~~Hatson~~

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Department of Chemistry

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50-320
(F)

April 24, 1979

Dr. Robert J. Budnitz
Office of Nuclear Regulatory Research
Nuclear Regulatory Commission
Washington, D. C. 20555

Dear Bob:

I am enclosing the summary of our telephone conversations and further thoughts on the accident which you requested.

Sincerely,

Harold A. Schwarz

Enclosure
HAS:bw

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Radiation Chemistry of the Three Mile River Accident

The bubble formed during the accident contained 1000 ft^3 of hydrogen at 1000 psi at around 400°F. This gas was above (and assumed to be nearly in equilibrium with) 10000 ft^3 of cooling water at nearly neutral pH, about ½ of which was in the reactor. The water was being irradiated by dissolved fission products and by γ-rays from inside the fuel rods. The question was whether or not hydrogen and/or oxygen would continue to be formed by water radiolysis.

Nearly all the radiation was absorbed in the water phase, consequently it was only necessary to consider the cooling water itself. The concentration of hydrogen in the cooling water was about 0.046 moles per liter, based on the pressure over the solution. In addition, the water might contain fission product iodine at a concentration as high as 0.1 ppm and several other fission products at comparable concentration. Part of the Zirconium cladding was oxidized to ZrO_2 which is essentially insoluble in water at neutral pH. Ferric and ferrous iron could conceivably be present from reaction with the core vessel, but ferric solubility is rather limited, probably about 1 ppm, and anyway there should have been no more iron present than is there during normal operating conditions. It was assumed that there was no copper present, other than fission product amounts. Consequently it would appear that the total concentration of dissolved species which were very reactive towards the free radicals produced in water radiolysis was about 1 ppm, certainly no more than 10 ppm.

Water radiolysis by fission products produces molecular hydrogen and hydrogen peroxide in small quantities and larger amounts of the hydroxyl radical, OH, and reducing radicals. Consider first the molecular hydrogen and the hydroxyl radical. They are formed in yields of 0.4 and 2.8 molecules per 100 ev, respectively. The hydroxyl radical reacts with hydrogen

$$OH + H_2 \rightarrow H + H_2O$$

and this is the only reaction which needs consideration in determining whether or not more hydrogen will be produced. If 1/7 or more of the OH radicals react this way, then no more hydrogen will be produced.

The rate coefficient for this reaction is

$$k = 9.2 \times 10^9 \exp\left(\frac{-1620}{T}\right)$$

or 3.0×10^8 M^{-1} sec^{-1} at 200°C (400°F). The maximum possible rate constant (diffusion-limited) for any OH reaction would be about 3×10^{10} at this temperature. The rate of the reaction is the product of the rate coefficient and the concentrations of the reactants $[k \times C(OH) \times C(H_2)]$, so the fraction of OH radicals reacting with hydrogen is at least

$$\frac{3 \times 10^8 \times 0.046}{3 \times 10^8 \times 0.046 + 3 \times 10^{10} C}$$

where C is the concentration in moles per liter of reactants with maximum possible rate constants. This fraction is greater than 1/7 if C is less than 2.8×10^{-3} M. For an atomic weight of 100, this would be 280 ppm. With less than 10 ppm of reactive impurity present, essentially all of the hydroxyl radicals reacted with hydrogen to produce water and hydrogen atoms. Thus all radicals produced by radiolysis will end up as reducing radicals, and whether they are all hydrogen atoms or half of them are hydrated electrons (as initially produced) is immaterial. Both react with oxygen at diffusion-limited rates. Oxygen could be produced by decomposition of the hydrogen peroxide with a yield of about 0.3 molecules per 100 ev and a steady state concentration is determined by reaction with H atoms. The total radical yield is 6 radicals per 100 ev. Four hydrogen atoms are required to reduce one oxygen molecule to water, so the steady state of O_2 will be reached when 20% of the H atoms (or electrons) react with O_2. Impurities which would compete with the oxygen are ferric ions, and many oxidized fission products. As before, the sum of their concentrations was at most a few parts per million in the reactor, so the steady-state of O_2 should have been about 1 ppm or less. This was about 10^{-4} of the hydrogen present in the water and since the distributions of O_2 and H_2 between solution and gas are nearly the same, there should have been less than one part in 10^4 of O_2 in the hydrogen gas at steady-state.

If significant O_2 was present initially it should have been reduced to water with a yield of one molecule disappearing for every four radicals produced, or with a yield of -1.5 molecules per 100 ev. Based on a dose rate of 6×10^4 rads/hour given for Sunday, April 1 (which seems very low to me) about 1.8 pounds of O_2 per hour, or 0.5 ft^3 at 1000 psi, would disappear, until the steady-state level was reached.

In the above analysis which has the benefit of checking some literature references, one figure is different from those given you over the phone, namely that the $OH + H_2$ reaction proceeds at 1% the maximum theoretical rate at 400°F, not 10% as stated. I did not remember the correct value for the activation energy. On the other hand, a safety factor of 10 was included, so the answer, that one or two hundred parts per million of oxidizable impurities would be required to prevent the back reaction was the same.

The above analysis is based on what is actually dissolved in the water, but the radicals could possibly diffuse to the surface of a solid and react. Most of the solid is ZrO_2 and so the hydroxyl radicals would find nothing to react with. The hydrogen atoms could diffuse up to 0.01 cm in their lifetime (though impurities probably limit this distance to about 10^{-4} cm). One might expect some reduction of ZrO_2, perhaps to a hydride of some sort, in which case hydrogen could slowly disappear.

Most of the parameters used in this analysis are accurately (±10%) known in the region of 0°C to 100°C. Extrapolation is required for 200°C, but should involve little error, certainly no worse than a factor of two. Lack of knowledge about impurity levels is the most doubtful part.

JUN 7 1979

MEMORANDUM FOR: File

FROM: Saul Levine, Director
Office of Nuclear Regulatory Research

SUBJECT: PRINCIPAL CONTACTS MADE WITH EXTERNAL ORGANIZATIONS
DURING TMI 2 ACCIDENT

1. I spoke with Robert Ritzmann of Science Applications concerning H_2 and O_2 generation rates in TMI 2 vessel in the period March 31 - April 1. He informed me that, although an increase without considerations of a reformation rate of H_2 and O_2 due to bubble back pressure, that the 1 percent rate was probably too high. He also said that he felt the rate was probably no higher than 0.1 percent per day and could be zero, but that he did not have the data to calculate an explicit rate.

2. I spoke with James Proctor of the Naval Surface Weapons Center about the effects of a Hydrogen explosion on vessel integrity. He said the cylindrical position of the vessel would be subjected to about 6 percent strain, which should not break it, and that it would also be subjected to a lifting force of about 1.5×10^8 lbs. He could not calculate whether the main loop piping could hold the vessel down when subjected to this force, since he did not have detailed information on plant layout.

Original Signed By
Saul Levine

Saul Levine, Director
Office of Nuclear Regulatory Research

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SLevine rdg

OFFICE	RES:D					
SURNAME	SLevine/kr					
DATE	6/[illegible]/79					

Dr Murley R

UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D. C. 20555

JUN 5 1979

MEMORANDUM FOR: Saul Levine, Director
Office of Nuclear Regulatory Research

FROM: Robert J. Budnitz, Deputy Director
Office of Nuclear Regulatory Research

SUBJECT: INFORMATION ABOUT INDIVIDUALS AND ORGANIZATIONS CONTACTED BY ME DURING FIRST FEW DAYS AFTER THE TMI ACCIDENT

I am responding to the memorandum of May 31, 1979, from E. K. Cornell, "Request for Information from Presidential Commission." I have gone over my log book for that period, and have found seven outside individuals with whom I had substantive contact. In each case, my contact was the only or the primary NRC contact. Besides these individuals, there is a large number with whom I spoke but for whom the primary contact was you or T. Murley. I assume that you and he are assembling your own lists, similar to mine, and that you will cover those other individuals.

For each individual, I will indicate their organizational affiliation, address and telephone number, as well as a brief description of what information was furnished.

1. Dr. Richard L. Garwin (I.B.M., Yorktown Heights, NY 10598, (914) 945-2555). On Saturday morning, March 31, I was called at home by Dr. Garwin, an old friend, and he provided a number of ideas to me about things that one might attempt to do to eliminate or reduce the pressure from hydrogen within the primary system of the TMI reactor. His ideas included putting a snake-like tube into the vessel, and using chemical means to combine hydrogen with other substances. He also gave me some insight into how important the back reaction is in calculating the shock pressure in a fast burn or detonation of hydrogen in a vessel like the TMI reactor vessel. He referred me to Dr. Harry Petschek of AVCO (see below) for assistance on the hydrogen combustion problem. Later that date, and again on Sunday, April 1, I talked with Dr. Garwin by telephone, to follow up on his understanding of pressure shock waves, something about which he had extensive advice.

2. Dr. Harry Petschek (AVCO Everett Research Laboratory, Everett, MA 02149, (617) 389-3000). On Dr. Garwin's suggestion, I called Dr. Petschek on March 31, finally reaching him at home in late

morning. He responded immediately by indicating that he and some colleagues could assist in understanding the issue of hydrogen combustibility and combustion kinetics in a reactor vessel such as at TMI. Later that day and through Sunday, April 1, I spoke, two or three times, to Dr. Petschek and one or two of his colleagues. They worked on the questions of what concentration of oxygen in pure hydrogen would be the threshold for combustion, particularly at the temperatures and pressures thought to be present at TMI (about 1000 psi at many hundreds of degrees F), and he reported back sometime Sunday on those. Dr. Petschek also referred me to Dr. Bernard Lewis in Pittsburgh, who turned out to be a highly-regarded expert in just these same issues.

3. Dr. Bernard Lewis (Combustion and Explosives Research, Inc., 1016 Oliver Building, Pittsburgh, PA 15222, (412) 391-3633). I finally reached Dr. Lewis, on referral from Dr. Petschek, on Sunday morning, April 1. He acknowledged expertise on the combustibility of hydrogen and oxygen; indeed, he is the coauthor of the definitive textbook on this subject. He and an assistant, reached at home on Sunday morning, worked through that day and part of Monday, April 2, and gave important advice on the issues that governed the physical behavior of hydrogen and oxygen burning in conditions such as were thought to exist at TMI. He gave information about the mixture of oxygen in pure hydrogen that would be a combustion threshold, talked at length to me about the physical difference between combustion and explosion, and what would be the impact of gaseous impurities. He reported back his preliminary conclusions sometime after midday on Sunday, April 1, and his final conclusions in midmorning of Monday, April 2. He calculated pressure ratios (pressure within a fast burning situation vs. starting pressure), detonation thresholds, heat release, flame temperatures, and other parameters. His insight was valuable in providing a perspective on which parameters were, and which were not, important in modifying the result of what was calculated using approximations.

4. Dr. Harold A. Schwarz (Brookhaven National Laboratory, Upton, NY 11973, FTS Tel. 666-4330). Dr. Schwarz was referred to us by Dr. H. J. Kouts of BNL, who called several times during the TMI incident to provide advice. Dr. Schwarz worked much of the weekend of March 31 and April 1 on calculating the production and recombination rates of oxygen in the TMI primary coolant water. He did these calculations at home mostly, I think; telephone contacts with him during the weekend were at his home. He reported on the considerations that were involved in his calculations, and showed definitively that oxygen generation from radiolysis would not result in much oxygen in the gas phase, because of the recombination reaction with the assumed large hydrogen gas overpressure and the associated dissolved hydrogen. We were apprised of the preliminary results of Dr. Schwarz' work early on the morning of April 1, in my memory, but it was not firmed up until sometime shortly after midday on that day. Dr. Schwarz continued with his work for several days after Sunday, April 1, and filed a description of his calculation with NRC on April 24.

5. Dr. Heinz Heinemann (Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720, (415) 486-6000). I telephoned Dr. Heinemann in early morning of Saturday, March 31 to follow up a suggestion of Dr. Garwin that the oil companies might have expertise in snake-like methods for extracting hydrogen from a pressure vessel like the TMI reactor vessel. Dr. Heinemann is a chemical engineer at my former laboratory in Berkeley and is a colleague and friend there, who spent most of his life working for Mobil Oil Corporation. Dr. Heinemann referred me to Dr. J. Penick of Mobil, whom I called subsequently. Dr. Heinemann also discussed with me the question of addition of catalytic chemical agents to reduce the hydrogen in water solution. Dr. Heinemann gave me the names of several catalysis chemists who might have expertise in this matter, and also enlisted in advice of two Berkeley colleagues. We talked several times over the weekend of March 31-April 1, but I turned over the entire problem of chemical hydrogen removal to others in NRC, and did not concern myself with the issue directly.

6. Mr. Joseph E. Penick (Mobil Oil Corporation, 150 E. 42 Street, New York, NY 10017, (212) 628-9757). I contacted Mr. Penick on Saturday morning, March 31, on referral from Dr. Heinemann. He said that he thought Mobil could assist NRC with advice on the availability of snake-like devices to extract gas from a TMI-like pressure vessel. He called back later during the weekend (I recall his return contact as occurring on Sunday, April 1) and indicated that devices such as we sought were not readily available in the Mobil Corporation, and unlikely to be available elsewhere in the petroleum industry. The problem was that the path into the reactor vessel from the outside to the upper dome was too tortuous for the use of the devices that did exist, and the fabrication of a special device would be quite difficult.

7. Dr. Laura Cherubini (17 Pandover Road, Billerica, MA 01821, (617) 667-9699. Dr. Cherubini called me on her own on Saturday, March 31, with a suggestion of chemical means to reduce or eliminate hydrogen dissolved in the reactor coolant water. I do not know how Dr. Cherubini received a reference to me. The method was to use algae that trap hydrogen from solution by presence of free electron acceptors. Since I was not expert in this matter I turned it over to others at NRC for follow-up. However, by the time anything more could be done with this suggestion, the perception of the importance of a "hydrogen bubble" had diminished, and I think that no further follow-up occurred.

Robert J. Budnitz, Deputy Director
Office of Nuclear Regulatory Research

cc: T. Murley

UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D. C. 20555

JUN 13 1979

MEMORANDUM FOR: The Files

FROM: Thomas E. Murley, Director
Division of Reactor Safety Research

SUBJECT: RECORD OF ACTIONS, THREE MILE ISLAND ACCIDENT
MARCH 28 - April 6

This memo records my major activities and lists the individuals with whom I had substantive contact during the Three Mile Island Accident and its immediate aftermath, March 28 - April 6, 1979.

On Wednesday, March 28, I learned about 9:30 a.m. that there had been an accident at TMI. Not much was known of the details except that there were high radiation levels in the plant and a general emergency had been declared by the utility. On Thursday morning I attended a briefing of the Commission by NRR staff where I gained the impression that the situation was generally under control, although the high radioactivity levels in the plant clearly indicated extensive fuel damage. On Friday, March 30, while on annual leave, I received a call from Saul Levine at 4:00 p.m. asking me to come to Tony Buhl's office to get some tests started to help resolve some problems at TMI. On the way to the office I heard a bulletin on the car radio that NRC had announced there was a danger of core melting at the Three Mile Island Nuclear Plant.

The following activities are listed by topic and are generally in chronological order.

Removal of the Hydrogen Bubble

Upon arrival in Tony Buhl's office I was informed that measurements at the site indicated there was a noncondensible hydrogen gas bubble in the reactor vessel having a volume of 1000-1500 cu. ft. at 1000 psi and 280°F. There was some concern that the bubble was growing and might lead to uncovering the core and potentially to fuel melting. One option being considered was to open the relief valve on the pressurizer and try to vent the hydrogen bubble out the valve to the containment building. It was recognized this would be a tricky maneuver since it would mean that the one pump operating at the time would have to be shut off and there was no assurance that it or any of the other three pumps could be restarted if they were subsequently needed.

At about 5:30 p.m., we called INEL (Larry Ybarrondo, Nick Kaufman, Hank Ziele and others), described the problem to them and asked if there were meaningful tests that could be done in the Semiscale facility to help decide whether and how to vent the hydrogen bubble. We described the TMI primary system layout and gave them the important plant dimensions and elevations. Later in the evening on Friday, they called back with the following information and suggestions:

- A test could be run in Semiscale using nitrogen gas to simulate the hydrogen venting maneuver in TMI.
- They recommended against such a maneuver in TMI, suggesting it was better to keep the plant in its then stable operating mode (this suggestion was relayed to the NRR personnel in the Incident Response Center).

After working all night to set up the Semiscale facility, the INEL staff ran a test on early Saturday morning (Enclosure 1). The results showed that the Semiscale system could be depressurized by opening the pressurizer relief valve and turning all pumps off but about half of the nitrogen gas in the bubble remained in the primary system -- principally in the steam generators. The electrically heated rods remained cooled during this maneuver. This information was passed on to the IRC and to B&W.

During the remainder of Saturday and Sunday, Wayne Lanning of the RES staff worked with B&W engineers and INEL to establish conditions for a second test using a larger helium gas bubble and injecting coolant from the High Pressure Injection System. This second test was run early Monday morning, April 2 (see Enclosure 2).

The Semiscale tests provided the following general information:

- They showed that the noncondensible gas in the bubble would not all vent out the relief valve -- in fact about half of the gas would remain in the primary coolant system.
- They showed that it would be difficult if not impossible to remove the gas from the primary system by subsequently restarting the primary pumps. Since the presence of gas in the high points of the steam generators could prevent natural circulation cooling, this information was a strong argument for leaving the gas bubble in the top of the vessel.
- They provided useful data for B&W in establishing the appropriate HPIS flow rate for their proposed emergency procedure in the event all primary pumps were lost.

Oxygen Production Rates

On Saturday, March 31, we received a question from the staff at the IRC whether there could be sufficient oxygen gas in the primary system to form an explosive mixture and thereby constitute a threat to the reactor pressure vessel. The answer to this question proved to be elusive.

I discussed this question with staff members from INEL (Sid Cohen, Ron Ayers and Jack Liebenthal). Concurrently, Saul Levine called Bob Ritzmann of Science Applications Inc., and we understood that Bob Tedesco of NRR was contacting staff at KAPL. The information I received from INEL was based on reported data from the Cooper plant (a BWR) and was scaled down to the power level of 25 MWt. Their conclusions, which they stressed were extremely conservative, were that the hydrogen bubble contained about 2.2% oxygen and that it would take at least 4 to 5 more days to reach 5% oxygen concentration. I was later given some data from the Advanced Test Reactor (ATR) that was purported to support the data from the Cooper plant.

I found it very difficult to piece together all of the information into a consistent story. The Cooper BWR data were not directly applicable to TMI (a PWR) although there was some boiling in the TMI core. Similarly, the ATR is a low pressure (150 psi) reactor and was also not directly applicable to TMI. Late on Saturday evening I received a call from Rob Ritzmann who reported that he was not having much luck in calculating the oxygen concentration, although he believed it was below the flammability limit.

Some time after midnight on Sunday morning, I went to the Incident Response Center where Roger Mattson asked what we were finding. I told him that the picture on oxygen concentration was confused, but that a conservative estimate seemed to be that the oxygen concentration in the hydrogen bubble was increasing at the rate of 1% per day after reactor scram.

Later that morning (around 9:00 a.m.) Roger Mattson met with Saul Levine, Bob Budnitz and me at the IRC prior to leaving for the TMI site. Chairman Hendrie, Commissioner Gilinsky and Commissioner Kennedy came and went throughout this short meeting as I recall. Mattson summarized the following information as the distillation of all of the input he had received:

Flammability limit	$\geq$ 5% O_2 in pure H_2
Detonation limit	$\geq$ 12% O_2 in pure H_2
Combustion limit	$\geq$ 18% O_2 in H_2/steam
O_2 production rate	$\simeq$ 1% O_2 per day in H_2 bubble
Current O_2 concentration	$\simeq$ 5% O_2 in H_2 bubble

After this meeting, I spent little further time on the oxygen concentration question.

Potential Pressures from Hydrogen Explosion

On Sunday morning someone suggested that I collect information on what pressures could be generated if there were a hydrogen explosion in the pressure vessel. I found that Vince Noonan of NRR was the focus in NRC for these analyses and I therefore was involved only peripherally.

I received information that Dr. Norman Slag of Picatinny Arsenal had made calculations showing a sharp peak pressure of 12,600 psi for the case of a detonation of a 1000 cu. ft. bubble containing a mixture of 83% H_2, 12% O_2 and 5% steam. This pressure appeared to be consistent with information received by Bob Budnitz from Dr. Bernard Lewis of Pittsburgh that pressures could reach 5 Po for deflagration and 13-14 Po for detonation (where Po = 1000 psi is the pressure of the bubble and the system initially).

This information was passed on to Vince Noonan and I had little further involvement after Sunday afternoon.

