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The lithium hydroxide formed during reaction 1 is caustic and must be neutralized to comply with RCRA. The radioactive component must also be considered for disposal, for example by immobilization (cementation) of the waste. These steps have not been included in this study.

EXPERIMENTAL SET UP

Figure 1 shows the experimental setup. The nitrogen flow rate is measured through a flow meter. The nitrogen gas enters and bubbles through a humidifier--a metal cylinder filled with glass beads--immersed in a water bath maintained at a constant temperature. The influence of water concentration in the gas stream (humidity) can be studied by changing the humidifier temperature. The humidity can be calculated by the weight loss of the humidifier.

Humid nitrogen then passes through the reactor. To prevent condensation, the tubing to the reactor and the reactor itself are maintained at a temperature higher than that of the humidifier, usually 5° C higher. Lithium hydride is placed in a ceramic crucible inside the reactor. A thermocouple immersed in the lithium hydride detects temperature changes.

The gas exiting the reactor goes through a hydrogen analyzer. The tubing to the analyzer is maintained at a temperature sufficient to prevent condensation. However, for experiments at high temperature that could damage the analyzer, the gas is dehumidified and cooled in an ice-cold moisture trap. Also, when hydrogen concentration exceeds the analyzer upper detection limit of 4%, the gas exiting the reactor is diluted with a known flow of nitrogen.

Finally, the gas passes through a flow meter which, by comparison with the inlet flow meter, indicates the presence of a substantial leak.

INFLUENCE OF GAS HUMIDITY

Introduction

The influence of gas humidity on the kinetics of hydration of lithium hydride was studied by running the humidifier at different temperatures. However, to prevent condensation, the humid gas in the reactor must be maintained at a temperature slightly higher than that of the humidifier, typically 5° C higher. Also, the reaction is quite exothermic, and the temperature of lithium hydride increases, sometimes substantially. Consequently, both moisture concentration and temperature of reaction changed simultaneously. The influence of temperature of reaction at constant humidity was investigated later in the program.

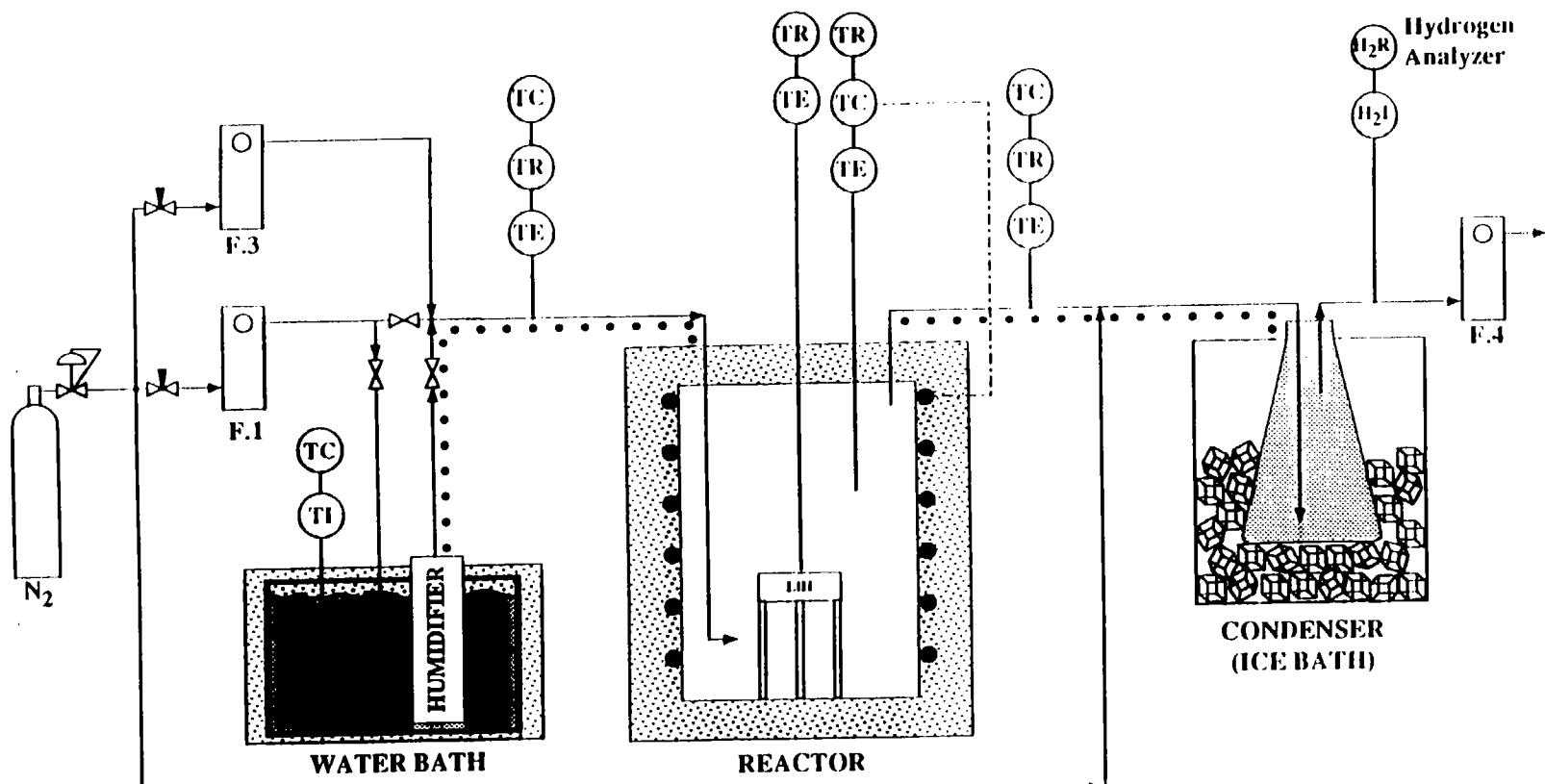
Hydrogen evolution rate was determined from its concentration in the exiting gas. An example of a recording of hydrogen concentration with time is shown in Fig. 2.

