD 8=-DATA
#09120733
TYPE 1 IF YOU WISH TO GET A PRINTOUT OF VARIABLES,
OTHERWISE TYPE 0
0
 &NUM1
DT=1.,TT=6000.,DTP=200.,DTG=60.,IN=1,
 &END
 &NUM2
IT=0,1,-1,1,1,1,-1,-1,1,-1,
 &END
 &NUM3
TM=1.,5...5,5...5,1...5,4.,0.,2.,
 &END
 &NUM4
ZNCL1=2.5,ZNCL2=.3,RK1=3.,RHA1=2.,ZN=0.,MHY=0.,
 &END
 &NUM5
VOL1=200.,VOL2=410.,VOLT1=230.,VOLT2=470.,
 &END
 &NUM6
P1=1.15,P2=1.15,P4=1.599999,P5=.4,PT2=1.,PT3=.57,
 &END
 &NUM7
T1=30.,T2=10.3,THYT=10.,TX1=5.,TX3=30.,TEX=25.,AU1=200.,
AU2=400.,AU3=20.,
 &END
 &NUM8
HX1=450.,HX3=50.,FHX1=.25,FHX3=.25,SH=1.,SHY=1.,
 &END
 &NUM9
VMIN=16.,CURCH=530.,CURDS=530.,CURMIN=80.,
 &END
 &NUM10
DVO=.9999998E-02,TMM=.3000000E-02,RB=2.,RE=2.,
 &END
 &NUM11
G=.2,M=6.25,HEI=10.,PAR1=44.,PAR2=6.,SER1=10.,SER2=1.,
 &END
 &NUM12
AR1CL=.1799999,AR1L=.4000000E-01,DPT3=.7999998E-01,
AR3R=2.5,AL=5.,
 &END
 &NUM13
DRP1=.2000000E-01,FR1=.5000000E-01,RP2=2.,DRP2=.4000000E-01,
FR2=.2000000E-02,FRY=.9999998E-02,MAX=600.,
 &END
 &NUM14
HC1=.7,HC2=.7,HC12=.3,MP1=300.,FP1=.9,MP2=500.,FP2=.9,
 &END
 &NUM15
JP1=0,1,0,1,1,0,1,0,0,0,
 &END
 &NUM16
JP2=1,1,0,0,0,0,1,0,0,0,
 &END
 &NUM17
JV1=1,1,0,0,0,0,0,0,0,0,
 &END
 &NUM18
JX1=1,1,0,0,0,0,0,0,0,0,
 &END
 &NUM19
JX3=1,1,0,1,1,0,1,0,0,0,
 &END
 &NUM21
JCUR=0,1,0,-1,-2,0,0,0,0,0,
 &END
 &NUM22
JIR=0,0,0,0,0,0,1,0,0,0,
 &END
 &NUM23
JH=1,1,1,1,1,1,1,0,0,1,
 &END
 &NUM24
FRIN1=.996,FRIN2=.996,MINHY=0.,RATIR=.2500000E-02,
RATIF=.2000000E-03,PERHY=.2,
 &END
```

Figure 9. Terminal session during which the simulated program was run.

MODEL VERIFICATION

The purpose of the computer model is to accurately simulate the operation of a zinc-chloride battery. To verify the model, its output was compared to data taken from a test run of the battery. The major difference between a simulated run by the model and an actual run of the battery is the way the flow of fluid in heat exchangers HX2 and HX3 is controlled. The model assumed that the flow in HX2 is controlled by the pressure in the store. Where in actual operation of the battery, the valve is manually controlled. For HX3, the model assumes the flow to be constant but in actual operation it is varied manually.*

*Operation of the most recent battery prototypes has become completely automated.

```
 TYPE IN THE NUMBER OF THE DATA SET YOU WISH TO CHANGE,
 IF YOU DO NOT WISH TO MAKE ANY CHANGES TYPE 00
 1
 TYPE IN YOUR CHANGES FOR DATA SET  1 : EXAMPLE X=5.,I=0
 TT=40000.