Hydrogen Gas Behavior

From the beginning of my involvement in the TMI accident one of the tasks being investigated, principally by Bob Budnitz, was how to eliminate the hydrogen bubble by mechanical or chemical means. During Saturday and Sunday I received a number of unsolicited suggestions from people calling in to NRC. One of the most novel suggestions came from Roger Billings, President of Billings Energy Co. in Provo, Utah. Billings specializes in hydrogen research and technology, and they had done work for DOE under a contract from DOE-Idaho. His suggestion was to inject into the primary coolant a large number of 2-4 micron diameter evacuated glass microspheres. The idea was that the hydrogen in solution would diffuse easily through the glass and be trapped in the spheres, thereby gradually deplenishing the hydrogen in the system. Billings claimed to have experience with these microspheres.

I felt the idea was worth a look, so I authorized INEL on Sunday night to have Billings start an experimental program on hydrogen behavior. The Billings staff began work on Sunday night and ran their first hydrogen solubility tests on Monday morning. Although the microsphere idea proved to be not feasible, Billings did some very good work over the following three weeks that proved very helpful in understanding hydrogen behavior in TMI (see Ecnlosure 3 for a complete report of their work).

Some of the conclusions reached from their work were the following:

- Adding nitrogen gas to TMI coolant to try to form ammonia (NH_3) and remove hydrogen would not work (reaction was too slow)
- Adding microspheres to trap hydrogen gas would not work (takes weeks)
- Adding hydrogen peroxide (H_2O_2) as a source of oxygen to combine with hydrogen in solution would not work (O_2 gas evolved within minutes)
- Measured H_2 solubility at TMI conditions
- Measured H_2 evolution rate if TMI were to depressurize
- Provided a means for determining the pressure at which H_2 saturation was reached if TMI were to depressurize (pressure rebound effect)

During the week of April 2-6, Billings was put in direct touch with the NRC team at the TMI site, and they continued to provide information to NRC during the following weeks.

Hydrogen Degassing

On Monday, April 2, I was asked to calculate how long it would take to remove hydrogen from the coolant by degassing through the letdown system and through the pressurizer spray system. I called Glen Jenks of ORNL for information on hydrogen removal through pressurizers, and he provided me with some useful data and several references to look up.

My calculations showed that it would take from 1 to 2 weeks to reduce the hydrogen in solution from 1600 scc/kg (saturated concentration at 850 psi and 280°F) to 300 scc/kg (saturated concentration at 300 psi and 140°F). These calculations also showed that it would take nearly a week to reduce the hydrogen bubble by degassing through the letdown system. The only way the hydrogen bubble could have been reduced from 1000 cu. ft. to zero in 2-3 days is by assuming high flow rates through the pressurizer spray line (15 gpm) and a high efficiency for hydrogen removal in the pressurizer (90%). I am skeptical that these flows and efficiencies were attained in TMI. I have not heard a convincing story of how the 1000 cu. ft. hydrogen bubble was reduced to nothing in 2-3 days.

Measurement of Water Level in Pressurizer

On April 5, I received a call from Tony Buhl to help with one of the instrument problems he was working on. The problem concerned what would happen if all the water level indicators were lost in TMI. Buhl was considering whether the resistance temperature device could be used as a backup level indicator by running a high current through the RTD and observing the change in temperature when the water level drops below the RTD in the pressurizer. I called Hank Ziele at INEL and put him in touch with Bob Shepard of ORNL to get the details of the RTD design. The INEL staff then ran a scoping test in an autoclave and determined that the technique could be used in principle to indicate water level in the pressurizer. I subsequently learned that there were practical problems at TMI that made this approach not feasible.

Follow-on Work

Since April 6, my staff and I have been involved in extensive analyses of the TMI accident. These activities are documented in the formal transmittals from RES to EDO.

TEMurley

Thomas E. Murley, Director
Division of Reactor Safety Research

Enclosures:
1. "Semiscale Pressurizer Relief Valve Venting from Three Mile Island Type Conditions" 3/31/79
2. "Second Semiscale Relief Valve Venting test from TMI Conditions" 4/2/79
3. "TMI Reactor Simulation Final Report," Billings Energy Corp., 4/20/79

cc: S. Levine
R. Budnitz
K. Cornell
J. Cummings

TO: W. D. LANNING

PRELIMINARY TEST RESULTS

SEMISCALE PRESSURIZER RELIEF VALVE VENTING FROM THREE MILE ISLAND TYPE CONDITIONS

.2 ft³ before venting

March 31, 1979

dupe

#1 [illegible]

A. SUMMARY

On March 30, 1979, NRC management personnel requested EG&G Idaho personnel to help evaluate alternative courses of action for securing the Three-Mile Island Plant (TMI). We conducted our evaluation. Amon several recommendations, we proposed conducting a venting test of the primary relief valve (PRV) in Semiscale from present TMI conditions to check the accuracy of calculations we performed on the response of TMI to such a venting condition.

We conducted the proposed test from 6:55 a.m. to 9:47 a.m. on March 31, 1979. Two-hundred forty channels of data were recorded. Th test was successful. We believe the test results may be of use to NRC in evaluating the probable TMI plant response if venting from present conditions is attempted.

The remainder of this report is divided into three sections. Section B presents a comparison of TMI and Semiscale significant parameters as best we know them. Section C provides the sequence of experimental events and significant pehnomena correlated with the time at which they occurred. Section D presents the calculated TMI plant response during venting from the PRV from the initial conditions provided by NRC. Section E presents our conclusions from pressurizer relief valve tests in Semiscale.

B. COMPARISON OF SEMISCALE AND THREE MILE ISLAND (TMI) SIGNIFICANT PARAMETERS

1. VOLUME RATIOS $\left(\frac{\text{Vol component}}{\text{Vol vessel}}\right)$

	B&W	Semiscale	SS/BW
Pressurizer	0.374	0.454	1.21
Cold Leg (one side) versus broken loop	0.118	0.255	2.16
Hot Leg (one side) versus broken loop	0.122	0.144	1.18
Total Loop (both sides)	0.974	1.596	1.639

2. ELEVATIONS (from ℄ Nozzle HL)

	B&W	Semiscale
Top of upper plenum	14 ft - 6 in.	13 ft - 2-1/2 in.
Top of core	4 ~~-4~~ ft - 0 in.	-6 ft - 0 in.
Surge line connection to HL	6 ft - 2-1/2 in.	4 ft - 0 in. ←
Surge line vertical drop (not from nozzle ℄)	12 ft - 8 in.	11 ft - 0 in.
Piping vertical height (total) (including pump suction)	68 ft - 0 in.	51.3 ft (BL) 21.3 ft (IL)
℄ Nozzle to top of tube (or pipe)	46 ft - 0 in.	41 ft (BL) 11 ft (IL)
Surge line below top of core	3 ft - 3-1/2 in.	2 ft - 0 in.

3. SIGNIFICANT DIFFERENCES

	B&W	Semiscale
Cold Leg	2 cold legs / side	1 cold leg / side (1 side scaled for 3/4 flow)
Hot Leg	1 per side	1 per side
Upper Plenum	Vent Valves	No Vent Valves
Hot Leg / Cold Leg Elevation Difference	None	8-1/2 in. (Hot Higher)
SG Elevations (difference)	None	IL @ 11 ft - 0 in. BL @ 41 ft - 0 in.

C. EXPERIMENTAL SEQUENCE AND SIGNIFICANT EVENTS

A description of the initial conditions for the TMI plant response test and a table of significant events follows. Also included is a description of the significant Semiscale system configuration or operating conditions that may not be typical of the TMI plant.

Initial Test Conditions

a. Nitrogen bubble initially established at a level of 43 in. above hot leg pipe upper invert (about 0.5 ft^3). The elevation of the bubble is higher than expected for the full scale plant.

b. No secondary side water was added to the steam generator. This lack of water would cause a lesser amount of energy to be transferred from ~~to~~ the primary fluid.

c. Pressurizer steam dome was established at 30% of the pressurizer volume.

d. Leak rate of the system was established since the flow out the simulated pressurizer relief valve flow was of the same magnitude as possible leak rate.

e. System was heated to 410°K utilizing the core and an initial pressure of 7.24 kPa was established.

Initial Test Conditions (Contd.)

f. Pumps were coasted down and an initial power of 7.64 kW was established. This power was about 2 kW above the scaled value to allow for energy losses to the structure.

TABLE OF SIGNIFICANT EVENTS

Time	Event
0	Experiment initiated (pressurizer steam bubble venting starte Initial clad temperature - 420°K (295°F) Initial core outlet water temperature - 411°K (280°F) Initial pressurizer pressure - 7.6 MPa (1100 psi) Initial inert gas / water interface at 1.35 m above (53.15 in. cold leg centerline Initial heat flux 4.1 kW/m^2 (1300 Btu/hr-ft^2)
0 - 1000 sec	Nitrogen bubble in upper head expands downward, pressurizer water level rises as steam is formed and vented. Pressure falls, temperatures rise slightly.
1000 sec	Pressurizer water level reaches vent connection Clad temperature - 435°K (323°F) Core outlet water temperature - 420°K (295°F) Pressurizer pressure - 4.7 MPa (680 psi) Gas / water interface - 0.36 m (14.17 in.) above cold leg centerline.
1000 - 3800 sec	Nitrogen bubble continues downward expansion, pushing water out pressurizer vent connection. Temperatures continue increasing, pressures fall.
3800 sec	Nitrogen / water interface reaches top of hot leg opening 0.25 m (9.84 in.) above cold leg centerline Clad temperature - 442°K (336°F) Core outlet fluid temperature - 427°K (309°F) Pressurizer pressure - 2.6 MPa (380 psi)

TABLE OF SIGNIFICANT EVENTS (Contd.)

Time	Event
3800 - 5000 sec	Nitrogen expands into loop piping. Steam generator drains through cold leg and downcomer forcing cool water into lower part of core. Clad temperatures generally decrease as well as pressure.
5000 sec	Steam generator tubes empty completely. Peak clad temperature - 456°K (361°F) Core outlet fluid temperature - 444°K (339°F) Pressure - 2.2 MPa (319 psi)
5000 - 7000 sec	Clad temperatures increase as core flow stagnates, fluid temperatures rise as pressure continues to fall.
7000 sec	Fluid temperature reaches saturation and bulk boiling begins in core. Core outlet fluid temperature - 452°K (354°F) Peak clad temperature - 456°K (361°F) Pressure - 0.8 MPa (116 psi)
7000 - 9000 sec	Low void fraction fluid rises in core, clad temperature decrease, fluid temperatures remain at saturation as pressure falls.
9000 sec	Test Shutdown. Nitrogen has expanded into steam generator but pressurizer appears to still be filled with liquid or very low void fraction fluid. Pressure - 0.34 MPa (49 psia) Clad temperature - 426°K (307°F) Fluid temperature - 423°K (302°F)

Core bulk boiling occurred when saturation conditions were reached. Max clad temperature - 456°K (361°F)

In several instances the Semiscale system configuration or operating conditions were not typical of the TMI Plant. The most significant instances include:

(1) Potential for structures to provide excessive cooling of the fluid.

(2) Lack of simulation of the PWR vent valves.

(3) Core elevation effects.

(4) Possible atypicality of power operated relief valve flow due to effects of size.

(5) Use of charging pumps to account for leakage from pump seals.

(6) Lack of steam generator secondary water.

The structures in the Semiscale Mod-3 system have excessive surface area which will cause atypical energy transfer during the course of a fluid temperature transient. During the simulation of a pressurizer relief transient the structures will absorb excess energy which would tend to increase the depressurization rate and provide cooler water to the core region. An attempt was made to provide more typical fluid conditions by increasing the core power level by about 35% above the scale value which was arrived at by determining the rate of energy transfer to the vessel structure and increasing the core power appropriately.

The Semiscale system cannot provide a particularly good simulation of vent valve actuation during a pressurizer relief drain test because of elevation differences between the hot and cold legs. However, this inability does not strongly influence the Semiscale test results since the influence of the vent valves on the TMI plant cold leg behavior is limited due to the cold leg geometry. No adverse effects on test results are expected in Semiscale pressurizer relief valve drain testing because of the lack of a vent valve simulation.

A particularly significant difference between the Semiscale facility and the TMI Plant is related to the location of the top of the core relative to the vessel nozzles. In the TMI plant the top of the core is approximately at the elevation of the vessel nozzles. In the Semiscale system, however, the top of the core is approximately 105 cm beneath the vessel cold leg nozzle. With these geometric differences, it is foreseeable that core uncovery could be accomplished more easily in the TMI plant than in the Semiscale Mod-3 system.

Flow through the Semiscale pressurizer relief valve simulation is not expected to completely duplicate, on a scaled basis, that which might occur in the TMI Plant. Critical flow through small orifices (e.g., the 0.030 in. diameter Semiscale flow area) has been shown to be different from that experienced in 2-in. diameter pipes, so that vent flow/pressure relief characteristics might reasonably be expected to differ somewhat between the two facilities.

Because of considerable leakage of pump seals (and other miscellaneous small leaks) it was necessary to provide makeup liquid to the system. The HPIS pump was run for brief periods at fixed intervals throughout the test to supply the additional liquid necessary to account for the pump seal leakage rate. Although the makeup rate was small compared to the discharge rate through the simulated pressurizer relief valve, the total amount of HPIS liquid injected into the system over the duration of the test was a substantial amount. Thus, considerable additional subcooling was added to the primary system liquid inventory through use of the HPIS pump. As a result, the core thermal response may have been less severe than would have otherwise occurred.

The secondary side of the steam generator was dry, i.e., no motive fluid for heat transfer. This condition minimized the influence of secondary heat transfer on the course of the PRV transient in Semiscale. If the temperature on the secondary side of the steam generator is lower than the primary system temperature the subcooling on the pump suction leg will be increased, thereby increasing the subcooling to the core. Conversely, if the secondary side temperature is higher than the primary side temperature the pump suction density will be reduced thereby reducing the core inlet subcooling. For a PRV transient the secondary side temperature should be less than or equal to the primary side temperature. Based on previous experiments conducted in Semiscale, steam generator heat transfer is not expected to have a significant influence on the pressurizer relief drain tests.

D. PRELIMINARY ASSESSMENT OF THE TMI PLANT RESPONSE DURING VENTING

Analysis

Simplified calculations were performed to evaluate expected response of TMI to the PRV release mode of depressurization. First, the heatup rate of the core fluid was calculated to be 480°F/hr if no circulation occurred (heating the core liquid volume only) and 170°F/hr if the total reactor vessel fluid volume were to be heated. (Neither calculation included fuel or metal mass heat capacity). From this it was concluded that makeup should be provided to assure core coverage as heat is removed by steaming. About 60 gpm was calculated as the required rate to meet the steam generation needs. The expansion of the (then assumed) 1500 ft^3 of gas to fill the hot leg, steam generator, and pressurizer to reach the point of gas venting and more rapid depressurization would reach this point at about 300 psi. At assumed liquid relief rate of 600 gpm and steam rate of 110,000 #/hr, this was calculated to take about one hour.

The Semiscale system depressurized slower; reaching about 350 psi in one hour with a smaller relative gas volume. Integrating the high velocity "gas" relief showed that the hot liquid in the pressurizer flashed to steam and separated yielding a larger total volume of steam to be relieved prior to the time of liquid relief. The data also showed that the pressurizer and surge line remained liquid full, thus not making that volume available for gas expansion. These features are being added to a more complex model. Initial indications are that a reasonable description of the pressure transient and volume change will result from this model, and it should be applicable to TMI.

E. CONCLUSIONS

(1) The Semiscale system can be depressurized via the proposed method to a level at which the RHR pumps can be activated and used to remove residual heat from the core.

(2) In the Semiscale system noncondensible gas did not vent easily or uniformly with the proposed method. The noncondensible gas bubble entered the hot leg at approximately 3800 seconds.

(3) Core uncovery in the Semiscale facility did not occur until after a point in time at which the RHR pumps could have been activated if desired (thus preventing core uncovery).

(4) The Semiscale results suggest that if ECC fluid is injected into the system at a rate comparable to that at which the system is being vented, significant benefits in the overall system response and core cooling may be realized.

(5) The heater rods in the Semiscale test remained in a mode of good cooling during the proposed transient and rod temperature rises were minimal.

(6) Depressurization from 1050 psia to 49 psia was accomplished in the Semiscale test in approximately 3 hours. Boiling in the core did not occur until approximately 6000 seconds after the vent relief transient was initiated.

TO: W. D. LANNING, NRC

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U.S. NUCLEAR REGULATORY COMMISSION
MAIL & MESSENGER BRANCH

PRELIMINARY TEST RESULTS

SECOND SEMISCALE RELIEF VALVE VENTING TEST
FROM THREE MILE ISLAND CONDITIONS

April 2, 1979

dupe
7904080415

A. SUMMARY

Results from the initial Semiscale Mod-3 test conducted at conditions similar to the Three Mile Island (TMI) plant provided significant insight into the growth and movement of an upper plenum bubble during continuous pressurizer relief valve (PRV) operation. On April 1, 1979 NRC management requested a second test to be conducted at conditions similar to the initial test except for a larger gas bubble volume and injection of a scaled amount of coolant from the HPIS.

The test was conducted between 1:18 a.m. and 4:35 a.m. on April 2, 1979. The test appears to be a success although some loss of data was experienced as a result of a malfunction in the data acquisition system. A preliminary evaluation of results indicates the test behavior was similar to the initial test. Injection of coolant from the HPIS maintained cooling in the core region. Pressurizer relief flow was terminated and recharging of the system with a high HPIS flow was initiated when the system pressure reached about 270 psia. The system was returned to a stable state where the primary coolant pump could be used to circulate flow within the primary system about one hour after termination of pressurizer relief flow.

B. INITIAL TEST CONDITIONS AND SEQUENCE OF EVENTS

A description of the initial conditions for the second TMI plant response test and a table of significant event follows. A table of the initial operating conditions Table I, and a description of significant Semiscale operating conditions are also included. A description of the system configuration that may not be typical are documented in the report on the initial Semiscale pressurizer relief test.

INITIAL TEST CONDITIONS

a) A Helium bubble was initially established at a level of 61 cm above the hot leg pipe upper invert (equivalent to 0.6 ft^3 of Helium). Helium was chosen for this test since its properties are relatively close to Hydrogen. The bubble size was chosen to provide a larger bubble volume than used on the initial test.

b) The diameter of the orifice used to simulate the relief valve was 0.091 cm. This diameter was slightly larger than the diameter used in the initial test (0.079 cm) and was adjusted based on results from the initial test to provide a steam flow more typical of the specified relief valve flow for the TMI plant.

c) The HPIS system was initiated at rupture at a constant rate of 12.6 ml/s (0.20 gpm). This rate was scaled to an average injection rate which was being considered for the TMI plant over a pressure range of 300 to 1000 psi. Additional injection was included to make up for the normal leakage from the Semiscale system.

d) The steam generator in the same loop as the pressurizer had a water level equivalent to 2/3 the total tube elevation. The initial steam generator fluid temperature was 416 K. The second steam generator was run with a dry secondary side due to difficulty in determining a consistent set of initial conditions.

e) An orifice was included in the intact loop hot leg to compensate for the difference in size, and hence elevation of the top invert (Figure 1), of the intact and broken loop pipes. This elevation difference was believed to have caused the intact and broken loops to behave differently in the initial test.

f) The core power was held constant at 21.5 kW throughout the test. This is substantially above the 3.9 kW level necessary to simulate the known TMI conditions. The additional 17.6 kW was included to make up for ambient and structural heat losses which are in excess of the TMI heat losses. The Semiscale heat losses were determined experimentally using initial test conditons. It is expected this excess power would cause the Semiscale core rod and fluid temperatures to be conservatively high compared to the TMI plant.

g) The initial pressurizer steam dome was about 50% of the pressurizer volume.

h) The system was heated to 416 K utilizing the core and an initial pressure of 7.24 MPa was established.

i) The pumps were coasted down and the initial power was established.