Test Results

Instant reaction rate versus test duration. For the design of the equipment to neutralize lithium hydride, the kinetics of the reaction is important. The kinetics is measured through the rate of hydrogen evolution.

Knowing the instant reaction rate permits calculating evolution at each point in time and the dilution of the reactor's exit gas stream necessary to keep hydrogen concentration below the flammability limit of 4% (and therefore below the explosive limit). Or, conversely, it permits adjusting operating conditions to stay below this limit at constant dilution.

FIGURE 1 EXPERIMENTAL SETUP



LEGEND	
.....	Heat Tracing
[Stippled Box]	Insulation
[Valve Symbol]	Needle Valve
[Valve Symbol]	Block valve

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Figure 1. Experimental Setup.

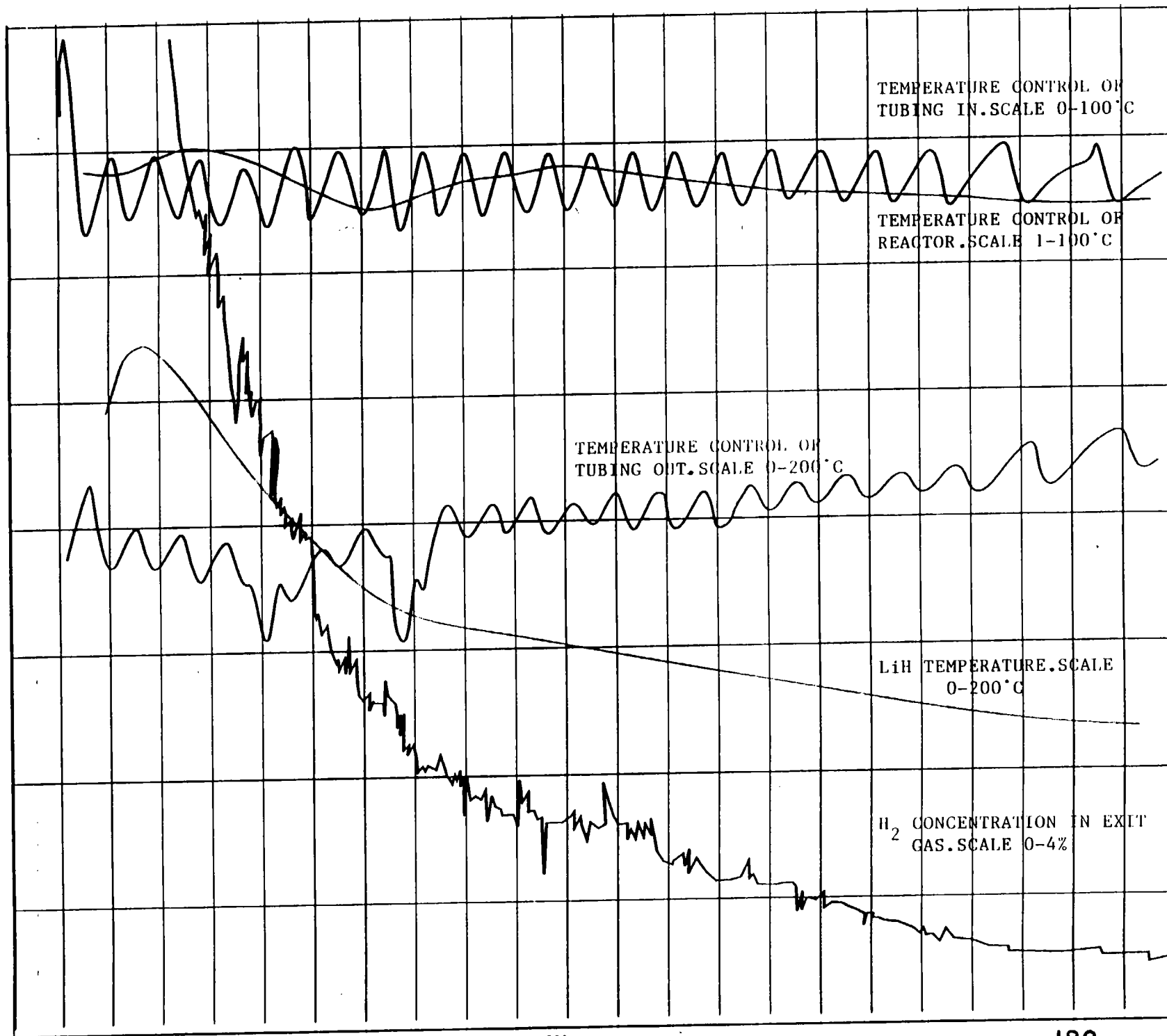


Figure 2. Recording for Test 16 (Humidifier Temperature 80.6° C).

The instant reaction rate may be a function only of the surface area of the unreacted lithium hydride, or it may be affected by the accumulation of a semi-impervious layer of hydroxide as the reaction proceeds. It may also vary with the humidity, temperature, gas retention time, etc. If a relationship between reaction rate and these variables can be determined, the equipment can be designed to treat larger quantities of lithium hydride.

The average reaction rate over the duration of treatment is another important factor. It indicates whether treatment can be effected in one shift or what conditions to use to complete treatment in a given period of time. The duration of treatment is somewhat imprecise because hydrogen evolution at the end of the test is very low. To compare tests, it is more accurate to determine, for example, the time required for evolution of 80% of the total volume of hydrogen.

Calculation of the instant reaction rate. A model of hydrogen evolution has been made. It assumes that, for a given set of operating conditions, the hydrogen evolution rate with time is a function only of the surface area of unreacted lithium hydride. With this assumption, the hydrogen generation rate, for example in liter/minute/gram, is given by an equation

$$R = ak(1 - bkt)^2; \quad (1)$$

a and b are constants that have been determined; t is the time; and k is the reaction rate per unit of time and surface area. With the assumption of this model, k is a constant.

The cumulative volume of hydrogen, V_c with time is given by

$$V_c = c[1 - (1 - dkt)^3]; \quad (2)$$

c and d are constants. V_c has been experimentally determined, which permits calculating k as

$$k = \frac{e}{t} \left[1 - (1 - fV_c)^{\frac{1}{3}} \right]; \quad (3)$$

e and f are constants.

Experimental determination of the instant reaction. Tests were run at various humidifier temperatures. These tests show a strong influence of the humidifier temperature on the instant volume of hydrogen generated and the time required to complete the reaction. This effect is illustrated in Fig. 3 and 4 for three selected temperatures. It is obvious that the kinetics of the reaction is greatly increased by higher temperature and humidity.

The instant reaction rate was calculated at different times for each test. The rate k is calculated from the theoretical hydrogen volume of 3 liters per gram of LiH at room temperature.

Figure 5 shows the relationship between the reaction rate and the humidity content of the gas. Humidity is given as the percentage by volume of the humid gas that is water vapor.