 &NUM1
 DT=1.,TT=40000.,DTP=200.,DTG=60.,IM=1,
 &END
 TYPE IN THE NUMBER OF THE DATA SET YOU WISH TO CHANGE,
 IF YOU DO NOT WISH TO MAKE ANY CHANGES TYPE 00
 2
 TYPE IN YOUR CHANGES FOR DATA SET  2 : EXAMPLE X=5.,I=0
 IT(6)=-1
 &NUM2
 IT=0,1,-1,1,1,-1,-1,-1,1,-1,
 &END
 TYPE IN THE NUMBER OF THE DATA SET YOU WISH TO CHANGE,
 IF YOU DO NOT WISH TO MAKE ANY CHANGES TYPE 00
 3
 TYPE IN YOUR CHANGES FOR DATA SET  3 : EXAMPLE X=5.,I=0
 IM(7)=3,
 &NUM3
 IM=1.,5.,.5,5.,.5,1.,3.,4.,0.,2.,
 &END
 TYPE IN THE NUMBER OF THE DATA SET YOU WISH TO CHANGE,
 IF YOU DO NOT WISH TO MAKE ANY CHANGES TYPE 00
 7
 TYPE IN YOUR CHANGES FOR DATA SET  7 : EXAMPLE X=5.,I=0
 T1=25.0,T2=10.2
 &NUM7
 T1=25.,T2=10.2,THYT=10.,TX1=5.,TX3=30.,TEX=25.,AU1=200.,
 AU2=400.,AU3=20.,
 &END
 TYPE IN THE NUMBER OF THE DATA SET YOU WISH TO CHANGE,
 IF YOU DO NOT WISH TO MAKE ANY CHANGES TYPE 00
 00
```

Figure 9. Terminal session during which the simulated program was run - (continued).

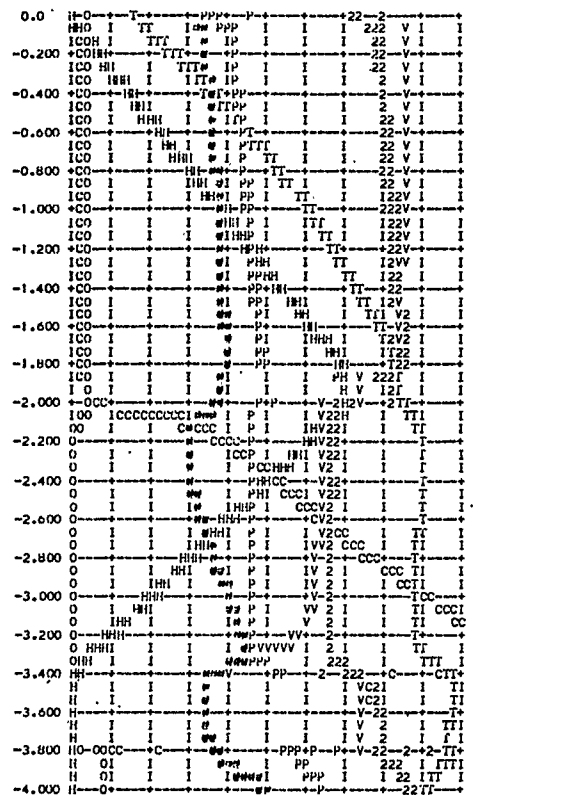


Figure 10. Output of Computer Simulation Run

Comparisons between the output of model and actual data from the battery should to first order provide a good basis for verification of the model. Since it is impossible to program the human factor involved in the actual operation of the battery, differences will exist between the actual data and the output of the model. The verification process started by determining as accurately as possible the initial parameters needed in the model to represent the battery. Then, the results of a computer run using those parameters were compared with data from an actual battery run.

The output of the simulation is found in Figure 11. The electrical charges, energies, and efficiencies calculated from the simulation run were transferred from the bottom of Figure 11 to Table 3 for comparison with results from the actual battery run. The comparison shows a match which is significantly better than 95%.