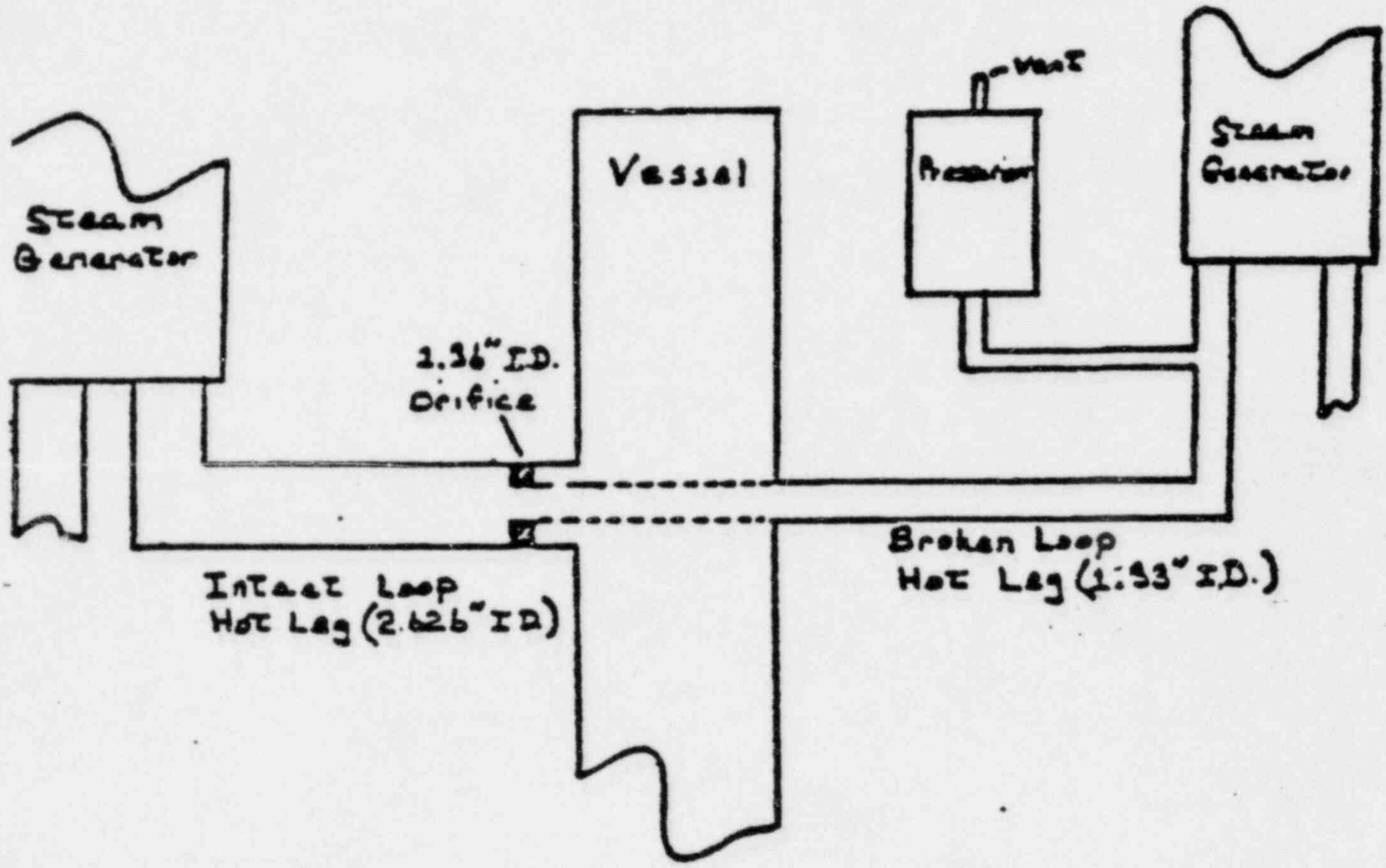

Figure 1 Schematic of the intact and broken loop hot legs.

TABLE OF SIGNIFICANT EVENTS

Time	Event
0	Experiment initiated (pressurizer steam bubble venting started Initial peak clad temperature - 442 K (336 F) Initial core outlet water temperature - 436 K (325 F) Initial pressurizer pressure - 7.3 MPa (1058 psi) Initial inert gas / water interface at 0.92 m above (36.4 in.) cold leg centerline Initial core power - 21.5 kW
- 200 s 0-200s	Helium bubble in upper head expands downward, pressurizer water level rises as steam is formed and vented. Pressure falls, temperatures rise slightly.
00 s 200s	Helium / water interface reaches top of hot leg opening 0.25 m (9.84 in.) above cold leg centerline Clad temperature - 442 K (336 F) Core outlet fluid temperature - 436 K (325 F) Pressurizer pressure - 6.0 MPa (870 psi)
00 - 700 s 200-700s	Helium continues to expand pushing water into pressurizer and filling intact and broken loop steam generators with gas.
00 s 700s	Pressurizer water level reaches vent connection Clad temperature - 465 K (378 F) Core outlet water temperature - 465 K (378 F) Pressurizer pressure - 4.45 MPa (640 psi)

TABLE OF SIGNIFICANT EVENTS (Contd.)

ime	Event
0 - 2200 s 700-2200 s	Helium bubble continues downward expansion, pushing water out pressurizer vent connection. Temperatures continue increasing, pressures fall.
00 - 2800 s 2200-2800 s	Intact and broken loop steam generators drain through cold legs and downcomer forcing cool water into lower part of core. Clad temperatures generally decrease as well as pressur
00 - 4800 s 2800-4800 s	Data acquisition system malfunctioned during this period. All data was lost. During this time the steam generators complete drained but some water remained in the bottom of the hot leg piping.
00 s 4800 s	Data acquisition system back on line. Recording of data continued.
00 - 5800 s 4800-5800 s	Temperatures continue to decrease as system pressure decreases,
00 - 6700 s 5800-6700 s	Clad temperatures increase as core flow stagnates, fluid temperatures rise as pressure continues to fall.
00 s 6700 s	Test terminated when vent valve was closed. HPIS injection ra increased to 0.63 gpm causing system pressure increase.
00 s 9100 s	System pressure peaked at 1050 psia. At maximum system pressur the broken loop pump was slowly brought up to speed and initial conditions were re-established. Helium was forced out of brok loop but collected in intact loop. It appeared impossible to restart and achieve full flow from both pumps since Helium woul collect in one pump when the other pump was being started, preventing the second pump from establishing a net positive suction head.

TABLE OF SIGNIFICANT EVENTS (Contd.)

Time	Event
12,000 s	Test Shutdown

TABLE I - LIST OF INITIAL CONDITIONS

CONDITIONS FOR SEMISCALE TEST 3MI2

PRIMARY SYSTEM

Pressure - 7.29 MPa (1058. psia)

Temperature - 416. K (289.4 F)

PRESSURIZER

Pressure - 7.29 MPa (1058. psia)

Temperature -	560 K	(548.8 F)	Top
	400 K	(260.6 F)	Bottom

Level - 80%

Heaters - Turned off after pressurizer conditions established

STEAM GENERATORS

Intact Loop
    Level - 0. (Dry Secondary)

Broken Loop
    Level - 1/3 - 2/3 full
    Temperature - 416 K (290 F)

CORE POWER

Decay Heat - 3.9 kW

Heat Losses - 17.6 kW

Total - 21.5 kW

TABLE I - LIST OF INITIAL CONDITIONS (Contd.)

UPPER PLENUM / UPPER HEAD

Helium Volume - $1.67 \times 10^4 \pm 567$ cm^3 (0.59 ± 0.02 ft^3)

Water volume above hot leg nozzles - 3400 cm^3 (0.16 ft^3)

HIGH PRESSURE INJECTION PUMP

Location - Intact Loop Cold Leg

Rate (constant) - 12.6 ml/s (0.20 gpm)

CORE FLUID TEMPERATURE DISTRIBUTION

TOP - 436 K (325.4 F)
MIDDLE - 430 K (314.6 F)
BOTTOM - 420 K (296.6 F)

LOOP COOLANT PUMPS

Standby conditions (power off)

C. CONCLUSIONS

1) The additional gas volume and the enlargement of the size of the scaled relief valve area influenced system response somewhat but did not change the general conclusion that the system could be depressurized to a level where the RHR system could be activated without significantly shocking the system.

2) The use of the HPIS pump during the early part of the experiment caused cold water to be supplied to the core. This additional cold water maintained high density fluid in the core and contributed to sustained effective cooling of the rods.

3) Based on a comparison of subcooled flow rates the simulated relief valve flow in Semiscale is 70 to 90 percent of the subcooled flow calculated for the TMI plant valves. This lower flow may be due to the presence of noncondensable gases or to orifice size. The possibility of reducing the subcooled relief valve flow when noncondensable gases are present should be considered in calculations performed for the TMI valves.

4) The need for higher core powers to make up for additional system heat losses resulted in higher rod temperatures and fluid temperatures in Semiscale than would be expected in the TMI plant. These higher temperatures would influence the depressurization rate late in the test when the pressure reached saturation levels.

5) After completion of the system depressurization, attempts were made to repressurize the system and re-establish initial operating conditions with both Semiscale pumps operating. It was discovered that when either one of the pumps was started gas was forced through the loops into the other loop pump and the remaining pump could not be started and maintained at full flow because a net positive suction head could not be established. Therefore, it appears that once Helium is present in the Semiscale loop piping it is unlikely that the gas can be removed from the system by operating both pumps simultaneously.

6) In Semiscale Test 3HI1, differences between the intact and broken loop pipe sizes allowed the expanding Helium bubble to reach the top invert of the larger intact loop pipe early in the transient. This produced preferential dispersion of the gas into the intact loop, which was felt to be atypical of a PWR. In Test 3HI2 an orifice was added to the intact loop hot leg nozzle to produce equal top invert elevations in the two hot legs. This geometry change produced more uniform gas dispersion into the hot legs and an increased venting of the gas out the pressurizer which is believed to be more typical of the TMI plant.

7) Semiscale results are definitely influenced by such scaling distortions as geometric size, one-dimensionality, structural heat transfer area, and elevation influences. Caution should be exercised in the interpretation and extrapolation of these results to any other size facility.

BILLINGS ENERGY CORPORATION
THREE MILE ISLAND REACTOR SIMULATION
FINAL REPORT

Billings
Energy
Corporation

Dupe

STATEMENT OF WORK REPORT

THREE MILE ISLAND
REACTOR SIMULATION FINAL REPORT

Contract No. K-2265

Submitted to

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Silver Spring, Maryland 20900

Submitted by

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1.0 EXECUTIVE SUMMARY

Billings Energy Corporation was contracted by the Nuclear Regulatory Commission to run various tests to provide information regarding (1) methods of predicting the maximum amount of hydrogen in the water circulating in the damaged reactor at Three Mile Island, Pennsylvania; (2) methods of scavenging gaseous hydrogen from the reactor system; and (3) the determination of the most efficient and also the safest means of depressurization.

This section contains a brief summary of the results of the experimental effort launched by scientists and engineers of Billings Energy Corporation to help solve the problem with a nuclear reactor at Three Mile Island, define depressurization procedures, and indicate possible alternatives to aid in the shut-down of the reactor.

Solubility of Hydrogen in Water (Theoretical Evaluation)

Calculations were made to determine the maximum amount of gaseous hydrogen that could theoretically be dissolved in water at various temperatures and pressures. These computations gave an indication of the potential hydrogen bubble growth in the reactor during depressurization. It was estimated that the maximum bubble growth in the Three Mile Island Reactor would be 1037 cubic feet at 300 psia (9% of the total volume), assuming the water in the reactor was completely saturated with hydrogen gas.

Solubility/Pressure Drop Tests

An experimental test apparatus was developed on a bench scale to investigate the solubility of hydrogen in water under conditions analagous to the Three Mile Island Reactor. Depressurizations of the test unit were performed for two cases: (1) continuous discharge, and (2) fast discharge with intermediate stops. Although the results were higher than the theoretical calculations (a bubble growth of 1781 cubic feet, 15.5% of total, and 1884 cubic feet, 16.4% of total, for the Continuous Discharge Test and the Fast Discharge with Intermediate Stops Test, respectively), the bench scale tests established a base for the Reactor Simulation Tests, as well as aiding in the definition of the experimental testing procedure.

Solubility Tests - Depressurization vs. Time

Using the bench scale test apparatus, the hydrogen bubble growth during depressurization was experimentally determined as a function of time at a constant temperature. The results of this test showed that a large pressure rebound could be an indication of saturation.

Catalytic System

Several different schemes were considered for catalytically causing the gaseous hydrogen in the reactor to react with oxygen to form water and thus reduce the pressure in the reactor vessel as well as reduce the hydrogen gas volume.

The first consideration was to analyze the materials in the reactor vessel itself and look at the possibility of these materials catalyzing a reaction between the gaseous hydrogen and oxygen. It was concluded that, although possible, it would be highly unlikely that significant reaction would take place.

A literature search identified some substances that could possibly be used to catalyze this reaction. This survey indicated that hydrogen forms complexes such as ReH_4^-, $HCo(CN)_5$ and $HPtBr[P(C_2H_5)_3]_2$. Four other materials that would possibly catalyze the reaction of hydrogen with oxygen are: (1) colloidal dispersion of sodium borohydride reduced nickel (or platinum); (2) a finely ground alumina-supported nickel (or platinum); (3) a homogeneous $Co(CN)_5^{3-}$ complex; and (4) catalyst coated glass microspheres.

To define the identified catalysts more adequately, several experiments were conducted.

Of the several catalyst systems considered, only the catalytic reduction of oxygen with hydrogen underwater on a platinum catalyst, and the colloidal nickel boride system showed positive experimental results.

Microsphere Test

Another alternative that was considered which might reduce the amount of hydrogen in the reactor vessel was the possibility of introducing glass microspheres to the circulating water system. The specifications that were received on the microspheres indicated that they would have a hydrogen scavenging effect. The experiments on the bench scale test apparatus indicated that there was a 10.6% decrease in pressure. The results did indicate that although the microsphere scavenging effect would not be an immediate solution to depressurization, the long term effects of the microspheres would have a significant result on the pressure of the system.

Reactor Simulation Tests

A pilot plant unit was constructed to simulate the reactor at Three Mile Island. The simulated reactor system consisted of the following major components: the steam generator, the high pressure circulation pump, the reactor vessel, and the pressurizer vessel. The pilot plant was fully instrumented to allow the monitoring of temperatures, pressures, flow rates, and volumes.

The purposes of the reactor simulator tests were: (1) to determine the effects of pressure and temperature reductions upon the behavior of the reactor system filled with water containing various amounts of hydrogen up to and including being saturated; (2) to obtain a model of these characteristics so that the degree of hydrogen saturation and bubble size might be ascertained through pressure and temperature and (3) to determine the most efficient and safest method for cold shut-down of a nuclear reactor system believed to contain a hydrogen water solution.

The various tests that were conducted defined the most critical condition which could exist for the reactor vessel at various temperatures and pressures. These results are plotted in graph form in Section 8.0 of this report.

It was concluded that the most efficient and safest procedure for cold shut-down was first to reduce the temperature of the reactor system. As shown in Figure 3 in the text, as the temperature is decreased there is simultaneously a decrease in the amount of hydrogen in solution, or, in other words, hydrogen evolves from the water. Since unsaturated water is added to the system during this period the actual amount of gaseous hydrogen does not increase significantly. Two phenomena occur during this period: (1) hydrogen is coming out of solution because of the decrease in temperature; and (2) hydrogen is going into solution because of the addition of unsaturated makeup water. After the temperature of the system has been decreased, the pressure can then be reduced.

Hydrogen Peroxide Test

An experimental apparatus was set up to evaluate the feasibility of introducing hydrogen peroxide into the reactor system which, upon decomposition, might react with the hydrogen and thus reduce the pressure of the system.

The experiment conducted indicated that the decomposition of the peroxide takes place at a much more rapid rate than the combining of the oxygen and hydrogen in the system. The results showed a net increase in pressure rather than a decrease in pressure.

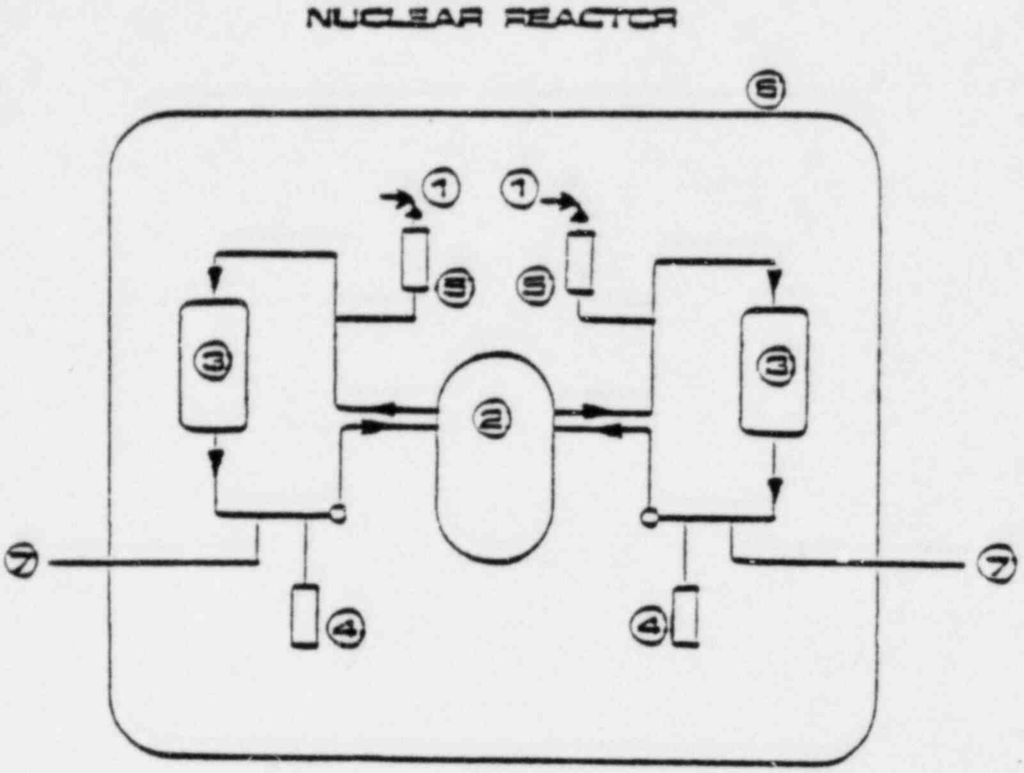
2.0 INTRODUCTION

As a consequence of the failure of a nuclear power reactor at Three Mile Island near Harrisburg, Pennsylvania, technological expertise was sought to assist in defining and solving the problem of safely cooling the reactor as a necessary step prior to shut-down, clean-up, and repair.

Based on the premise that a bubble of hydrogen existed above the water in the reactor, Billings Energy Corporation was asked by the Nuclear Regulatory Commission to investigate means of removing the hydrogen so that the reactor could be safely cooled and depressurized.

Information supplied to Billings Energy Corporation by the Nuclear Regulatory Commission relative to the damaged reactor indicated that the reactor contained approximately 12,000 cubic feet of highly radioactive and slightly acidic water, which was circulating at the rate of 95,000 gallons per minute. Apparently some debris (presumably from the damaged core) was also circulating with the water. The pressure and temperature inside the reactor were 1000 psig and 280°F, respectively. Various estimates of the size (as of April 1, 1979) of the bubble above the liquid in the reactor ranged from 350 to 1500 cubic feet with some indications that the bubble was slowly decreasing in size.

It was presumed that the hydrogen bubble resulted from a reaction of zircalloy and water at the elevated temperatures



1. Relief Valve
2. Reactor Vessel
3. Steam Generator
4. Letdown Cooler
5. Pressurizer
6. Containment Vessel
7. Injection System

Figure 1. A Schematic of the Nuclear Reactor System at the Three Mile Island Nuclear Station.

which are thought to have been produced when a portion of the core was exposed.

It was considered possible that the bubble contained not only hydrogen but also oxygen, and there was concern as to whether or not there existed or could exist an explosive gaseous mixture during depressurization. It was also possible that the bubble contained no hydrogen.

The reactor vessel was inaccessable, because of high radiation levels in the containment area. Compounded with inaccessability of the reactor was the lack of or unreliable reactor instrumentation. Consequently, there was some diversity of opinion as to the nature of the problem and the possible solution. A quick solution was necessary to minimize the danger to the surrounding area and inhabitants.

Resolution of this problem may prevent similar problems from recurring or, at least, may provide a quicker solution should the same problem occur elsewhere.

Figure 1 shows a schematic diagram of the nuclear reactor and containment vessel.

A bubble of a gaseous hydrogen/oxygen mixture in a reactor chamber presents two major problems: (1) If the void space at the top of the reactor increases sufficiently to expose the reactor core to the gaseous mixture, cooling will be lost to the exposed portion of the core, resulting in possible damage to the core with possible release of radioactive material into the cooling water; (2) The second major concern with a hydrogen/oxygen mixture above the liquid in a reactor chamber is the potential for an explosion of the hydrogen/oxygen mixture.

To delineate the problem and provide possible solutions, the following statement of work was drawn up:

Task 1. Calculations of Hydrogen Solubility

Using known data determine the solubility of hydrogen in water at conditions similar to the reactor's present operation and proposed depressurization program.

Task 2. Laboratory Test Unit

Develop a laboratory bench scale test unit to investigate the solubility of hydrogen in water under conditions analagous to the Three Mile Reactor i.e. 1000 psig to 300 psig at 280°F.

Task 3. Hydrogen Solubility Continuous Discharge

Determine, using the bench scale test unit, the hydrogen solubility in water for a range of pressures from 1000 psig to 300 psig at a constant temperature of 280°F (138°C).

Task 4. Hydrogen Solubility - Fast Discharge with Intermediate Stops

Determine, using the bench scale test unit, the hydrogen solubility in water for a range of pressures from 1000 psig to 300 psig at a constant temperature of 280°F.

Task 5. Depressurization and Bubble Growth vs Time

Determine, using the bench scale test unit, the hydrogen bubble growth during depressurization at constant temperature.

Task 6. Catalytic Systems

1. Investigate catalysis of the hydrogen-oxygen reaction by stainless steel.
2. Undertake a literature search for other possible catalytic systems.
3. Assess, using material balances and a thermodynamic study, the present reactor conditions.
4. Investigate the catalytic reduction of oxygen with hydrogen under water using a platinum catalyst.
5. Investigate the catalytic reduction of oxygen with hydrogen under water using nickel based catalysts.