TEST #'S (6,10 & 21). HUMIDIFIER TEMP deg C (36.1,69.4 & 80.6) RESPECTIVELY

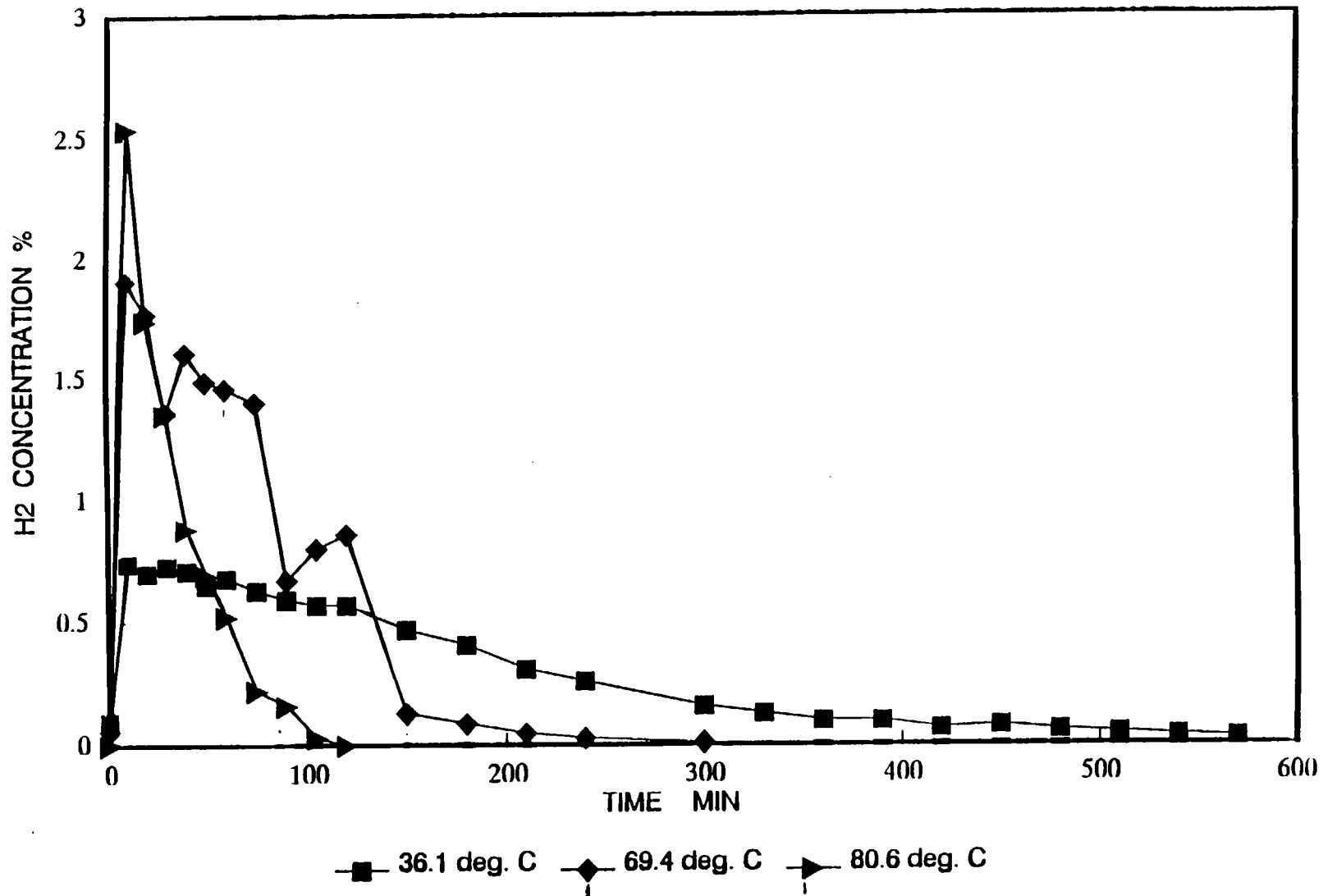


Figure 3. Hydrogen Concentrations Vs. Time.