To verify that the behavior of the variables in the model as a function of time follows the same behavior as the data from the battery, Figures 12 through 15 may be examined. Each figure contains the computer graphic output with one or two variables highlighted by thick solid lines. The corresponding data from the actual battery run are represented by dots. In Figure 12, the battery cell voltage is highlighted and there is an excellent match. Figure 13 shows the pressure in the store and in the stack. During charge, there is good agreement between the actual data and the

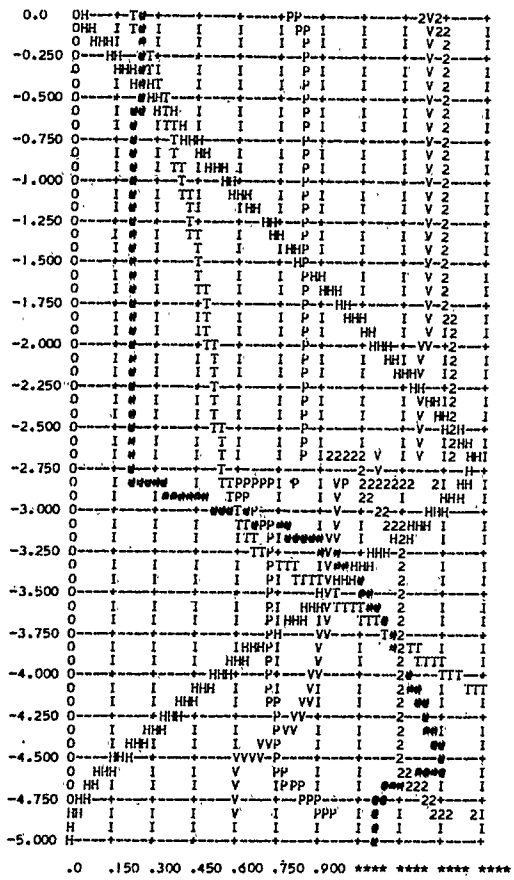
Table 3

COMPARISON OF CHARGE, ENERGY, AND EFFICIENCY BETWEEN SIMULATION RUN AND AN ACTUAL BATTERY RUN

	Simulation Run	Actual Run	Percent Difference
Coulombic Input (kAh)	3.878	3.886	0.2
Coulombic Discharge (kAh)	2.768	2.798	1.1
Energy Input (kWh)	88.419	90.000	1.8
Energy Output (kWh)	51.559	53.240	3.2
Energy Efficiency (%)	58.3	59.2	1.5
Coulombic Efficiency (%)	71.4	72.0	0.8
Voltaic Efficiency (%)	81.7	82.2	0.6

simulation. The deviation during discharge is a result of valve V2 being manually controlled during the actual operation of the battery. Looking at the temperature of the store shown in Figure 14, it can be seen that again, there is excellent agreement. The stack temperature shown in Figure 15 does not show a good correlation. This is due to the manual manipulation of the flow in heat exchanger HX3 during actual operation.

Ample verification of the computer simulation model is provided by Table 3 and Figures 12 through 15. The major discrepancies are due to the manual operation of valves V2 and V5.



CHARGE IN KAMPH; ENERGIES IN KWH

CHARGE IN=3.878 ELEC ENERGY IN=88.419 ENERGY INTO P1=3.900 ENERGY INTO HX1=4.195
CHARGE OUT=2.768 ELEC ENERGY OUT=51.559 ENERGY INTO P2=6.486 ENERGY INTO HX3=3.574

ELEC EFF=0.583 COU EFF=0.714 VOLT EFF=0.817
TYPE 1 TO CONTINUE, 0 TO STOP

Figure 11. Output of computer run which simulates an actual battery run. The plot is of battery variables as a function of time. A description of the symbols is found in the previous section. A more detailed breakdown of the plot is found in Figures 12 through 15.

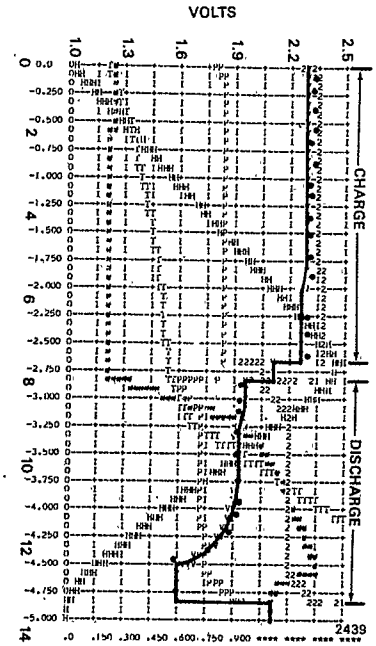


Figure 12. Cell voltage vs. time - computer output with the simulated voltage shown by the broad solid line and data from the battery represented by the dots.