Task 7. Microspheres

Investigate, using microspheres, the possibility of scavenging hydrogen in the reactor.

Task 8. Pilot Plant Unit

Develop a pilot plant unit to simulate the reactor-pressurizer-steam generator systems for operation under pressures and temperatures analagous to the Three Mile Island Nuclear Plant. Install all equipment necessary to measure and record full data requirements and to simulate present reactor conditions and standby cooling conditions; i.e., Pressure, Temperature, Flow Indication, etc.

Task 9. Simulation Tests

Using the pilot plant undertake a series of tests to simulate reactor conditions during the depressurization of the reactor-steam generation system.

Test A. Hydrogenate system to simulate saturation at a pressure of 300 psig. Lower reactor pressure from 1000 psig to 300 psig by discharging water medium maintaining constant temperature.

During discharge lower system pressure by increments of about 100 psi and correlate discharge pressure, bubble volume (water volume extraction) and time.

Test B. Hydrogenate system to simulate saturation at 1000 psig. Lower reactor pressure from 1000 psig to 300 psig by discharging water medium maintaining constant temperature.

During discharge lower system pressure at increments of about 100 psi. Plot and correlate discharge pressure, bubble volume (water volume extraction), and time. Observe pressure rebound following each incremental discharge.

Test C. Calibrate differential pressure gauge.

Test D. Lower reaction pressure from 1000 psig to 300 psig by discharging water medium maintaining constant temperature. Partially hydrogenate system.

During discharge continuously lower reactor pressure maintaining an even water flow from the system. Plot and correlate discharge pressure, bubble volume and time.

Test E. Lower reactor pressure from 1000 psig to 300 psig by discharging water medium maintaining constant temperature of 280°F. System to be fully saturated with hydrogen at 1000 psig and 280°F.

During discharge continuously lower reactor pressure maintaining an even water flow from the system.

Plot and correlate discharge pressure, bubble volume, and time. Compare bubble volume in reactor and steam generator.

Test F. Repeat Test D discharging water from pressurizer as an alternate to discharge from vessel.

Plot and correlate discharge pressure, bubble volume, and time. Compare bubble volume in reactor and steam generator.

Test G. Install a Bailey Differential Pressure Gauge from central reactor location to reactor discharge line.

Bring system up to a temperature of 240°F and 40 psi, release pressure and degasify system.

Pressurize system to remove vapor bubble. Bring total system up to 1000 psig pressure and 280°F temperature.

Depressurize system using depressurizer discharge. Measure discharge volume to reduce system pressure to 300 psig.

This test to be undertaken without hydrogenation of the water medium.

During the test the following data are to be recorded: Time, System Pressure, System Temperature, and Differential Pressure (ins. W.G.). Appropriate plots are to be made for comparison with prior data and observations are to be made regarding the differential pressure reading against temperature changes and pressure changes. Differential pressure is to be recorded on a strip chart recorder to observe and document noise signals.

Test H. The depressurized and unsaturated system following Test G will be saturated using measured volumes of hydrogen. The system will be maintained at constant temperature of 280°F.

Following each pressurization step the pressure decrease will be observed to establish degree of hydrogen saturation.

During Test H the following data are to be recorded: Time, System Pressure, System Temperature, and Differential Pressure.

Appropriate plots are to be made for comparison with prior data and the differential pressure recording plotted against temperature and pressure to assess any changes. Differential pressure shall be recorded on a strip chart recorder.

Test I. The proposed sequence of reactor temperature and pressure changes to bring the reactor down to standby cooling condition is to be simulated on the pilot unit.

The sequence of testing will be as follows:

1. Bring the pilot unit up to pressure and temperature to simulate the system at 1000 psig and 280°F.
2. Saturate the system with hydrogen.
3. Drop the temperature from 280 to 130°F at a constant pressure of 1000 psig.
4. Drop the pressure from 1000 psig to 300 psig at constant temperature.

During the above sequence the following will be recorded: Time, Pressure, Temperature, and Differential Pressure. The results will be recorded and the appropriate graphs charted.

<u>Task 10</u>. A full report will be made on the above tasks.

The report will document equipment used, tests undertaken, calculations and graphs made, observations, conclusions, and recommendations.

The following sections summarize the specific experiments conducted by BILLINGS, as outlined above. The objective, experimental procedure, experimental apparatus, results, and discussion for each section are included.

3.0 THEORETICAL EVALUATION OF HYDROGEN SOLUBILITY IN WATER

3.1 Objective

To determine the maximum solubility of hydrogen in water at different temperatures and pressures based on Henry's Law.

3.2 Results

The results of calculations are shown in Figures 3 and 4. The tabulated values are shown in Tables I and II. Corresponding results are shown in Figures 3 and 4 respectively.

TABLE I

Pressure	Temperature	Moles H_2/kg H_2O	LBM H_2/ft^3 H_2O
1000 psia	280°F	.0714	.00891
"	200°F	.0551	.00698
"	130°F	.0483	.00604
250 psia	280°F	.0179	.00224
"	200°F	.0138	.00173
"	130°F	.0121	.00151

Reference: Dr. Angus Blackham

TABLE II

Theoretical Calculations of Hydrogen Solubility in Water Based on Henry's Law

(All Gas Volumes are ft^3 Based on 12000 ft^3 of Liquid Volume in 3 M.I. Primary System)

PRESSURE PSIA	VOLUME OF DISSOLVED GAS AT STP	VOLUME OF GAS EVOLVED AT STP ΔV PER STEP	VOLUME OF GAS EVOLVED AT LOWER PRESSURE AND 280°F	
			ΔV PER STEP	ΔV FROM 1000 PSI
1000	1.97 E4			Base
		2.00 E3	51.7	
900	1.77 E4			51.7
		2.00 E3	58.0	
800	1.57 E4			116.1
		1.90 E3	62.9	
700	1.38 E4			195.2
		2.00 E3	76.9	
600	1.18 E4			303.9
		1.96 E3	90.0	
500	9.84 E3			453.0
		1.97 E3	112.3	
400	7.87 E3			674.6
		1.97 E3	148.0	
300	5.90 E3			1037

REFERENCE - WAPD TM 633

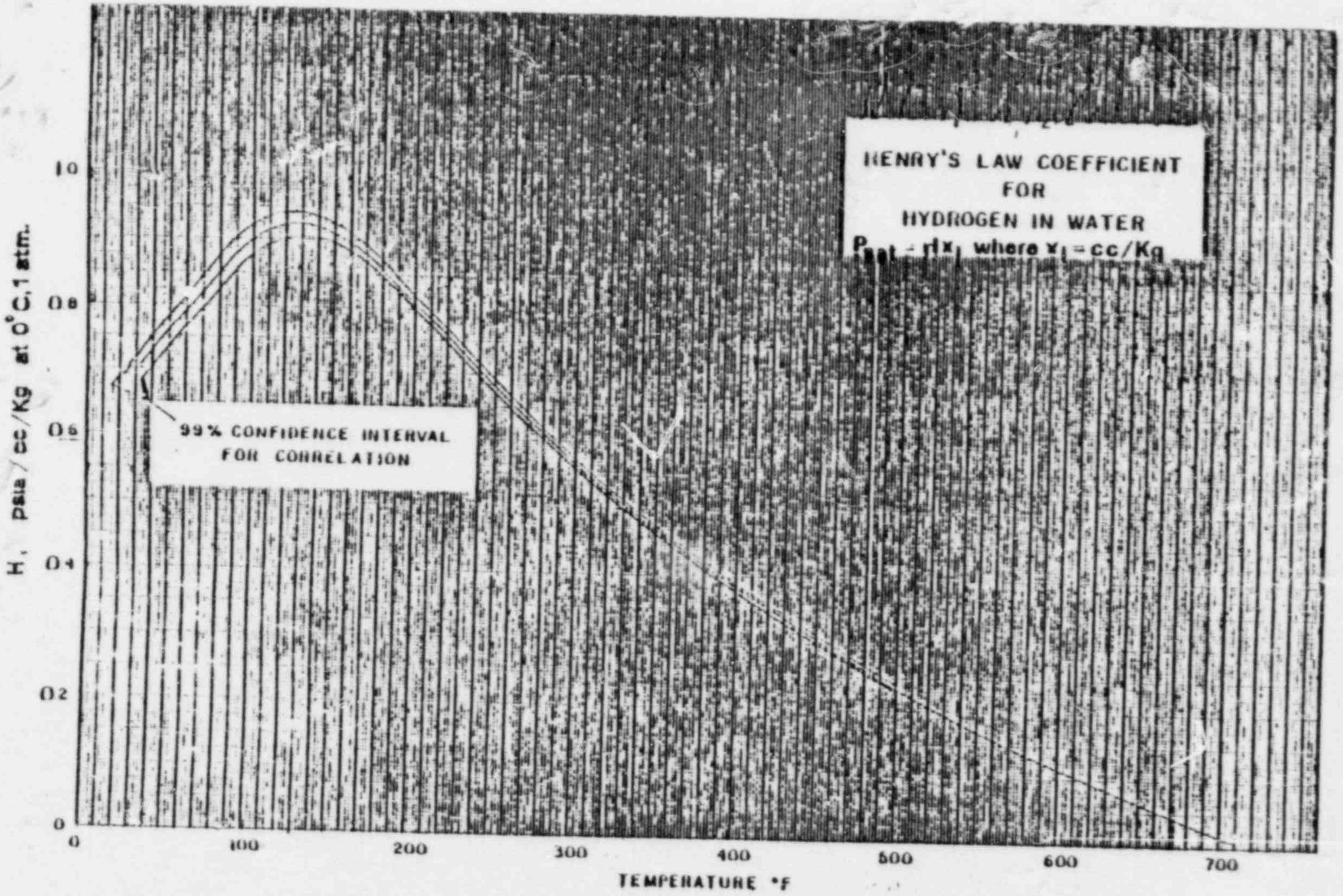


Figure 2 Henry's Law Coefficient for Hydrogen in Water

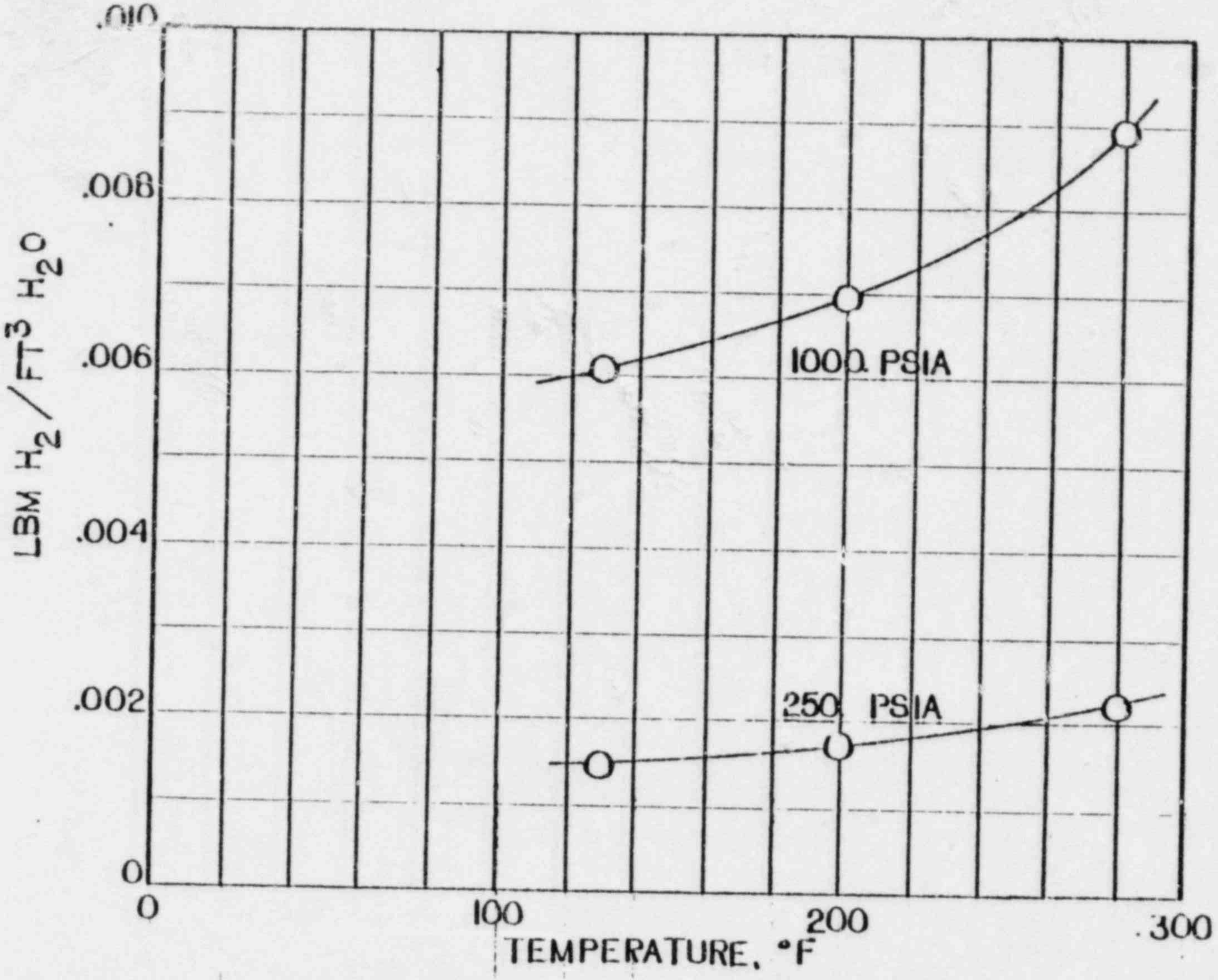


Figure 3 Theoretical Plot of Hydrogen Solubility in Water as a Function of Temperature and Pressure

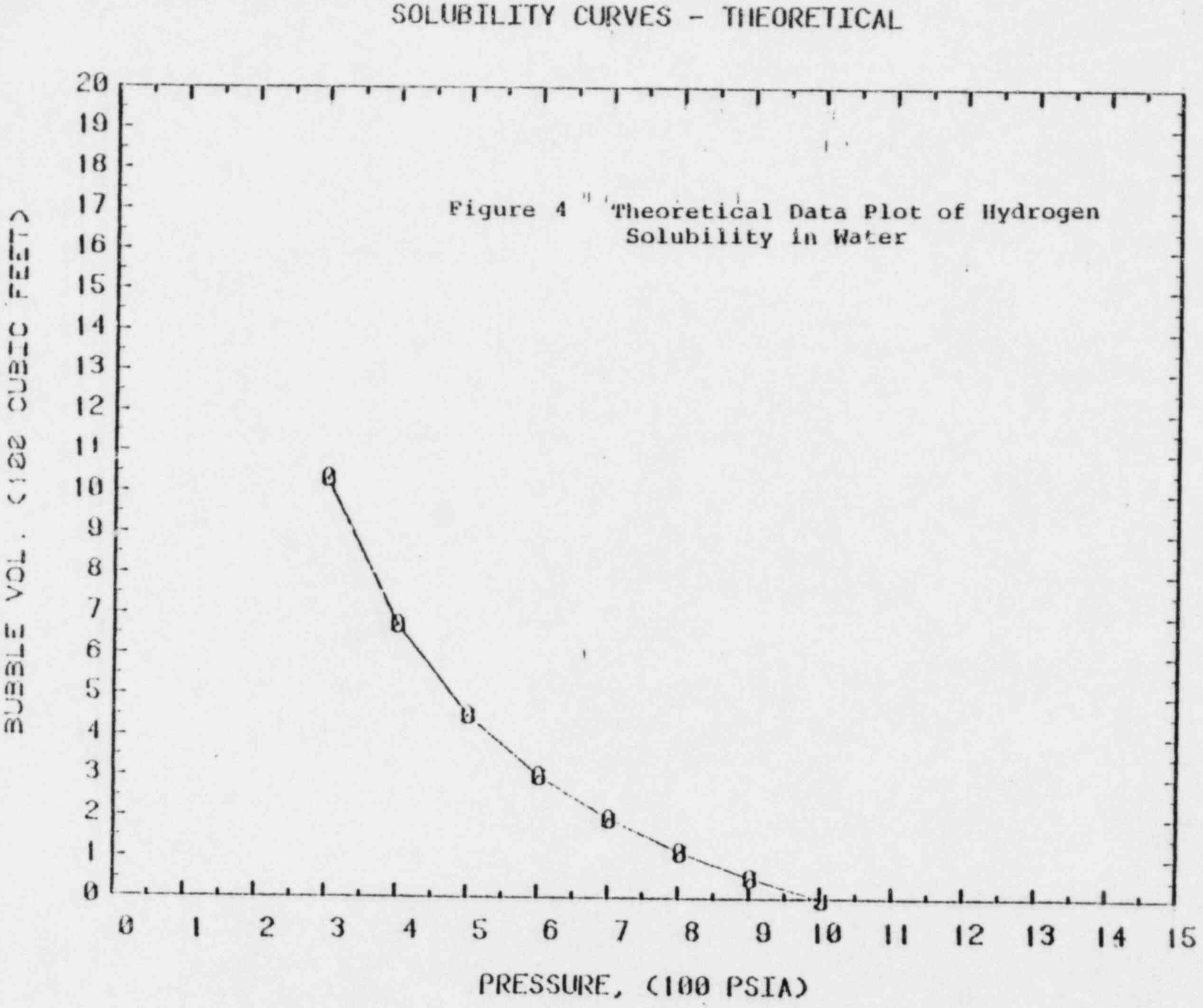


Figure 4 Theoretical Data Plot of Hydrogen Solubility in Water

4.0 SOLUBILITY TESTS/PRESSURE DROP TESTS, CONTINUOUS

4.1 Objective:

To determine experimentally the amount of gaseous hydrogen that comes out of a saturated water solution during depressurization.

4.2 Introduction

Experiments were conducted to determine the amount of hydrogen that would dissolve into water at various temperatures and pressures. An apparatus was constructed which allowed monitoring of the following temperatures and pressures: (1) the temperature of the hydrogen gas in the void space above the water, the temperature of the water, the ambient temperature, the pressure inside the vessel, and the barometric pressure. The experimental procedures used for Tests 1 and 2 are described in Section 4.4

4.3 Assembly of Bench Test Apparatus and Data Acquisition System

See Figures 5, 6, 7, 8.

4.4 Experimental Procedure - Test 1

Test 1 was set up to give pressure/temperature information for continuous discharge. The experimental procedure is outlined below:

1. Fill vessel chamber with deionized water.
2. Drain water from vessel. Measure in graduated cylinder.
3. Fill vessel chamber again with deionized water. Drain out 50 ml.
4. Heat to 137°C.