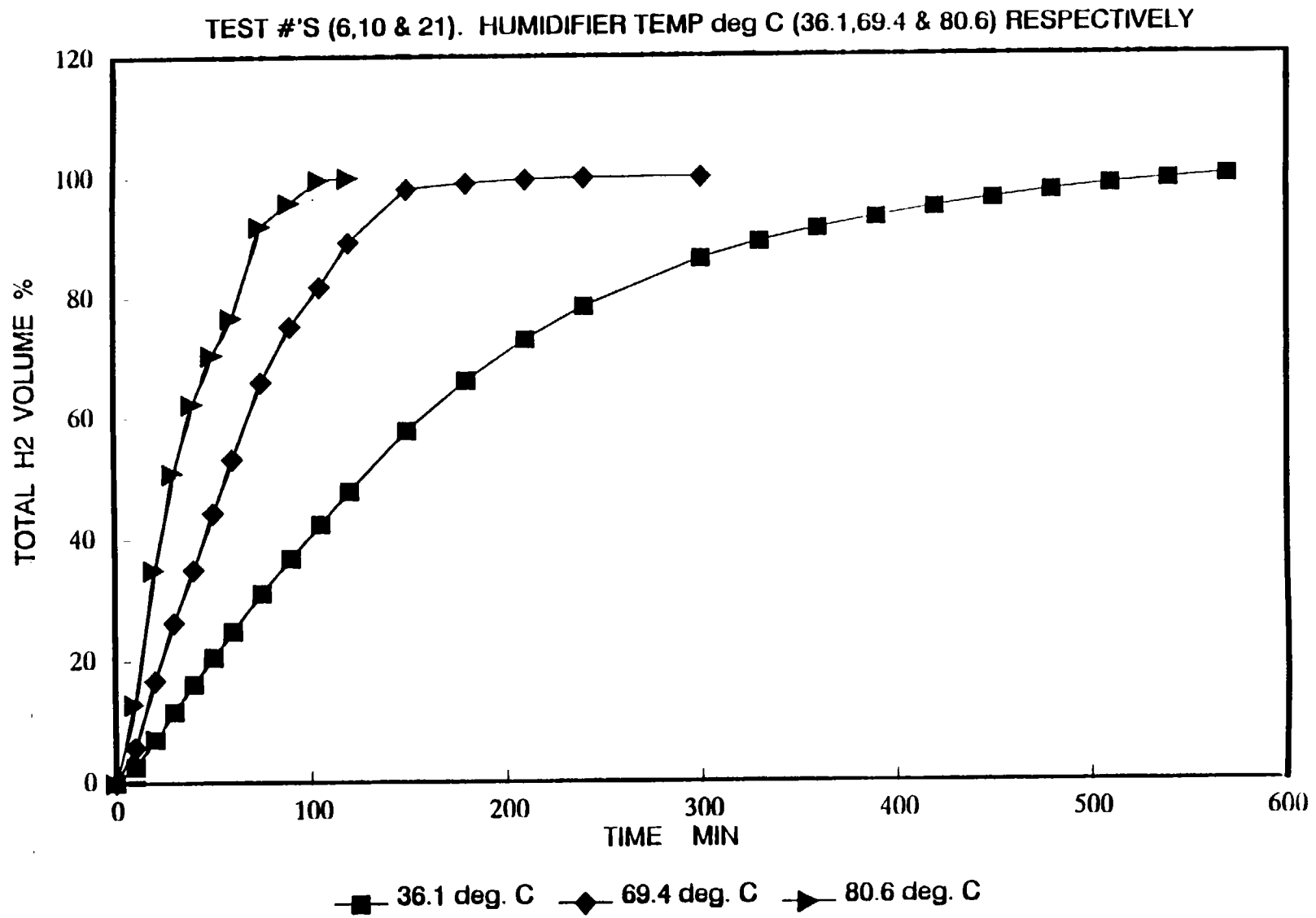


Figure 4. % Total H₂O Volume Vs. Time.

Data evaluation. Figure 5, which is on a semi-logarithmic scale, shows a relatively linear relationship. The points do not line up better for several reasons.

- The product of hydration is a function of the temperature. As mentioned previously, humidity was increased by increasing the humidifier temperature, and hydration also had to be done at a higher temperature to prevent condensation. Figure 6 shows the hydration ratio--the weight ratio of hydrated lithium hydride to the starting weight--as a function of the temperature. At about 80° C and above, it is close to the theoretical ratio of 3.0 for LiOH. Between 35° C and 70° C, the ratio falls between LiOH, H₂O (5.25) and LiOH, 0.5 H₂O (4.1). During the test, the lithium hydride temperature increases substantially for some time because of the exothermicity of the reaction. For example, Fig. 7 shows the lithium hydride temperature for a test run at a reactor temperature of 53° C. It increases to about 60° C for about 100 minutes. It is possible that the hydration product is a mixture of LiOH, H₂O, and LiOH, although no positive identification (such as by x-ray diffraction) was made. Typically, the high-temperature product of hydration was dry and grainy, while low-temperature products were deliquescent.

It is believed that below 35° C, the reaction rate was too slow, and complete hydration was not reached.

- Most tests were fairly reproducible. For example, Fig. 8 shows three tests run at 80.6° C. However, tests run with the humidities at near boiling were more erratic. Test runs at room temperature were too slow to be completed in a day's time.
- The calculation of the rate of reaction assumed a single particle size. Under the microscope, it is obvious that there is a relatively wide range of sizes. The sample used for the test was quite small (0.5 g) and differences in size distribution from one test to the next are likely.
- Drifting of the hydrogen analyzer calibration was fairly common.

CONCLUSION

The influence of gas humidity on the reaction rate with lithium hydride was determined and can be used for preliminary treatment equipment design. To prevent formation of a deliquescent compound--which could impede the reaction for large quantities of chunky lithium hydride--and have a relatively rapid reaction rate, it was decided to run further tests at 80° C.

More accurate values of the reaction rate will be determined by using well-defined screen sizes as well as chunks of lithium hydride. This will also permit verifying the assumption that the reaction rate is a function only of the surface area when other conditions are kept constant.

Other tests will study the influence of reactor temperature above the minimum required for a given humidity level and others will aim at decreasing nitrogen consumption. Other water-reactive wastes will be tested.