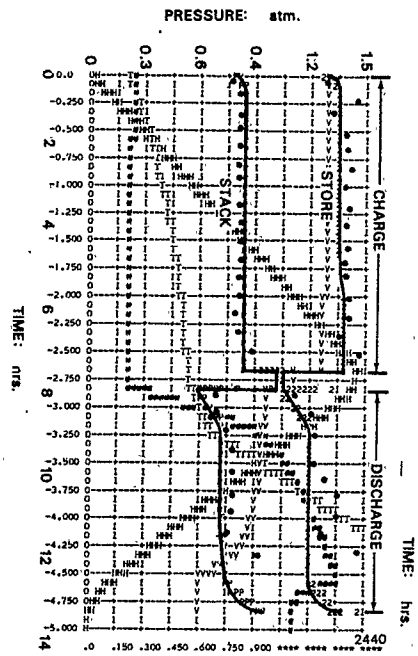


Figure 13. Store and stack pressure vs. time - computer output with the simulated pressures shown by the broad solid line and data from the battery represented by the dots.

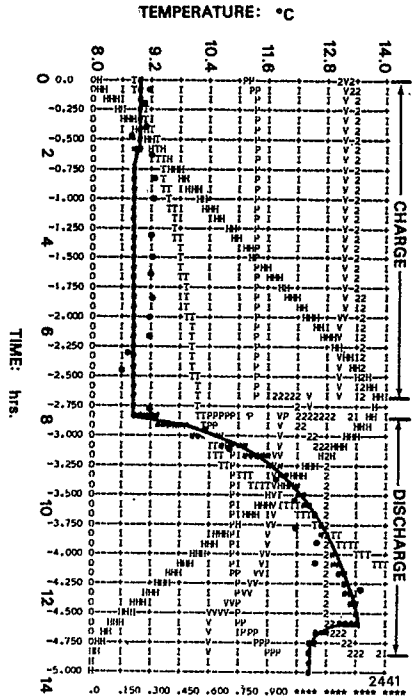


Figure 14. Store temperature vs. time - computer output with the simulated temperature shown by the broad solid line and data from the battery represented by the dots.

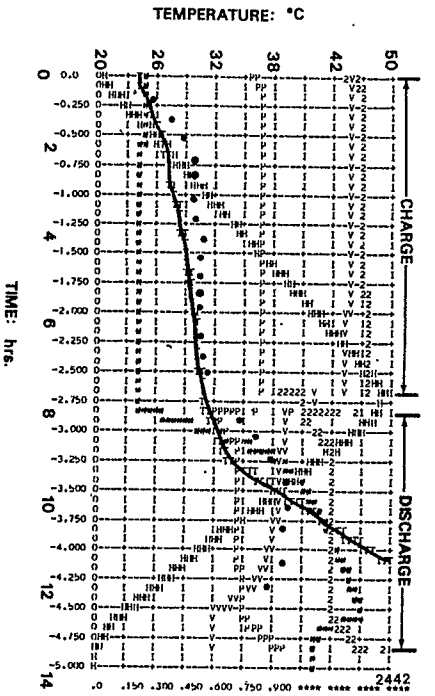


Figure 15. Stack temperature vs. time - computer output with the simulated temperature shown by the broad solid line and data from the battery represented by the dots.

DISCUSSION

After successfully developing the computer simulation, its value to the battery development program became apparent in many ways. These include:

- Providing a better understanding of the interrelationships between components of the battery.
- Yielding information needed to help design the battery control system.
- Allowing one to predict the consequences of battery design changes.
- Providing a basis for the modeling of a battery system made up of many individual batteries.
- Providing a centralized location for information about the battery as well as indicating areas where knowledge is lacking.
- Facilitating optimization of the operation and performance of the battery.

These benefits make the simulation model an extremely valuable design/development tool.

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