4.2 Test Apparatus

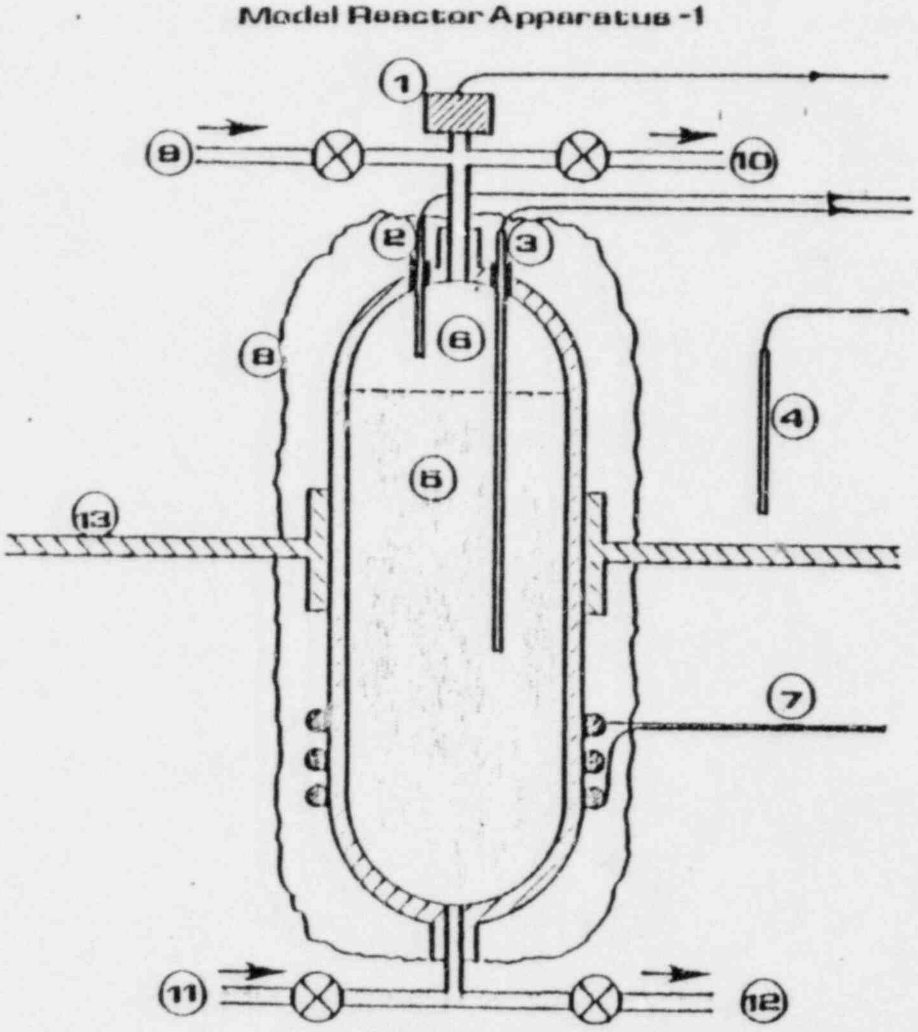


Figure 5 Experimental Setup to Model Hydrogen Solubility in Water

Reaction Chamber
    Maximum Working Pressure 6000 psia
    Internal Volume 1095 ml
    Material - 316 SS
    Length - 34 cm(outside dimension)
    Diameter - 9.5 cm (outside dimension)

1. Bournes Pressure Transducer
   Model #2900
   Input Pressure 0-2000 psia
   Maximum Pressure 4000 psia
   Input Voltage 10.0 vdc
   Output Voltage 100.0 mvdc

2. Thermocouple #1
   type J - Iron-Constantan
   1/8 inch stainless steel probe
   Manufacturer-Love Controls

3. Thermocouple #2
   type J - Iron-Constantan
   1/8 inch stainless steel probe
   Manufacturer-Love Controls

4. Thermocouple #3
   type J - Iron-Constantan
   1/8 inch stainless steel probe
   Manufacturer-Love Controls

5. Deionized Water

6. Hydrogen Bubble

7. Heater
   Input voltage 0-110 volts
   Output 0-1500 watts

8. Kaowool Insulation
   5/8" thick

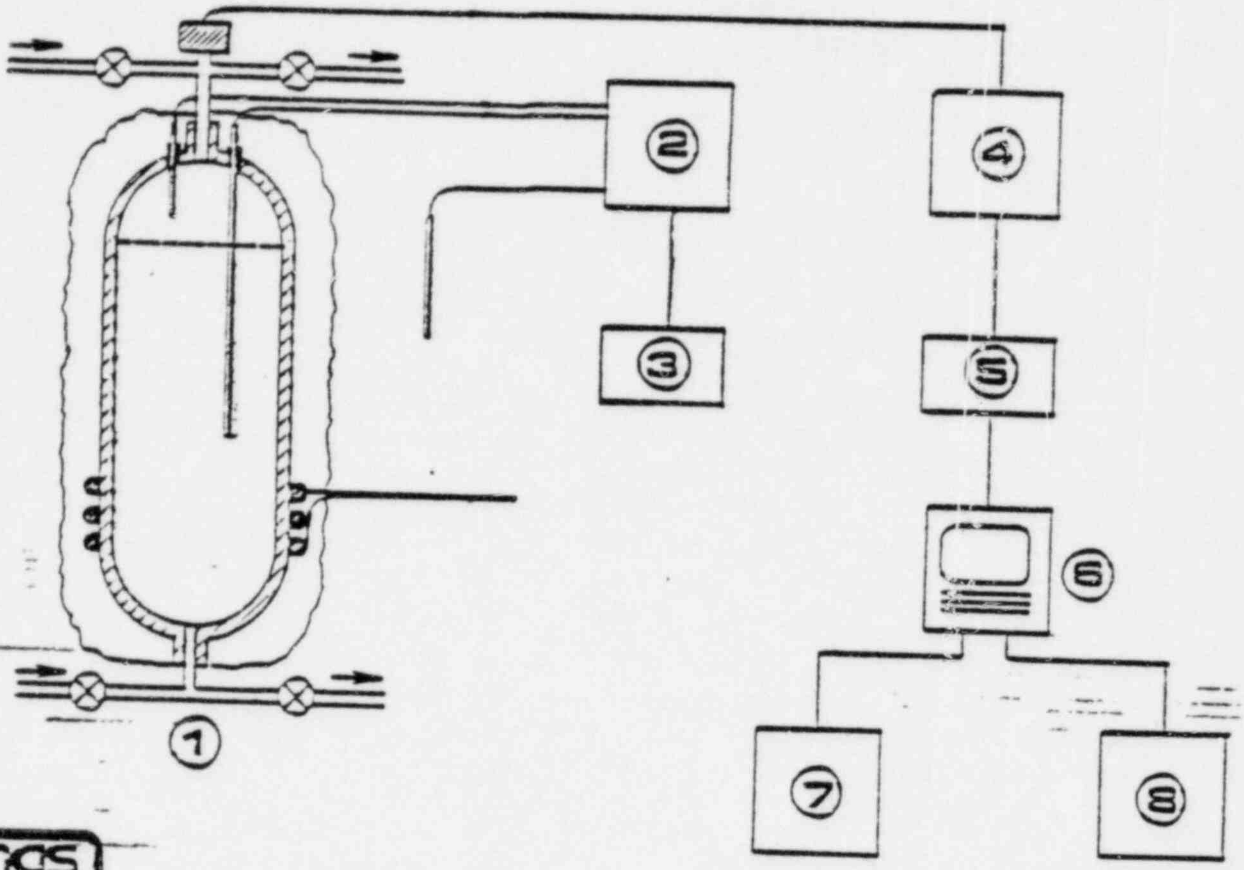
9. Hydrogen Inlet

10. Hydrogen Outlet to mass flow meter

11. Water Inlet

12. Water Outlet - to drain

13. Support



Billings

1. Reactor Chamber (see Figure 5)
2. Thermocouple Switch
    - Loue Controls Corporation
    - Model No. 101
3. Digital Pyrometer
    - Newport Co.
    - Model No. 267
4. D.C. Amplifier
    - Dynamics Corporation
5. A to D Board
    - Billings Computer Corporation
    - 12 bit
    - Conversion time 40,000/sec.
    - 16 channel
6. Computer
    - Billings Computer Corporation
    - Model B-100
7. Printer
    - Billings Computer Corporation
    - Model 701
8. Interactive Digital Plotter
    - Tektronix Corporation

Figure 6 Schematic of Data Acquisition System for the Solubility Tests.

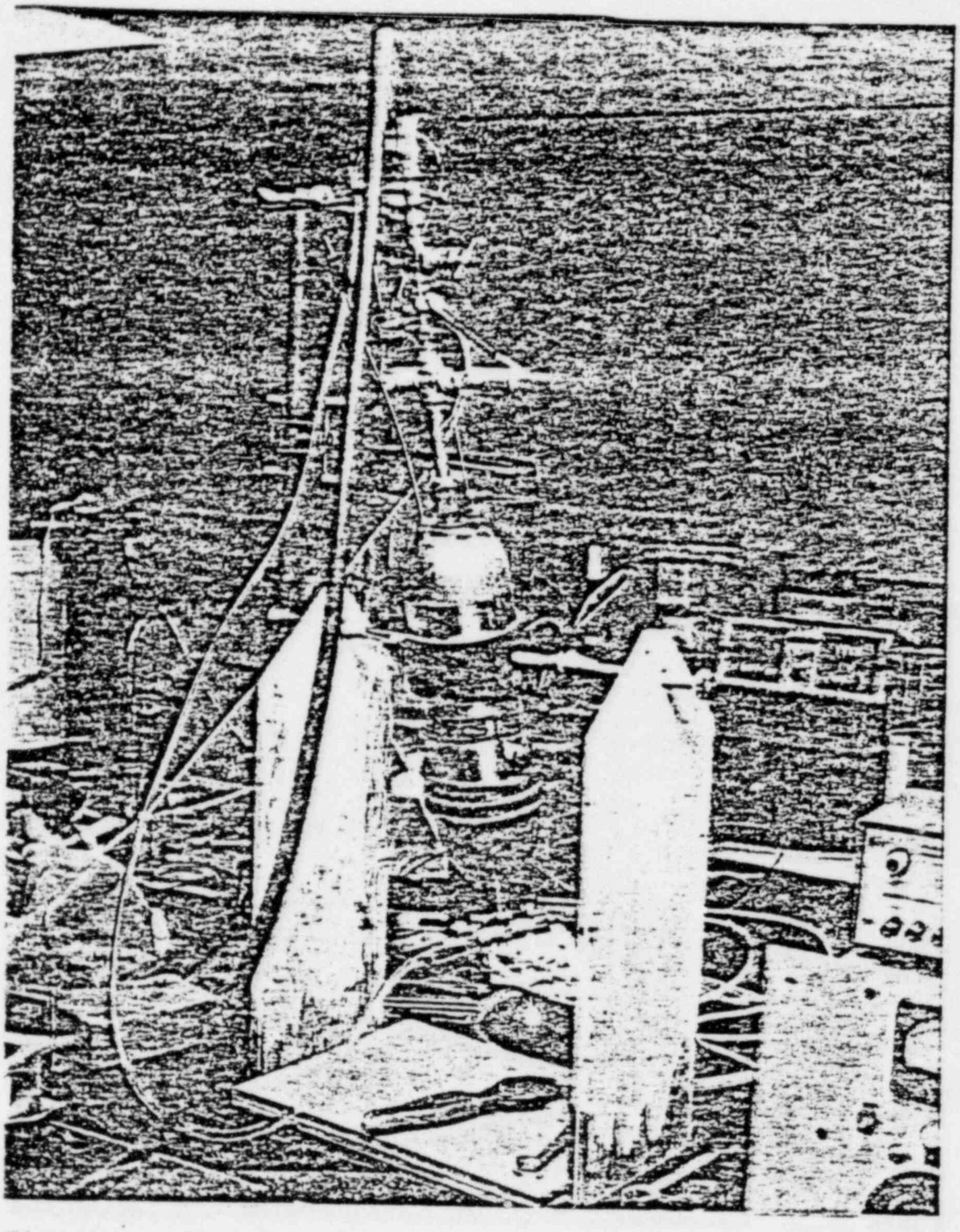


Figure 7 Photograph of Test Apparatus

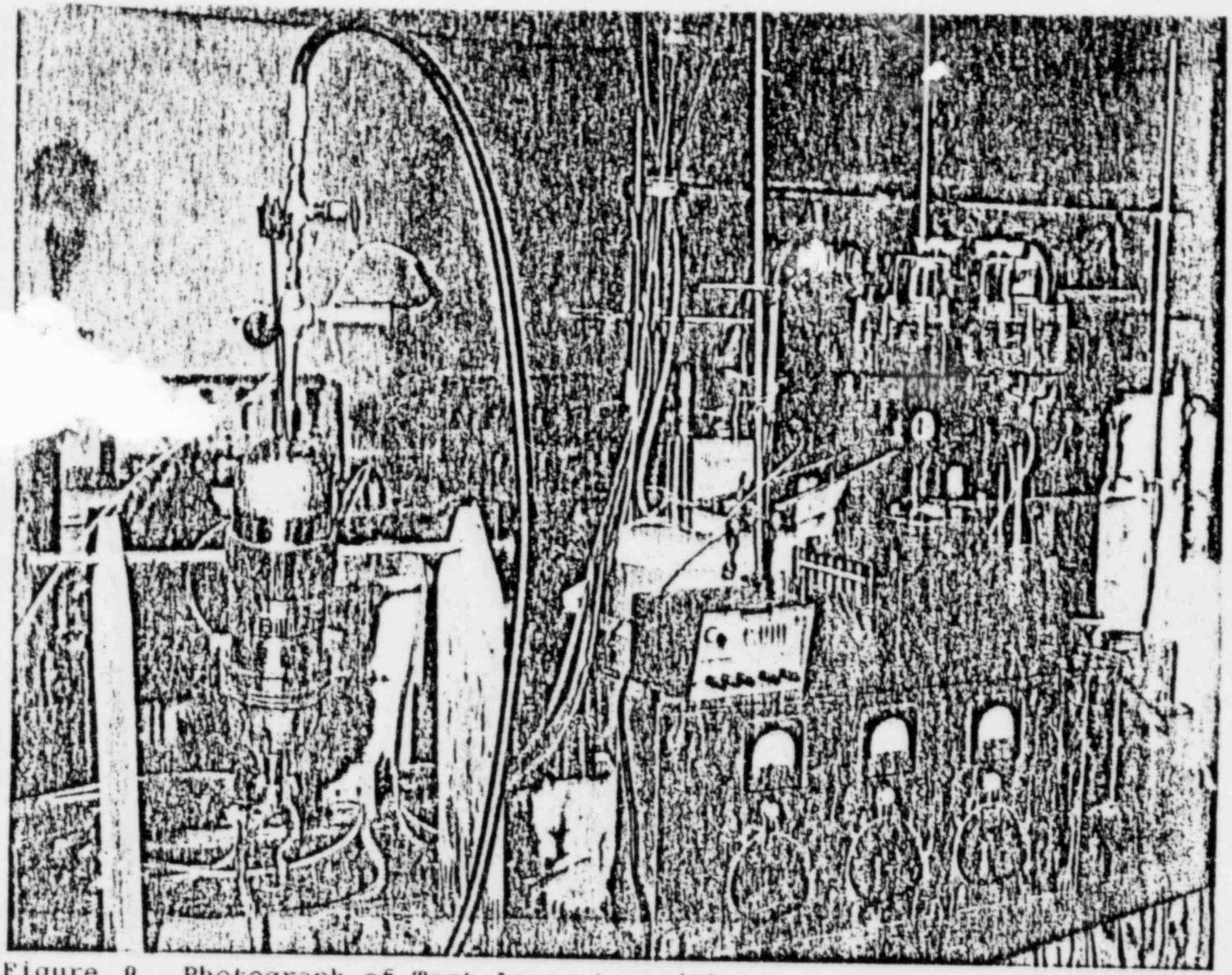


Figure 8 Photograph of Test Apparatus with Instrumentation Equipment

5. Pressurize vessel with hydrogen to 1050 psig.
6. Rock vessel to help saturate water with hydrogen. Adjust pressure to 1050 psig.
7. Begin pressure drop tests by opening hydrogen outlet valve which is connected to a mass flow meter and then to a water displacement vessel. Allow pressure to drop slowly.
8. Record temperature, pressure, time, and volume of displaced water at 50 psig increments.

Experimental Procedure - Test 2 - 4/4/79

Test 2 was set up to give pressure/temperature information for a fast discharge with intermediate stops. The experimental procedure is indicated below:

1. Retain water in vessel from Test 1.
2. Maintain temperature at 137°C and pressurize with hydrogen to ≈1050 psig.
3. Rock vessel to help saturate water with hydrogen. Adjust pressure to ≈1050 psig.
4. Begin pressure drop tests by opening hydrogen outlet valve. Rapidly drop pressure to predetermined value and hold for several minutes (until pressure is stable).
5. Record temperature, lowest pressure achieved, pressure at end of hold period, hold time, time, and volume of displaced water at 100 psig increments.
6. At conclusion of test drain water from vessel. Measure in graduated cylinder. Measure temperature of the water.

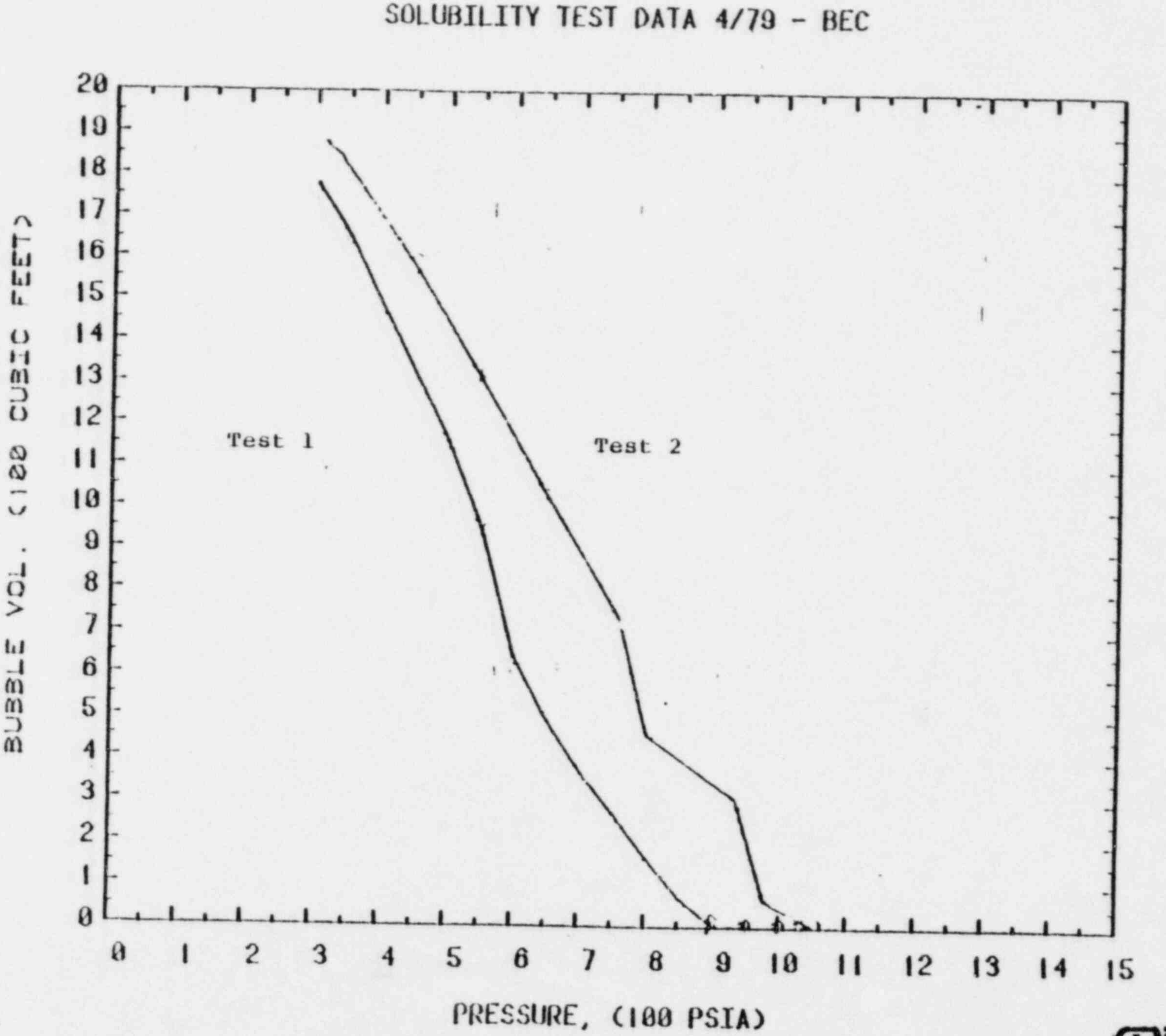


Figure 9 Plot of Bubble Volume as a Function of Pressure

TABLE III

RUN 1. 4/3/79 H_2 Solubility Data - Continuous Discharge

Time	Pressure (psia)	Temp (^{o}C)	Z	M Gas (lbH_2)	V sample (ml)	cc H_2/kg*	V Bubble (ft^3)
23:02	1033	136	1.034364	.000	0	0	0
23.03	1000	136	1.033344	.0002528	10	-36(0)	-27(0)
23:05	950	136	1.031795	.0002405	125	-9(0)	-6(0)
23:06	900	136	1.030239	.0002282	230	10.1	7.6
23:07	850	136	1.028678	.0002159	415	95.6	70
	800	136	1.02711	.0002035	650	222.5	167
	750	136	1.025534	.0001910	904	365.0	273
	700	137	1.023915	.0001782	1150	498.2	372
	650	137	1.022327	.0001657	1429	661.3	493
	600	137	1.021732	.0001532	1785	888.3	647
	550	138	1.019102	.0001403	2348	1285.5	955
	500	138	1.017489	.0001277	2769	1566.3	1162
	450	138	1.01586	.0001152	3129	1796.1	1330
	400	138	1.014225	.0001025	3469	2009.1	1485
	350	139	1.01256	.0000896	3832	2239.8	1653
	300	138	1.010899	.0000771	4168	2443.5	1781

*The ratio of the Volume of gas at standard conditions leaving solution to the mass of solution.

TABLE IV

RUN 2 H_2 Solubility Test - Fast Discharge with Intermediate Stops

Time	Pressure (psia)	Temp (^{o}C)	Z	M Gas (lbH_2)	V sample (ml)	cc H_2/kg	V Bubble (ft^3)
24:	1055.0	136	1.035042	.0002663	0	0	0
24:53	978.5	136	1.032678	.0002[illegible]75	225	83.3	62.7
24:56	933.2	136	1.03127	.0002364	690	408.6	307.2
1:13	799.6	137	1.02705	.0002029	1160	613.9	459.6
1:18	755.7	137	1.025674	.0001920	1690	994.77	743.7
1:41	645.1	137	1.02217	.0001644	2359	1398.9	1042.3
1:50	543.1	137	1.01890	.0001389	2993	1784.8	1325.6
2:04	446.1	137	1.01575	.0001144	3582	2139.5	1584.1
2:14	334.0	137	1.01205	.0000860	4207	2501.9	1845.7
2:24	306.0	137	1.011107	.0000788	4320	2556.4	1884

4.6 Discussion

The results of Tests 1 and 2 seem to indicate that more hydrogen can be dissolved in water at 1000 psi and 280°F than suggested from theoretical calculations. This difference may be due in part to certain experimental conditions which might have contributed to the high results obtained. Those conditions were:

1. Deionized water was used, but no effort was made to degasify it prior to hydrogen absorption.
2. Some air bubbles could have remained in cavities in the pressure transducer and gauges.
3. A small amount of water was retained on all inside surfaces of the vessel and tubing during volume measurement.