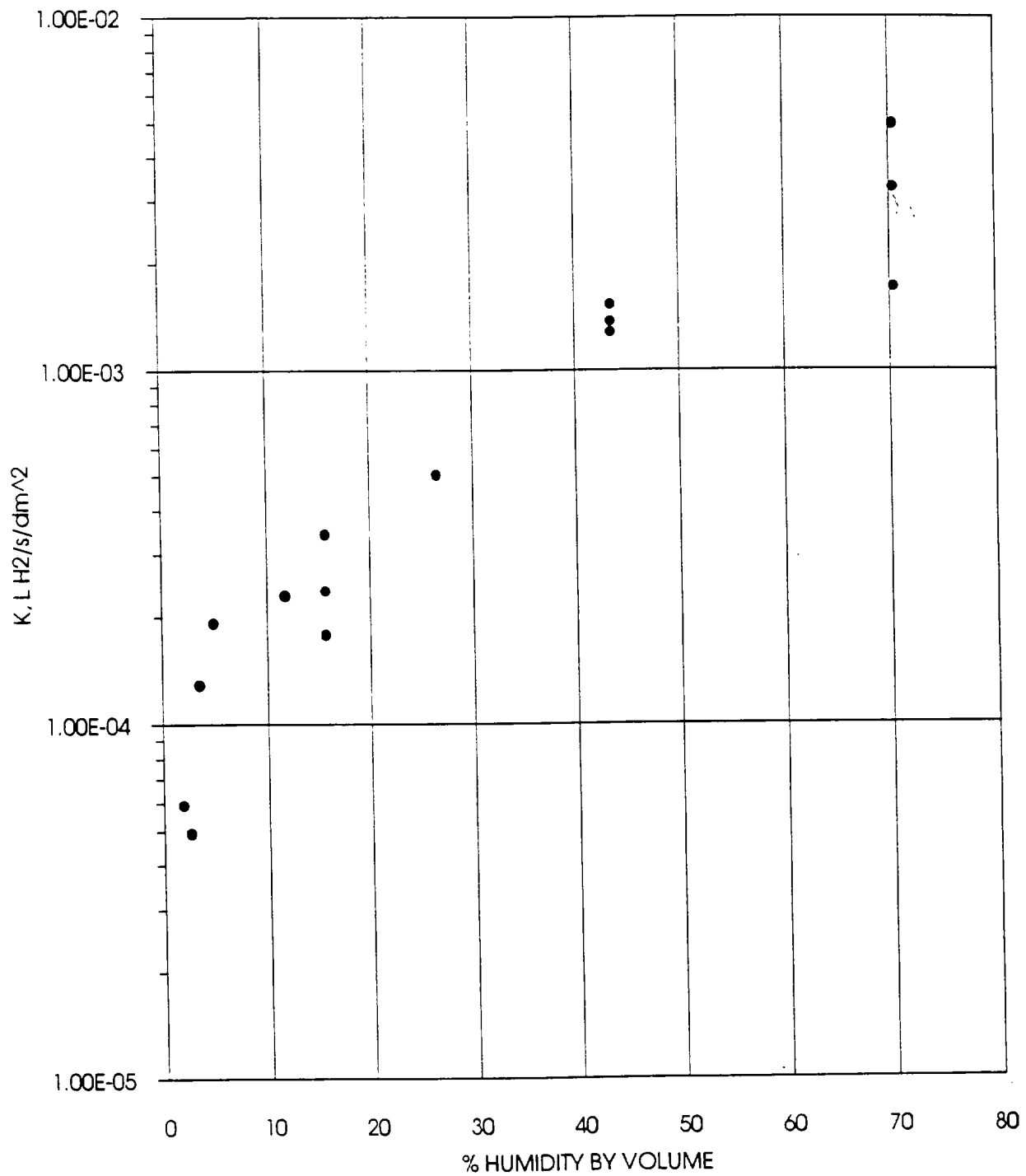


Figure 5. K Vs. % Humidity.