Since the water was not degasified by boiling and since air is more soluble in water than is hydrogen, more gas would evolve from solution than if hydrogen had been the only gas in solution.

Any air bubbles initially trapped in any of the small tubes would be evolved during the tests, thus giving high results. Trapped air bubbles would result in the assumption that the vessel has a lower volume than it actually has.

Water retained in the vessel during a volume determination would indicate a lower vessel volume than actual thus contributing to high results.

It is estimated, however, that these experimental errors can account for probably not more than 20% of the difference between the experimental and theoretical calculations for the solubility of hydrogen in water.

5.0 SOLUBILITY TESTS - DEPRESSURIZATION AS A FUNCTION OF TIME

5.1 Objective:

To define the parameters and general characteristics associated with the depressurization of water saturated with hydrogen.

5.2 Introduction

The experimental apparatus, used to determine the solubility of hydrogen in water, was modified such that depressurization and bubble growth could be measured as a function of time. (Compare Figures 5 and 10).

Summarized below is the operational procedure carried out under controlled experimental conditions in order to determine solubility rates of hydrogen in water.

5.3 Experimental Apparatus

See Figure 10.

5.4 Experimental Procedure:

1. Fill test chamber with boiled, deionized water through Valve L with make-up water unit disconnected.
2. Rock chamber until water fills all spaces. Tilt chamber from side to side and upside down.
3. Repeat steps 1 and 2 until only water comes out of chamber.
4. Heat chamber to test conditions (137°C).
5. Pressurize to 1070 psig with hydrogen through Valve L.

Model Reactor Apparatus - II

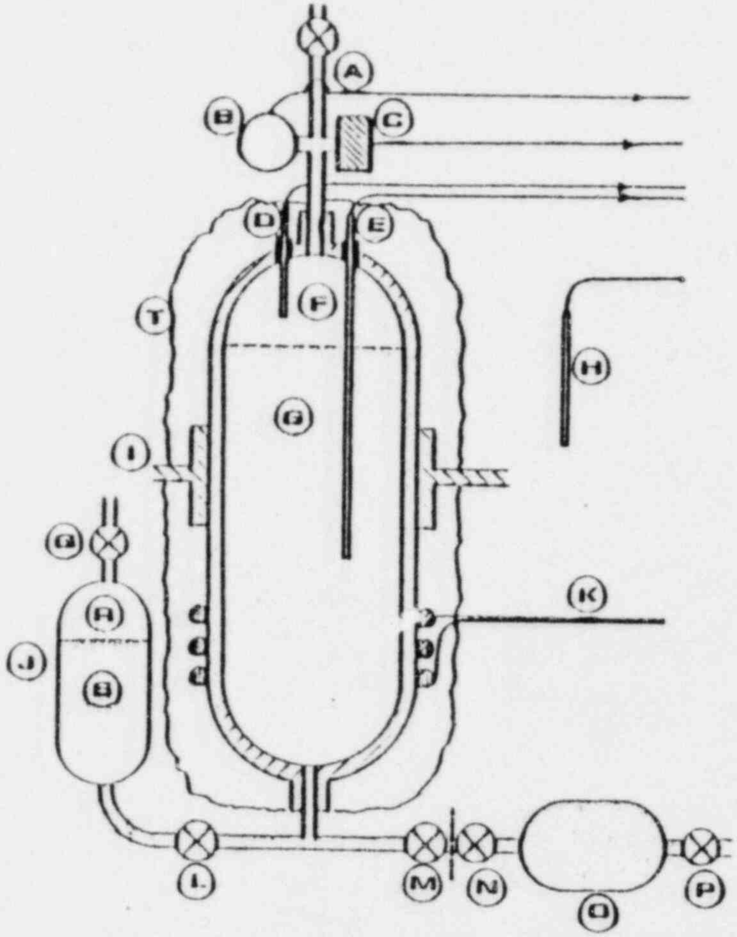


FIGURE 8 Modified Reactor Experimental Aparatus - used for determining time response of hydrogen dissolution in water.

A. Vent Valve

B. Gauge Pressure Transducer
  Manufacturer - Bourns
  Input Pressure 0-3000 psig
  1000 ohm

C. Pressure Transducer
  Manufacturer - Bourns
  Model No. 2900
  Input Pressure 0-2000 psia
  Maximum Pressure 4000 psia
  Input Voltage 10.0 vdc
  Output Voltage 100.0 mvdc

D. Thermocouple #1
  Manufacturer - Love Controls Corp.
  Type J - Iron-Constantan
  1/8 inch stainless steel probe

E. Thermocouple #2
  Manufacturer - Love Controls Corp.
  Type J - Iron-Constantan
  1/8 inch stainless steel probe

F. Hydrogen Bubble

G. Boiled Deionized Water

H. Thermocouple #3 - (Room Temperature)
  Manufacturer - Love Controls Corp.
  Type J - Iron-Constantan
  1/8 inch stainless steel probe

I. Support Structure

J. Makeup Water Unit

K. Heater
  Input Voltage 0-110 volts
  Output 0-1500 watts

L. Inlet Makeup Water Valve

M. Outlet Valve

N. Inlet Valve
  note: apparatus is made such that the system can be disconnected between M and N

O. Cylinder Water Displacement Sample Cylinder (used for measuring the mass of water leaving reactor vessel.)

P. Drain Valve

Q. Inlet Hydrogen Pressurizer Valve

R. Pressurized Hydrogen Gas

S. Degasified Hydrogen Saturated Makeup Water

T. Kaowool Insulation

6. Bleed hydrogen through Valve L into chamber at 1070 psig controlling bleed rate and pressure with Valve A.
7. Periodically stop flow of hydrogen and rock and shake vessel.
8. Repeat Steps 6 and 7 until pressure remains constant after rocking and shaking. (Hydrogen saturation point).
9. Disconnect hydrogen pressure line and connect to make-up water unit J. (J contains hydrogen saturated water).
10. Pressurize system through Valve Q to force water into test chamber through Valve L while bleeding hydrogen through Valve A. Continue until water discharges from Valve A.
11. Close all Valves.
12. Connect water displacement sample cylinder O as shown in Figure 10.
13. Begin PRESSURE DROP TESTS.
14. Open Valve P and crack open Valve M allowing pressure to drop.
15. Cool connecting line between vessels.
16. Disconnect water displacement sample cylinder and weigh cylinder with water sample.
17. Repeat Steps 14 through 16 until 300 psig is reached.

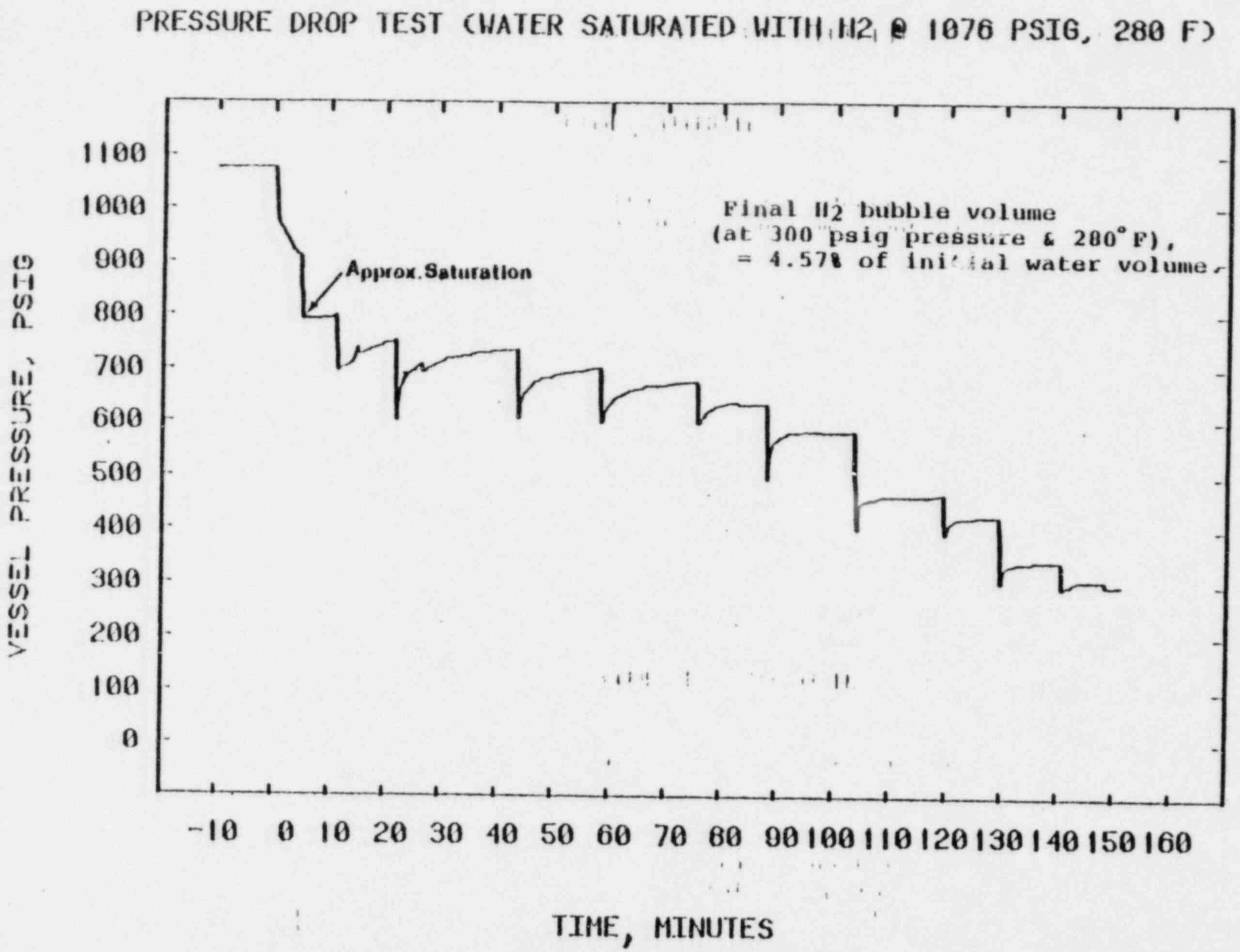
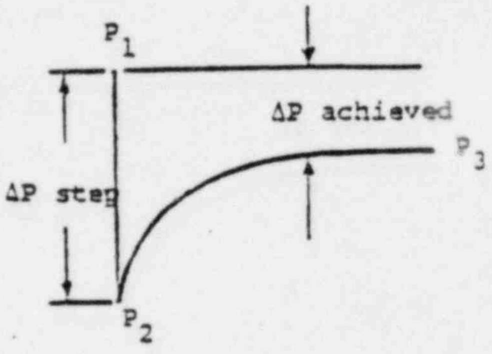


Figure 11. Pressure – Time Trace Showing Changes and Subsequent Pressure Recovery as Hydrogen Comes Out of Solution.

TABLE V

Numerical Values for Step Changes in Pressure as Recorded by Computer

Time At Start Of Test (Min)	P_1 (Psig)	P_2 (Psig)	P_3 (Psig)	Per Cent Pressure Drop
11.150	801.6	696.6	755.0	44.4%
21.783	755.0	603.3	737.5	11.5%
43.466	737.5	605.4	702.4	26.6%
58.25	702.4	599.6	678.4	23.3%
73.483	678.4	601.8	634.6	57.2%
88.016	634.6	496.0	584.3	36.3%
103.633	584.3	402.0	465.4	65.2%
119.633	465.4	396.1	426.8	55.6%
129.5	426.8	303.5	342.2	68.6%
140.517	342.2	293.3	298.4	89.6%



PRESSURE DROP TEST 4/4/79

(WATER SATURATED WITH HYDROGEN @ 1076 psig, 280 F)

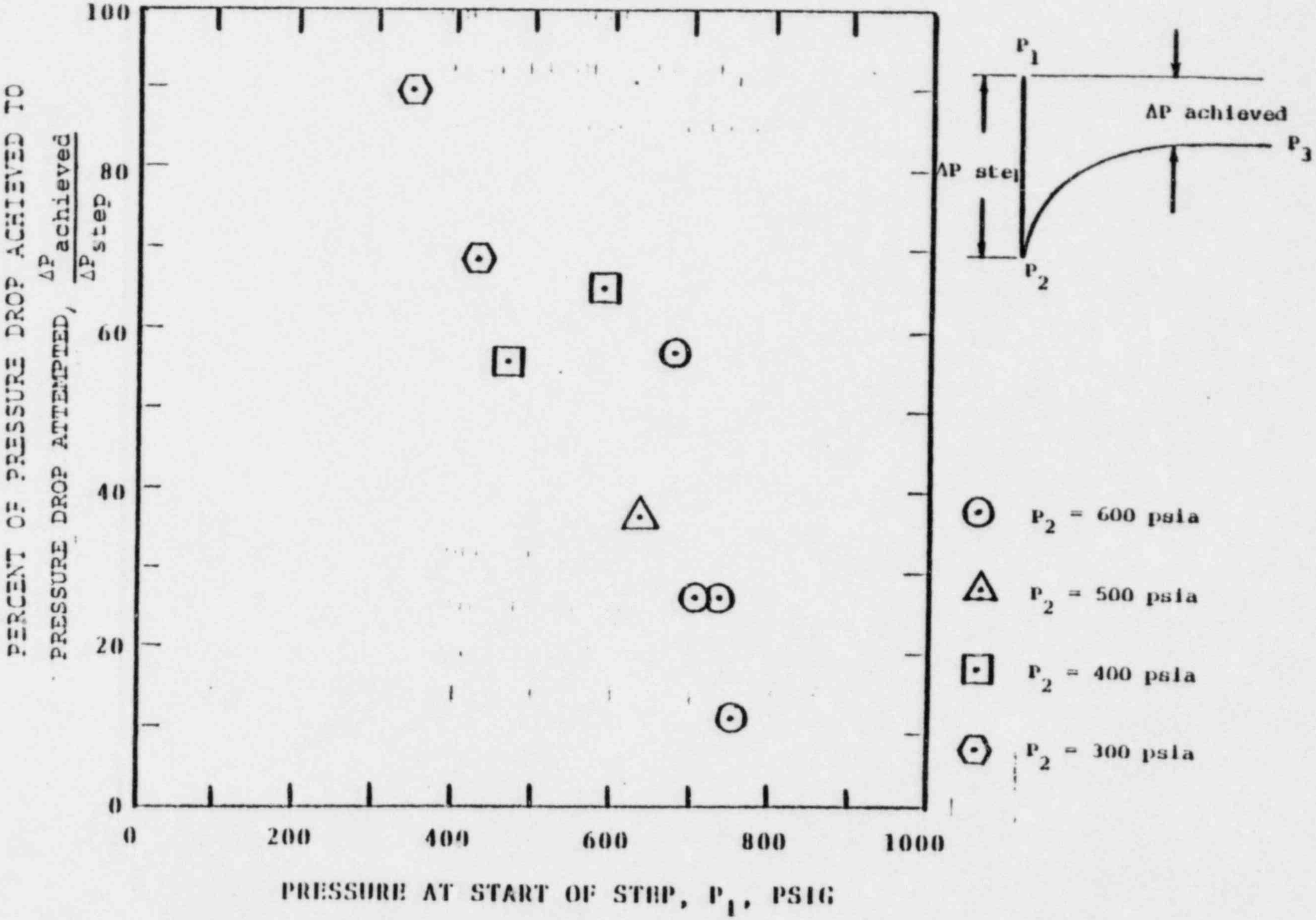


Figure 12. Interpretation of Data in Figure 11 .

5.6 Discussion:

This test represents the reactor depressurization procedure, in that a liquid-full system is depressurized by venting water. In the experiment the water was apparently not initially H_2 saturated. Once saturation was reached, a large pressure recovery took place after venting. 10 to 20 minutes were required for the pressure recovery to line out.

Four attempts to reach 600 psi, depressurizing from ≈750 psi, brought the pressure to ≈630 psi after about an hour. This slow response indicates that attempts to reduce pressure and infer reactor level from pressure are uncertain.

Two items seem apparent:

(a) The saturation point appears to be at about 770 psig at the start of the test instead of 1076 psig, the pressure at which hydrogen was bubbled through the liquid.

(b) The 600 psig and 300 psig data seem to fall on a line connecting the saturation pressure with the target pressure for the step change. This is not entirely substantiated by the 400 psig and 500 psig data although they are bounded by the other data.

6.0 CATALYTIC SYSTEMS

6.1.0 Catalysis of the Hydrogen-Oxygen Reaction by the Reactor Vessel

6.1.1 Objective:

To consider the possibility of the H_2-O_2 reaction being catalyzed by the stainless steel tank or reactor contents in contact with the hydrogen bubble.

6.1.2 Observations Regarding the Possibility of Reaction of H_2 in the Reactor Vessel.

(a) The stainless steel head in contact with the gas does not significantly catalyze oxidation of H_2 with O_2 because

1. The stainless steel was previously passivated and the surface consists primarily of Fe_2O_3, NiO, and Cr_2O_3 which exhibit low catalytic activity ($r = 6 \times 10^{-5}$ moles/m^2h) based on data from Boreskov et al. [Adv. Catal., 15, 285 (1964)].
2. The surface area is low (100-300 m^2) depending upon the size of the H_2 bubble. Naturally, this conclusion should be verified experimentally.

(b) It is not possible to quantitatively assess the extent of H_2-O_2 reaction that might occur in the liquid phase catalyzed by minute particles (of Ni, Zr, UO_2, etc.) produced during the temperature transient. The extent of reaction depends upon (i) the amount, (ii) particle size, (iii) chemical state, and (iv) amount of available O_2. Unfortunately, none of these factors is known quantitatively. It is speculated that most of the particulates are oxides of low catalytic activity produced by reaction of steam with metals having diameters greater than 50-100 microns. However, a significant depletion of H_2 via catalysis by these particles cannot be ruled out.

6.2.0 Literature Search for other Catalytic Systems

6.2.1 Objective:

The objective of the literature search is to explore the possibility of catalyzing a reaction that will remove hydrogen gas either by adding oxygen or some other reactants in addition to the catalyst or by utilizing species already available in solution.

6.2.2 Discussion of Literature Search Findings

A literature search was made for information concerning the catalytic activation of hydrogen. Information in "Homogeneous Catalysis by Metal Complexes" by Khan and Martell indicates that hydrogen forms complexes such as ReH_4^-, $HCo(CN)_5$, and $HPtBr[P(C_2H_5)_3]_2$. This indicates that hydrogen might be activated by metals which could be added to the cooling water of the reactor or which are already there because of the damage to the fuel rods in the reactor. For example, if rhenium forms a hydride complex such as ReH_4^-, then technetium, with properties similar to rhenium, may also form a complex hydride.

Catalysts which might be added to the reactor to induce reaction of H_2 were considered as follows:

(a) Four alternative catalyst systems were considered (and are listed in order of preference):

1. A colloidal dispersion of sodium borohydride reduced nickel (or platinum) [R. C. Wade, Catal. Rev., 14, 211 (1976)].
2. A finely ground (micron size) alumina-supported nickel (or platinum).
3. A homogeneous $Co(CN)_5^{3-}$ complex. [B. DeVries, J. Catal., 1, 489 (1962)].
4. Catalyst coated glass microspheres.

(b) Advantages and disadvantages of each system are listed in Table VI. Colloidal nickel boride is recommended as the leading candidate because (1) it has been used successfully in liquid phase hydrogenation reactions, (2) since the nickel metal crystallites are submicron, they will be uniformly distributed throughout the liquid with negligible settling or clogging of the system, and (3) the metal crystallites are stable toward thermal degradation to 350-400°C. Moreover, the chance of explosion with this catalyst is very small and the rate of the liquid phase reaction is easily controlled by the rate at which oxygen is added to the make water. Last, but not least, because heat of reaction is absorbed by the liquid, formation of hot spots accompanied by runaway reaction is prevented.

TABLE VI

Advantages and Disadvantages of Four Different Catalyst Systems

Catalyst	Advantages	Disadvantages
colloidal nickel boride	Extremely well dispersed, active, will not settle, controlled liquid phase reaction minimal chance of explosion	preparation complex and slow
supported nickel powder	well dispersed, active, commercially available, minimal chance of explosion	may settle, may plug portions of system
$Co(CN)_5^{-3}$	Soluble, homogeneous reacts directly with H_2, relatively stable complex, very little chance of explosion	reacts with H_2O, rate of reaction with H_2O catalyzed by acid. HCN?
Catalyst coated glass microspheres	stay afloat	could initiate explosion, relatively inactive, difficult to recover

The use of finely ground Ni/Al_2O_3 is a viable 2nd choice alternative to nickel boride. It has essentially the same advantages as mentioned for the nickel boride. However, it may tend to settle and plug portions of the reactor system.