TESTS #S 2 - 24

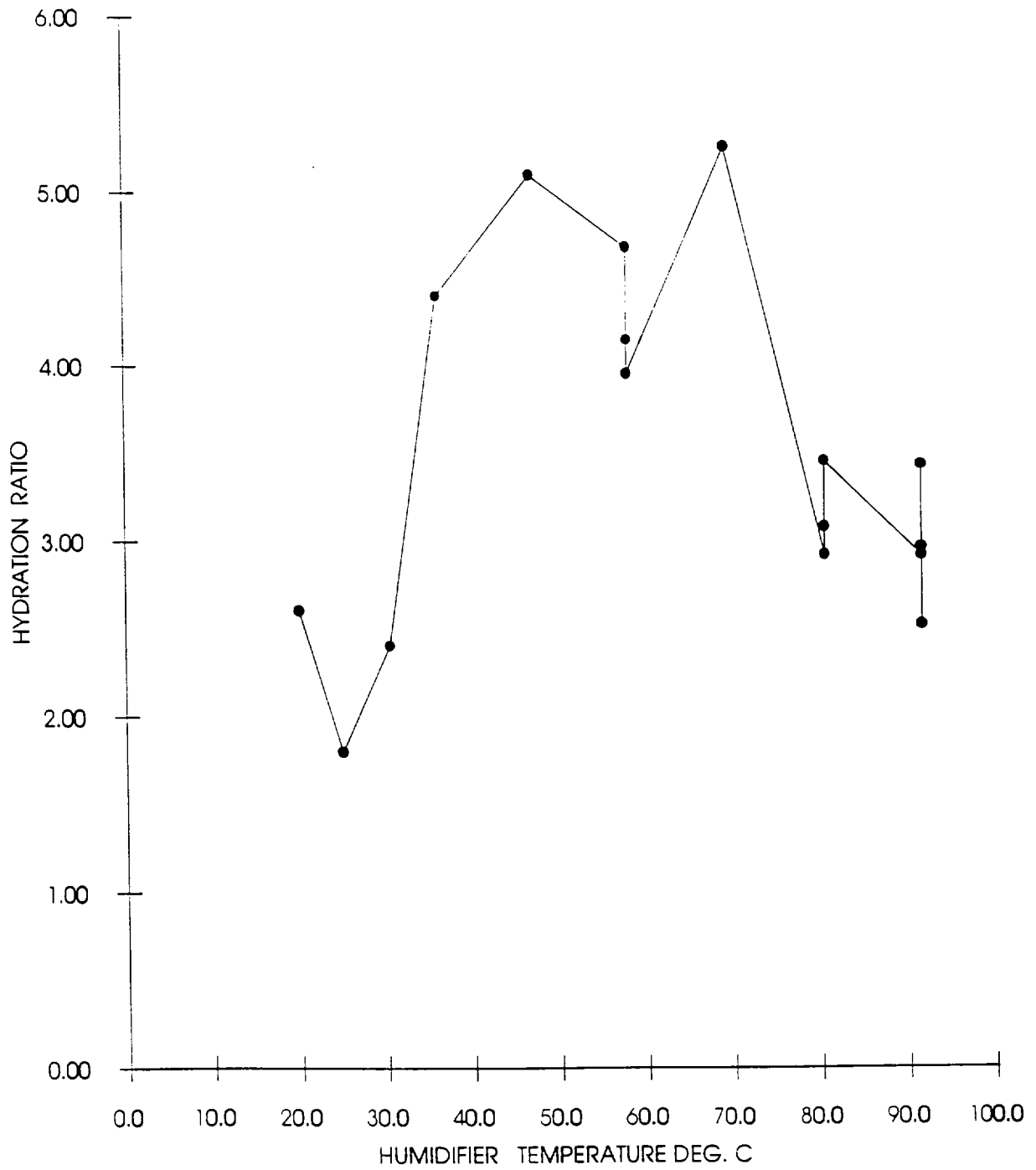


Figure 6. Hydration Ratio Vs. Humidifier Temperature.