TABLE VII

Catalysts Prepared by $NaBH_4$ Reduction

Catalyst	Solvent Used in Chemical Reduction	Physical Characteristics
Ni-A	H_2O	Initially black; turned green because of hydrolysis; coarse precipitate
Ni-B	H_2O	Black; reasonably fine precipitate
Ni-C	Ethanol	Initially very fine, black ppt. Turned to gray-black and moderately fine precipitate when water was added and the solution was boiled
Ni-D	Isopropanal	Same as for ethanol; precipitate was initally finer than all other catalysts
Pt-A	H_2O	Heavy black flakes; prepared from aqueous solution of H_2PtCl_6
Pt-B	Ethanol	Reasonably fine black precipitate; prepared from Pt DNS plating solution

The last two alternatives are not recommended, the $Co(CN)_5^{3-}$ complex because it reacts rapidly with water as well as H_2 in acid solution and catalyst-coated microspheres because they could possibly initiate an explosion in the gas phase, but would do little to remove H_2 dissolved in the liquid.

(c) Estimates of catalyst requirements:

Reliable kinetic data for H_2 oxidation in the H_2-rich region are available only for Pt [Hansen and Boudart, J. Catal., 53, 56(1978)]. However, work by Boreskov et al. [J. Chim. Phys., 51, 759 (1954)] suggests that Pt, Pd, and Ni are "the best" catalysts and reasonably close in activity. However, Ladachi et al. [J. Catal., 4, 239 (1965)] obtained data showing Ni to be 10-100 times less active than Pt. Leder and Butt [AIChE J., 12, 718 (1966)] studied the H_2-O_2 reaction on Pt in the oxygen-rich region. Their data show reasonably strong inhibition by the product water. Accordingly, the reaction in aqueous phase will be significantly lower because of the high P_{H_2O} and because of slow diffusional rates in the liquid.

The specific initial gas phase rate of the H_2-O_2 reaction on Pt (see attached calculations) is 5.5 x $10^2 \frac{\text{gmoles}}{\text{h m}^2}$. The gas phase rate on Ni is 5.5 to 55 $\frac{\text{gmoles}}{\text{h m}^2}$ and for liquid phase 1-2 orders of magnitude lower in rate. If it is assumed that 5 x 10^4 gmoles are present in the reactor water and bubble and it is desired to remove the hydrogen by reaction in 5% O_2 over a period of 8 hours, the nickel boride catalyst requirement is estimated at 27 lbs. (12,500 g) (see attached calculations). Since this figure could be high by a factor of 10 and low by a factor of 10-100, it was recommended that the rate be determined experimentally so closer estimates could be made.

6.3.0 Material Balance and Thermodynamic Study

A rough calculation was made as to how much uranium had undergone fission since the plant started. This was calculated to be 3 x 10^5 grams. Six percent of the uranium that undergoes fission ends up as technetium-99. Similar amounts of palladium and rhodium are formed. If it is assumed that 10% of the core was damaged accessing water to the fission products and that 10% of these products is carried into the water in dissolved or finely divided form, there could be approximately one pound (600 g) of technitium, palladium, and rhodium circulating with the cooling water. As indicated in the previous section, these elements are known to interact with hydrogen in catalytic reactions. Perhaps these elements are in part responsible for the reduction of the hydrogen bubble in a reaction sequence in which hydrogen forms a complex with these metals and these complexes slowly reduce some of the metallic oxides to the metals and water. If a high temperature reaction converted water and metals to hydrogen and metallic oxides, then at lower temperatures there would be a thermodynamic tendency for hydrogen to reduce the metallic oxides. The technetium, palladium, and rhodium may have provided a catalytic path with favorable kinetics for this reduction.

6.4.0 Catalytic Reduction of Oxygen with Hydrogen under Water

6.4.1 Objective:

To obtain empirical evidence as to whether or not platinum and/or nickel catalysts added to the reactor system might assist in the removal of hydrogen by reduction of oxygen.

6.4.2 Catalytic Reduction of Oxygen with Hydrogen under Water on a Platinum Catalyst

Experiment No. 1. 54 mg of [illegible]$_2$ were added to 425 ml of water in a 500-ml glass reaction bottle and placed in a Parr low-pressure hydrogenation system. Therefore, 75 mls of air at one atmosphere pressure were trapped in the bottle. Hydrogen was added to give a gauge pressure of 50 psi. Therefore, the relative pressure due to O_2, N_2, and H_2 are, respectively, 3, 12, and 50 units. If all of the oxygen combines with hydrogen, there will be a 9 psi pressure drop. The hydrogen necessary to reduce the PtO_2 should give a 2.4 psi pressure drop. Shaking of the reaction bottle was started and the pressure drop during one hour was observed as indicated in Figure 13. The drop of 11.5 psi compares closely with what was predicted. However, solubility of hydrogen in water was not considered.

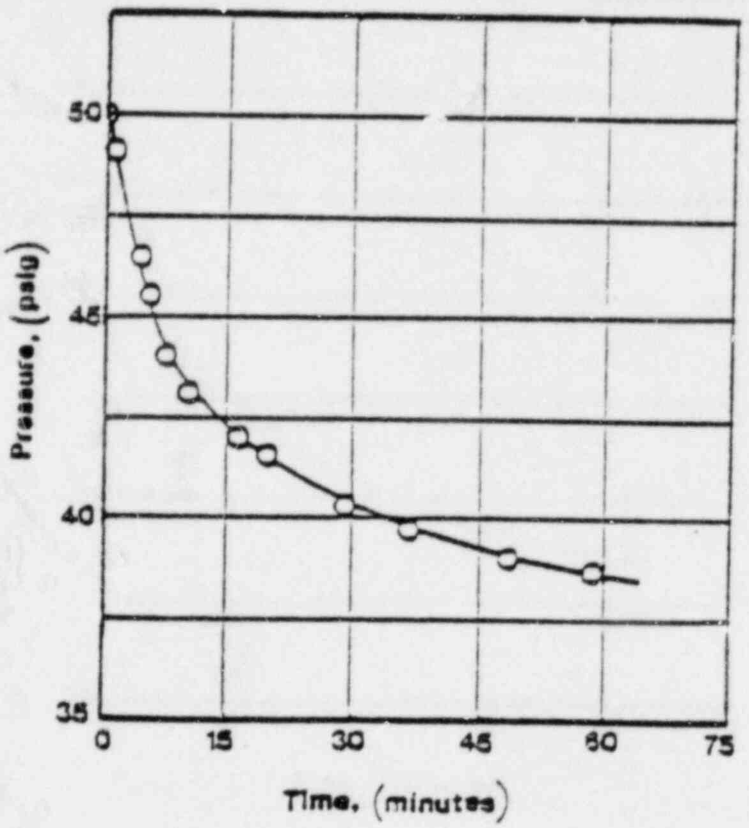


Figure 13 Pressure-Time Plot for the Catalytic Reduction of Oxygen with Hydrogen Under Water on a Platinum Catalyst

Experiment No. 2. A similar run with only water indicated a pressure drop of 2.5 psi due to solubility of the hydrogen.

Experiment No. 3. A similar run was made with 10 grams of catalytic pellets that had been impregnated with a platinum plating solution and heated at 600°F. In 10 minutes the pressure had dropped 4.3 psi. Since the platinum had already been reduced, this pressure drop was due to solubility and to the reaction of H_2-O_2 on the pellets which remained on the bottom of the reaction bottle even when it was being shaken.

Experiment No. 4. The water was poured off and the conditions of Experiment 3 repeated. In 10 minutes the pressure drop was 7.5 psi. This means that 56% of the oxygen had reacted catalytically on the pellets at the bottom of the reactor.

Experiment No. 5. Another run similar to Experiments 3 and 4 was run for 1½ hours with the same pellets. A pressure drop of 8.2 psi was observed. Overnight, without shaking, the pressure dropped an additional 2.5 psi.

The H_2-O_2 reaction on a Pt catalyst underwater is thus shown to occur.

6.4.3 Nickel Catalyzed Reactions

Four different Ni catalysts prepared by sodium borohydride reduction of nickel nitrate and two Pt catalysts prepared by borohydride reduction of chloroplatinic acid and Pt DNS (plating solution) are briefly described in Table VII. Each catalyst was prepared in a well-stirred flask containing the metal salt solution to which $NaBH_4$ (solid) was added slowly. The reaction rate was controlled by cooling the flask in an ice bath. In the case of catalysts prepared in ethanol and isopropanol, the solvent was partially boiled off after the reduction was complete; then water was added and boiling continued to a temperature of 98°C.

Two of the Ni catalysts, Ni-B and Ni-D, were tested in a 300-ml stainless steel reactor for activity in aqueous phase oxidation of hydrogen by oxygen (5% oxygen in hydrogen) at 25 and 140°C and 700 and 1000 psia (50-75 atm).

6.4.4 Results - Nickel - Catalyzed Reaction

Tests and results of the Ni catalyst experiments are summarized in Table VIII. Chromatographic analysis for catalyst B indicated that essentially all of the oxygen (originally

TABLE VIII

Results of Activity Tests for Borohydride Reduced Ni

Conditions: 25 or 140°C, 600-1000 psia (50-75 atm)

Apparatus: 300-ml stainless steel bomb

Catalyst	Time at 25°C	Time at 140°C	Initial Pressure
Ni-B	3.5 hours	1.5 hours	675 psig
Ni-D	2 hours	4 hours	675 psig

Chromatographic Analysis of Products after reaction Catalyst A:

about 5% Oxygen

about 5% Nitrogen

remainder Nitrogen

present in a concentration of ≈5%) was still present in the reactor following reaction for two hours at 140°C and eight hours at 25°C. In other words, the Ni catalyst did not catalyze the reaction of hydrogen and oxygen in aqueous phase. Based on the limited data available at this point, two possible reasons for this behavior are suggested:

1. The finely dispersed nickel particles are passivated or oxidized by hot water.
2. The surface reaction is strongly inhibited by water and the product or reaction

Evidence that colloidal Ni was oxidized was obtained during the preparation of catalysts. The catalysts prepared by addition of water followed by heating to remove the nonaqueous solvent were a gray-black color, characteristic of nickel oxide, rather than dark black, which is characteristic of finely divided metals.

6.5.0 Appendix

Calculation of Rate of $H_2 - O_2$ Reaction of Pt, Fe, Ni Metals

1. Pt at 410K (138°C) and 75 atm

$$k = \frac{0.1\ \text{cm}^3}{\text{cm}^2\ \text{S}} \quad \text{[Hansen and Boudart]}$$

$$r = k\ C_{O_2} \qquad \text{where } C_{O_2} = P_{O_2}/RT$$

$$r = \frac{0.1\ \text{cm}^3}{\text{cm}^2\ \text{S}} \quad \frac{5\ \text{atm}}{82\ \frac{\text{cm}^3\ \text{atm}}{\text{K gmole}}\ (400\text{K})} = 1.52 \times 10^{-5}\ \frac{\text{g moles}}{\text{cm}^2\ \text{S}}$$

$$= 5.5 \times 10^2\ \frac{\text{g moles}}{\text{m}^2\ \text{h}}$$

If reactor were made of Pt

$$R - 5.5 \times 10^2\ \frac{\text{gmoles}}{\text{h m}^2}\ (100\ \text{m}^2) = 5.5 \times 10^4\ \text{g moles/h}$$

No. moles of H_2 in reactor is 4.7×10^4 = 1 hour to react

2. Ni at 410°K and 75 atm

According to Ladachi the rate of Ni is 10^2 lower than Pt.

$$r = 5.5\ \frac{\text{gmoles}}{\text{h m}^2}$$

$$R = 5.5\ (100) = 500\ \frac{\text{gmoles}}{\text{h}} = 80 \text{ hours to react at the wall}$$

NOTE: These are initial rates. There will be strong inhibition by H_2O (see Leder and Butt). Moreover, the passivated surface is probably Cr_2O_3, NiO, and Fe_2O_3.

Calculation of Catalyst Requirement:

1. Nuclear reactor with 5×10^4 gmoles H_2

   Assume rate for Ni is 1-2 orders of magnitude lower in liquid phase:

$$r = 0.05 - 0.5 \ \frac{\text{gmoles}}{\text{h m}^2}$$

Ni SA = 10 m^2/g (lower limit)

Allow 8 hours for reaction; upper limit

$$\text{Amt. of Cat.} = \frac{5 \times 10^4 \text{ gmoles}}{0.05 \ \frac{\text{gmoles}}{\text{h m}^2} (8 \text{ hours})} \times \frac{1 \text{ g}}{10\text{m}^2} = 12{,}500\text{g} \quad (27 \text{ pounds})$$

2. Lab reactor with a 10cc vapor space:

$$n = \frac{PV}{RT} = \frac{75 \text{ atm } (10 \text{ cm}^3)}{82 \ \frac{\text{cm}^3 \text{ atm}}{\text{K gmole}} \ (800 \text{ K})}$$

$$\text{amt. cat.} = \frac{0.02 \text{ gmoles}}{0.05 \ \frac{\text{gmoles}}{\text{h m}^2} \ (0.5 \text{ h})} \ \frac{1 \text{ g}}{10 \text{ m}^2} = 0.1 \text{ g}$$

by Dr. Robert J. Teitel (Consultant - Microsphere Specialist):

1. SI Grade

    Ratio of Diameter to thickness of wall is 35.3

    Thickness of wall is 1.9 micrometers

    Thickness of Diameter is 67 micrometers

    The pressure requirement of the microspheres bed is immaterial. Example: @1000 psi, then in 10.1 hours the microsphere bed will be at 500 psi.

    Then at room temperature the microsphere bed would lose 1/2 its charge in 1200 hours.

2. 3 M Grade B38/4000

    (a) At same pressure conditions, it would take 59 days to build up to the same pressure as referenced above. Thus, 1000 psi would result in a microsphere bed of 500 psi.

    (b) At room temperature the microsphere bed would loose 1/2 its charge after ten (10) years.

7.3 Experimental Apparatus (See Figure 14)

7.4 Experimental Procedure

The microspheres test was performed according to the following procedure using SI grade microspheres:

1. Place 150 ml microspheres in 300 ml pressure vessel.
2. Fill with boiled, deionized water.
3. Pressurize with hydrogen through bottom valve of vessel. Displace some water from vessel through top valve to create "bubble."

7.3 Experimental Apparatus

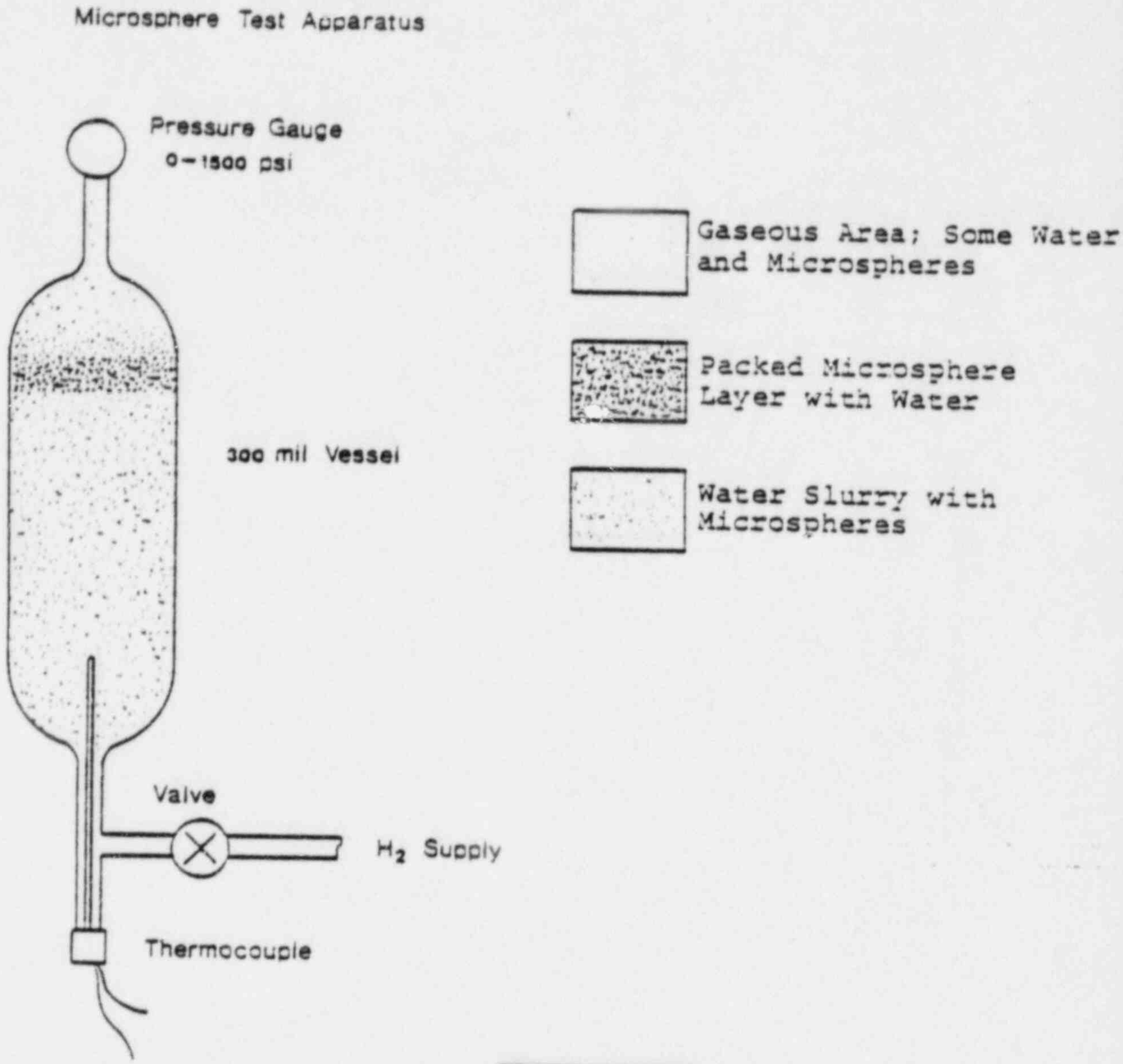


Figure 14 Microsphere Test Apparatus

TABLE IX

Pressure Data for Microsphere Test No. 2

Temperature (°C)	Pressure (psig)	Time and Date
286	990	12:10 am April 5
280	975	12:12 am
279	975	12:14 am
277	975	12:16 am
277	975	12:20 am
282	975	12:25 am
281	975	12:30 am
280	970	12:45 am
278	950	1:45 am
275	910	8:25 am
275	900	9:00 am
275	900	9:30 am
274	895	10:30 am
274	895	11:30 am
273	885	2:00 pm
	≈ 600	12:00 pm

This was done to see if the amount of hydrogen absorbed could be detected from the weight difference between constant weight at 220°F and the weight after heating to 600°F. The following data were recorded:

	Drying Time @600°F					
	30 min	90 min	3 hrs	6 hrs	After Outgas (gm)	Hydrogen (gm)
Sample A (Gaseous Area)	9.2903	9.2893	9.2886	9.2867	9.2723	.0144
Sample B (Packed Microsphere Layer with Water)	9.3730	9.3707	9.3700	9.3683	9.3414	.0272
Sample C (Water Slurry with Microspheres)	10.2011	10.1883	10.1832	10.1759	10.1095	.0536

The data indicated that a significant larger amount of hydrogen was absorbed by the microspheres in the water slurry than the microspheres in the gaseous area of the test apparatus. It was concluded that additional tests would be required to fully define the characteristics of hydrogen absorption in the glass microspheres. It was however concluded that the S.I. grade responded much more rapidly than did the 3M microspheres.

8.0 REACTOR SIMULATOR TESTS

8.1 Objective

The objectives of the reactor simulator tests are (1) to determine the effects of pressure and temperature reduction upon the behavior of the reactor system filled with hydrogen containing water of varying degrees of saturation. (2) To obtain a model of these characteristics so that the degree of hydrogen saturation and bubble size might be ascertained through pressure and temperature measurements. (3) To assist in the eventual cold shut-down of a nuclear reactor system believed to contain a hydrogen water solution.

8.2 Introduction

A reactor simulator was constructed so that the characteristics of hydrogen bubble formation in the reactor and steam generator might be observed as a function of pressure, temperature, and hydrogen concentration. Manipulation and documentation of these parameters in accordance with conditions current or anticipated at the Three Mile Island Reactor were expected to reveal means of controlling the effects of hydrogen gas in the reactor system and to forewarn engineers as to what to expect given any set of circumstances relative to changes in temperature, pressure, and hydrogen concentration.

8.3 Experimental Apparatus and Data Acquisition System

A schematic of the simulated reactor apparatus is presented in Figure 15, followed by a description of the components. Figure 16 shows the completed reactor simulator system in service.

The simulated reactor and data acquisition instrumentation are pictured in Figure 17. Figure 18 is a photograph of the simulated reactor system under construction, wherein the major elements of construction are visible prior to being covered with insulation.