TEST #8. HUMIDIFIER TEMPERATURE: 47 Deg C

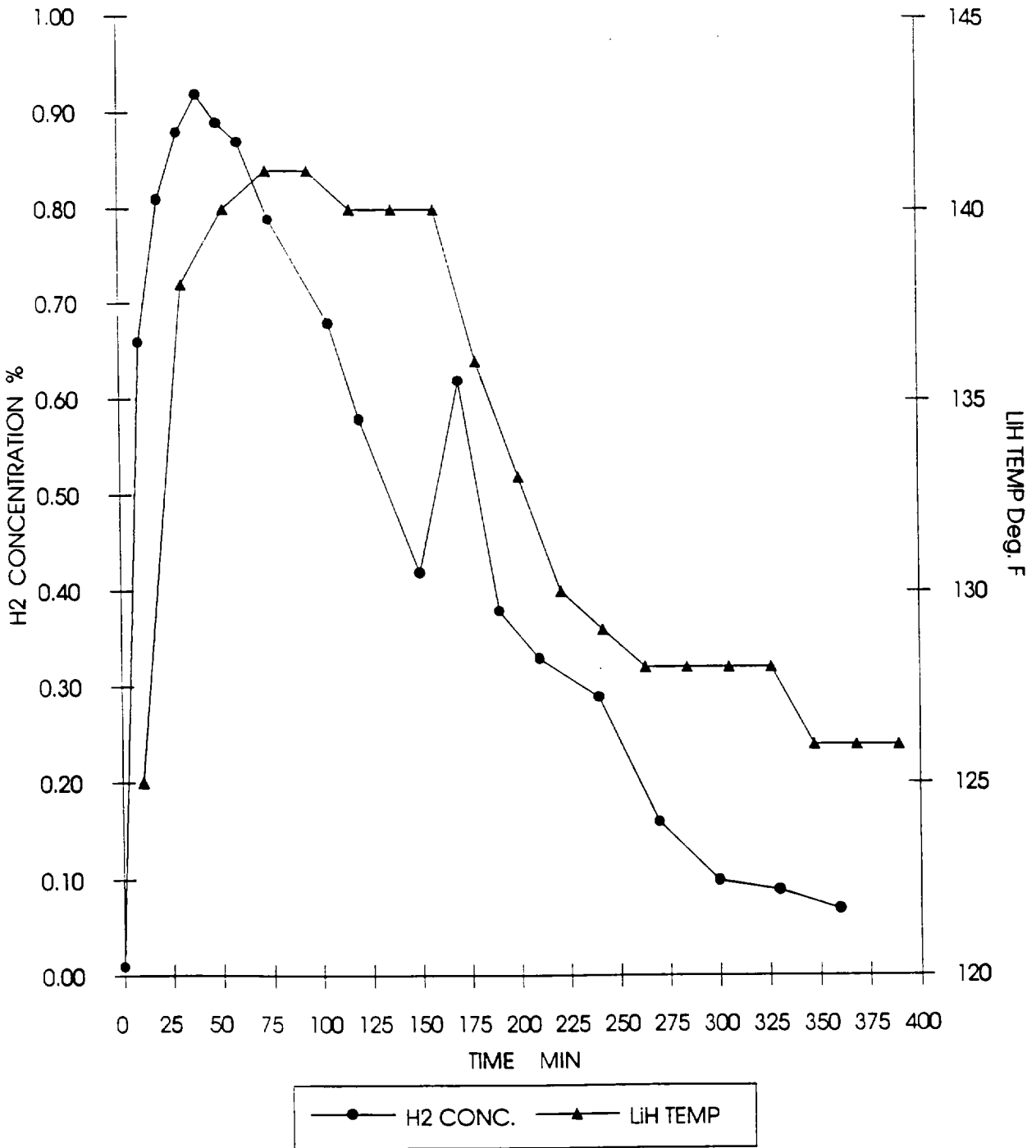


Figure 7. Hydrogen Concentration/LiH Temperature Vs. Time.

TEST #'S 16,20 & 21. HUMIDIFIER TEMP AT 80.6 deg C

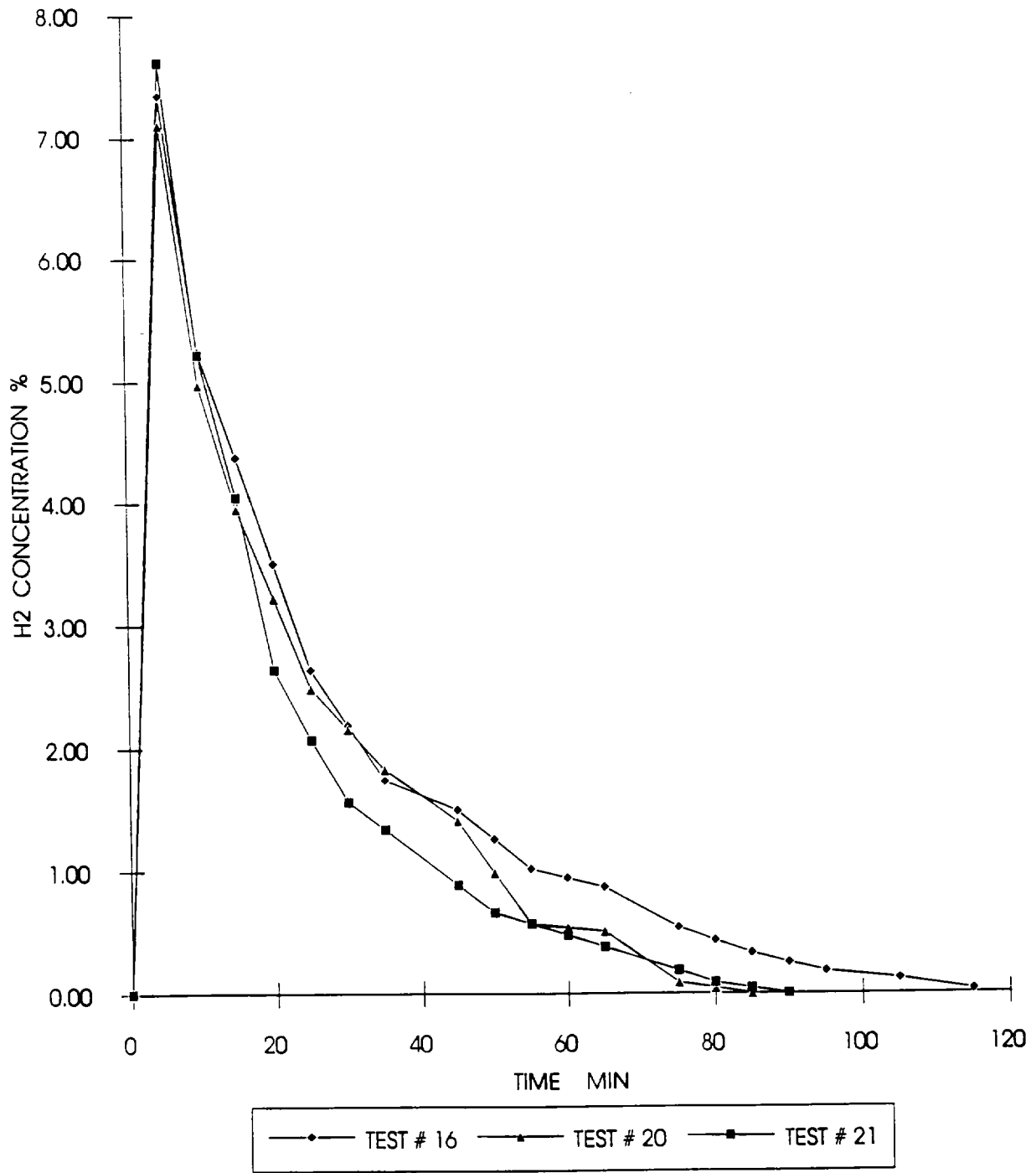


Figure 8. Reproducibility of H2 Evolution.

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