No commercial pumps could be obtained, within the time constraints of this project, which could withstand the pressures anticipated. A Grunfos #25-42 sf pump was thereby encased in a heavy steel shell and immersed in hydraulic oil. The pump casing oil was then pressurized or depressurized in concert with the reactor system through a large diaphram to which was attached a lead line from the pump on one side and a lead line from the reactor on the other. The encased pump is shown in Figure 19.

The data acquisition system is shown in Figure 20. A Billings B-100 computer with 48K memory and dual floppy disk drive system was used to access and store data from the various thermocouples and pressure transducers of the system as a function of real time. In addition, the data were printed on paper with a Billings 701 printer. Further backup redundance was accomplished by printing the time and temperature readings on paper tape via a model 9300 data logger by Monitor Labs.

8.4 Discussion - Reactor Simulation Tests

8.4.1 Experimental Procedure

For the experiments requiring saturation or varying degrees of hydrogen saturation the following procedure was common:

1. Fill the system with tap water from the hot water heater through V 14 with V1, V2, V4 and V8 open. (See Figure 15).

2. Close V2, V1, and V4, respectively, when water begins to flow out.
3. Manipulate pump and valves to dislodge and remove bubbles from the system.
4. Heat to boiling at ambient pressure with circulating pump on.
5. Remove bubbles from system by opening and closing valves V1 and V2 intermittantly.
6. Pressurize through V4 to 1200 psig. Relieve 1/8 - 1/4 volume of pressurizer, PV, through V7.
7. While proceeding to heat to the desired temperature (280°F), release hydrogen bubble from PV through V4 while admitting H_2 into R at V13. Hydrogen bubble forms in R.
8. Saturate with hydrogen through V13 with V8 closed and V9, V10, V11, V12 open. Vent hydrogen slowly at V2 during hydrogen charging.
9. Pressurize PV to 1100 psi and release hydrogen bubble in R slowly (maintaining at least 1050 psi) through V2.
10. Test saturation by reducing pressure at V7 in 100 psig increments. Look for pressure rebound. Repeat until pressure rebound is observed. Saturation will have been achieved for the pressure at which rebound first occurs.
11. Water and/or gas samples removed from the system batchwise or continuously according to the intent of each individual tests. The sampling port differed also according to the design of individual tests.

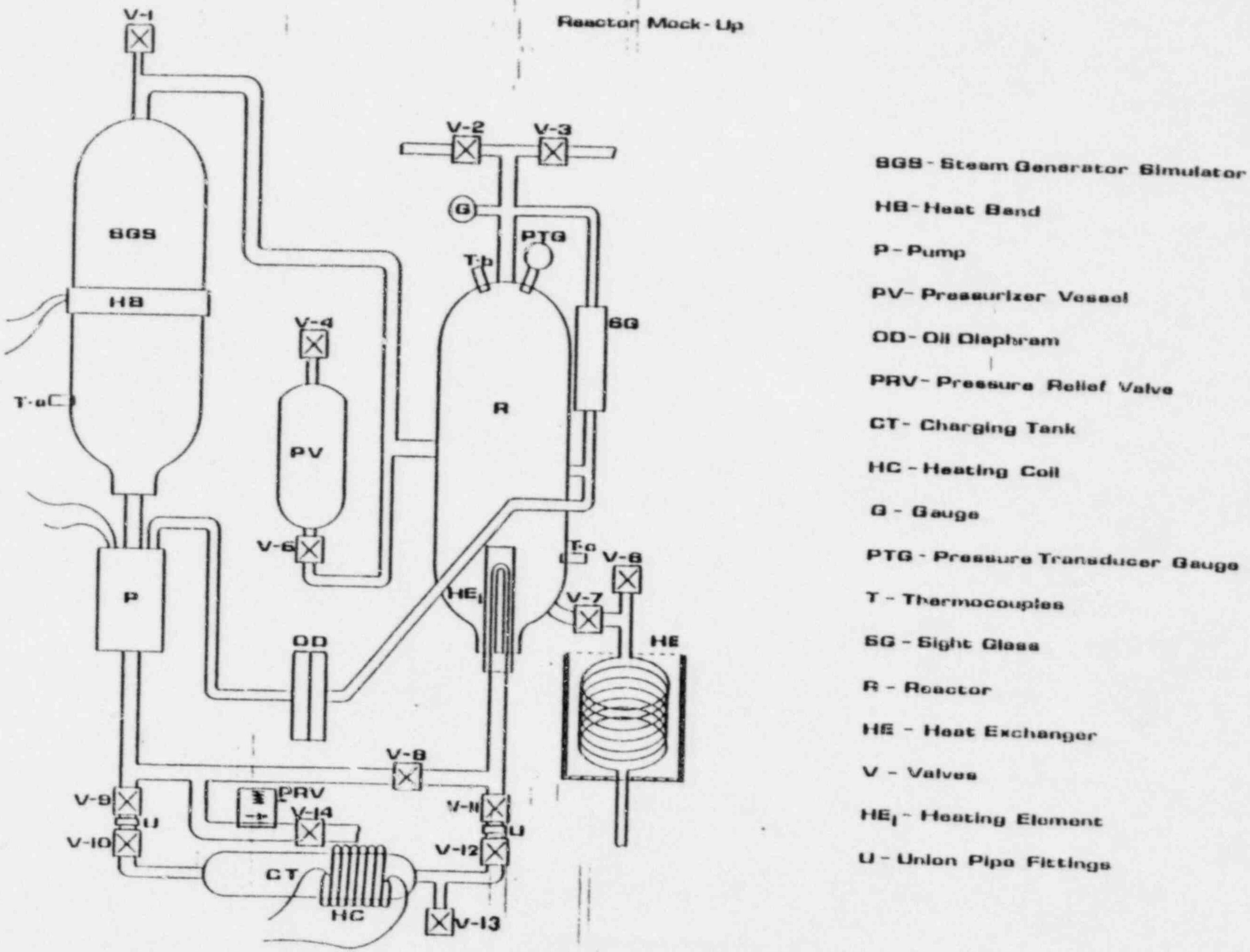


Figure 15 Schematic of the Simulated Reactor Apparatus

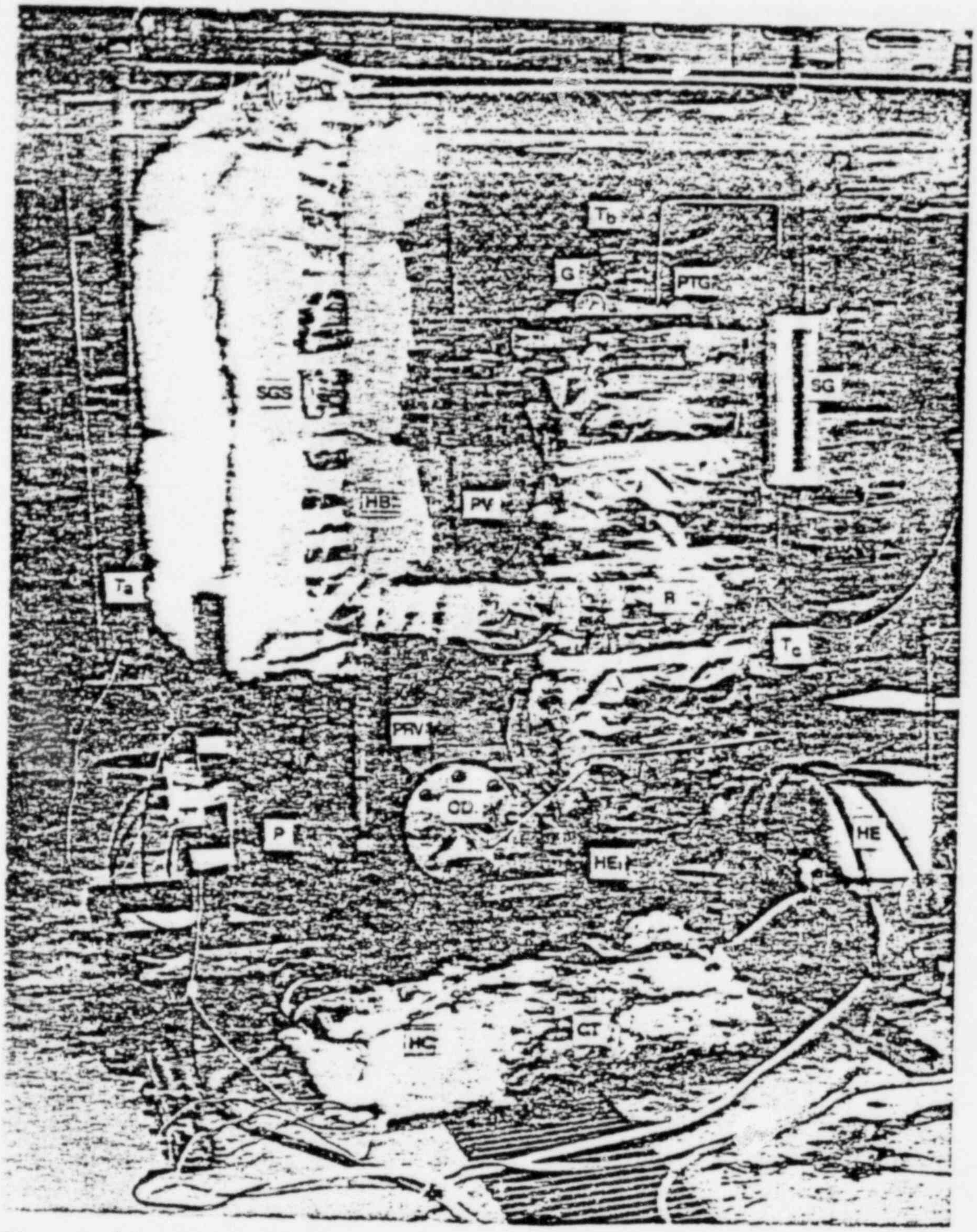


Figure 16 Photograph of the Reactor Simulator Test Apparatus

Description of Components:

SGS - Steam Generator Simulator

Description: Government surplus pressure vessel

Dimensions: O.D. = 16" Length - 48" x .875 wall thickness.

Function: Simulate conditions in and represent the actual steam generator

HB - Heating Band

Description: 750 watt 110 volt heating band

Function: Heat water contained in the steam generator

P - Pump

Model: Grunfos #25-42 sf

Description: 15-20 GPM delivered flow rate

Encasement: BILLINGS in-house construction 1000 psi design

Function: (Encasement) pressurize outside of pump to equalize pressure pumping conditions

Function: (Pump) water system circulation

PV - Pressurizing Vessel

Description: Luxfer 2,000 psi pressure vessel

Dimensions: O.D. = 7" Length = 15"

Function: Simulation of total system pressurization

OD - Oil Diaphram

Description: BILLINGS in-house construction

Dimensions: O.D. = 10" Length 3"

Function: Prevent pump pressurizing oil from entering water system

PRV - Pressure Relief Valve

Model: Consolidated

Description: Standard relief valve 3,000 psi capacity

Function: To allow pressure escape beyond control pressure

CT - Charging Tank

Description: Steel cylinder 2,000 psi capacity

Dimensions: O.D. 4" Length - 24"

Function: Heat exchange, decreased heating time for water, also sample and material addition

HC - Heating Coil

Description: 6,000 watt, 220 volt heat coil
Function: General water heating

G - Gauge

Description: Standard gauge - range 0-4,000 psi
Function: Monitor reactor temperature

PTG - Pressure Transducer Gauge

Description: Standard gauge - range 0-3,000 psi
Function: Monitor reactor temperature and interface with Billings T-100 computer

T - Thermocouples

Description: Standard type J-iron constantan 1/8" stainless steel
t-a Function: Monitor water temperature in steam generator
t-b Function: Monitor gas temperatures in reactor
t-c Function: Monitor water temperatures in reactor

SG - Sight Glass

Description: 1,700 psi capacity; liquid level style
Dimensions: width: 4" thickness: 3½" length: 13"
Function: Monitor liquid level in reactor

R - Reactor

Description: Government surplus pressure vessel
Dimensions: O.D. 16" length 48" x .875 wall thickness
Function: To simulate conditions in and represent actual reactor

HE - Heat Exchanger

Description: Billings in-house construction; coil 3/4" finned stainless steel tubing
Function: Cool samples

HE_1 - Heating Element

Description: 4,500 watt 220 volt heating element
Function: Heat water contained in reactor and simulate actual core conditions

U - Union Pipe Fittings

Description: 3/4" union pipe fittings (2 req)
Function: To afford a disconnection of the charging tank from the main system.

V - Valves

V-1 Description: ½" ball valve
Function: Venting for steam generator simulator

V-2 Description: ½" regulator valve
Function: Venting for reactor

V-3 Description: ½" regulator valve
Function: Venting and filling valve for reactor

V-4 Description: ½" ball valve
Function: Venting and filling valve for pressurizing vessel

V-5 Description: ½" ball valve
Function: Isolation valve for pressurizing vessel

V-6 Description: ½" regulator valve
Function: Purge valve for reactor sample line

V-7 Description: ½" Regulator valve
Function: Sample isolation valve

V-8 Description: 1½" ball valve
Function: Bypass valve for charging tank

V-9 Description: ½" ball valve
Function: Isolation valve from charging tank

V-10 Description: ½" ball valve
Function: Isolation valve for charging tank

V-11 Same as V-9

V-12 Same as V-10

V-13 Description: ½" regulator valve
Function: Bleed valve for charging tank

V-14 Description: 1" ball valve
Function: System drain and fill valve for charging tank

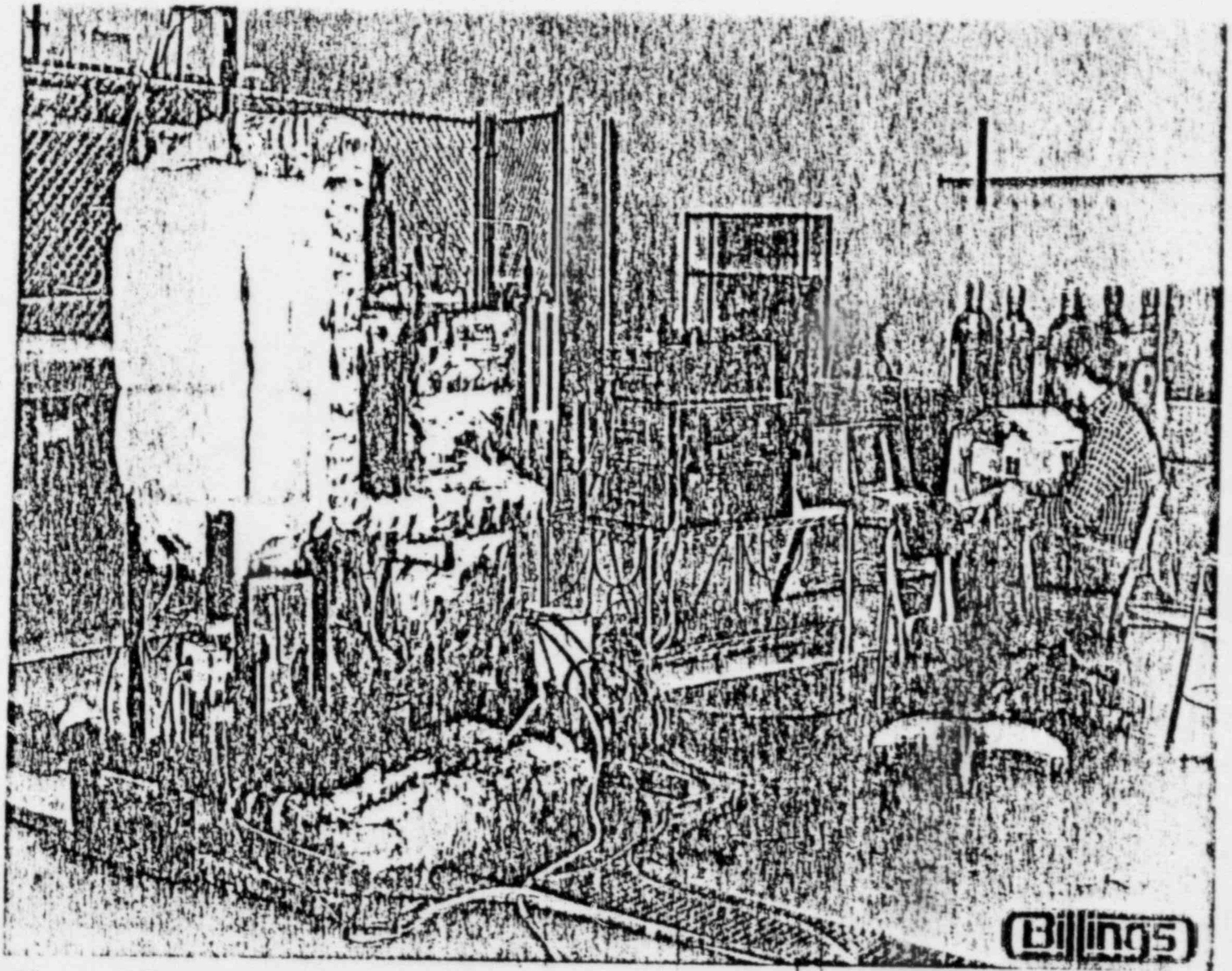


Figure 17 Photograph of the Simulated Reactor Including Instrumentation

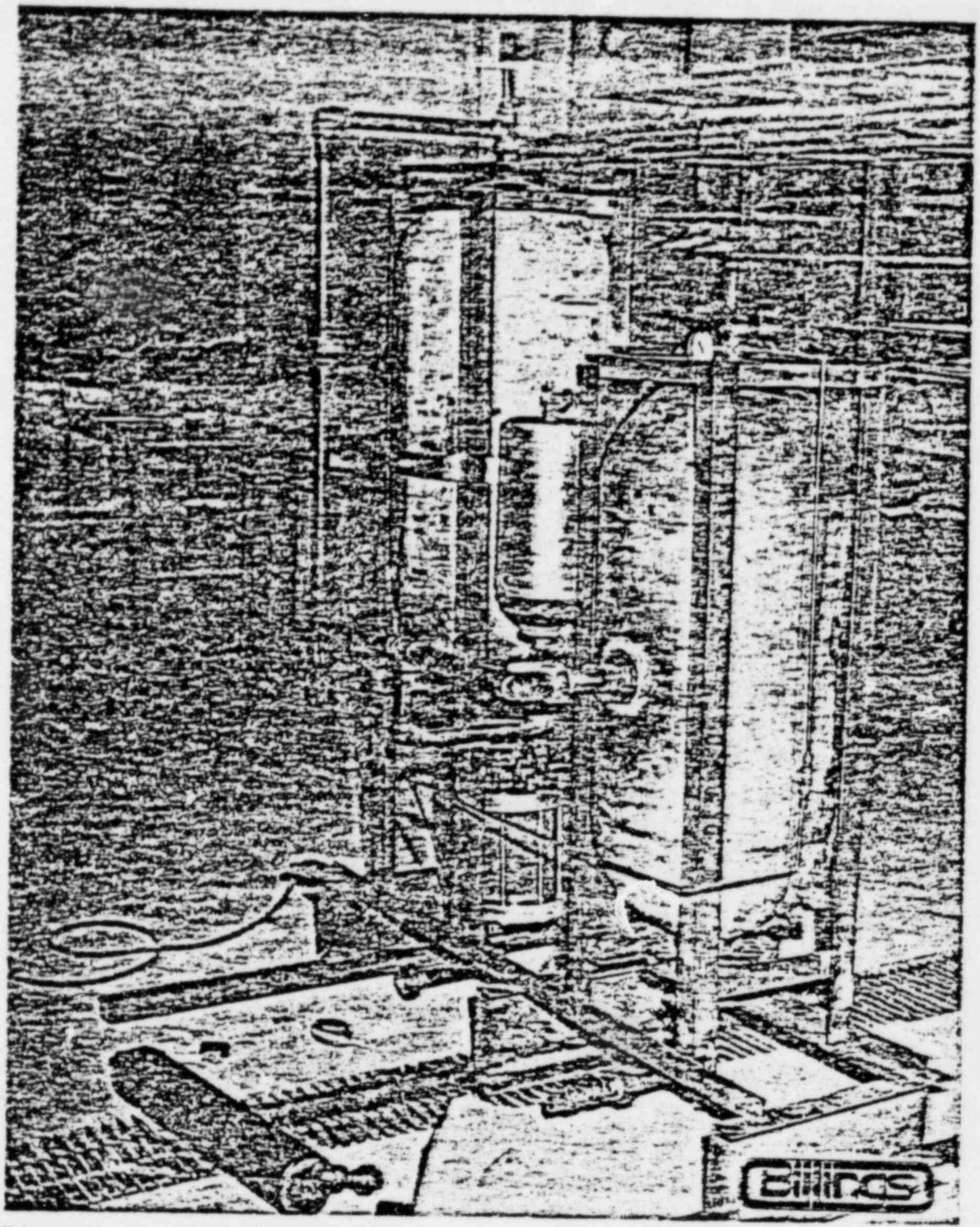


Figure 18 Photograph of the Simulated Reactor System
Under Construction

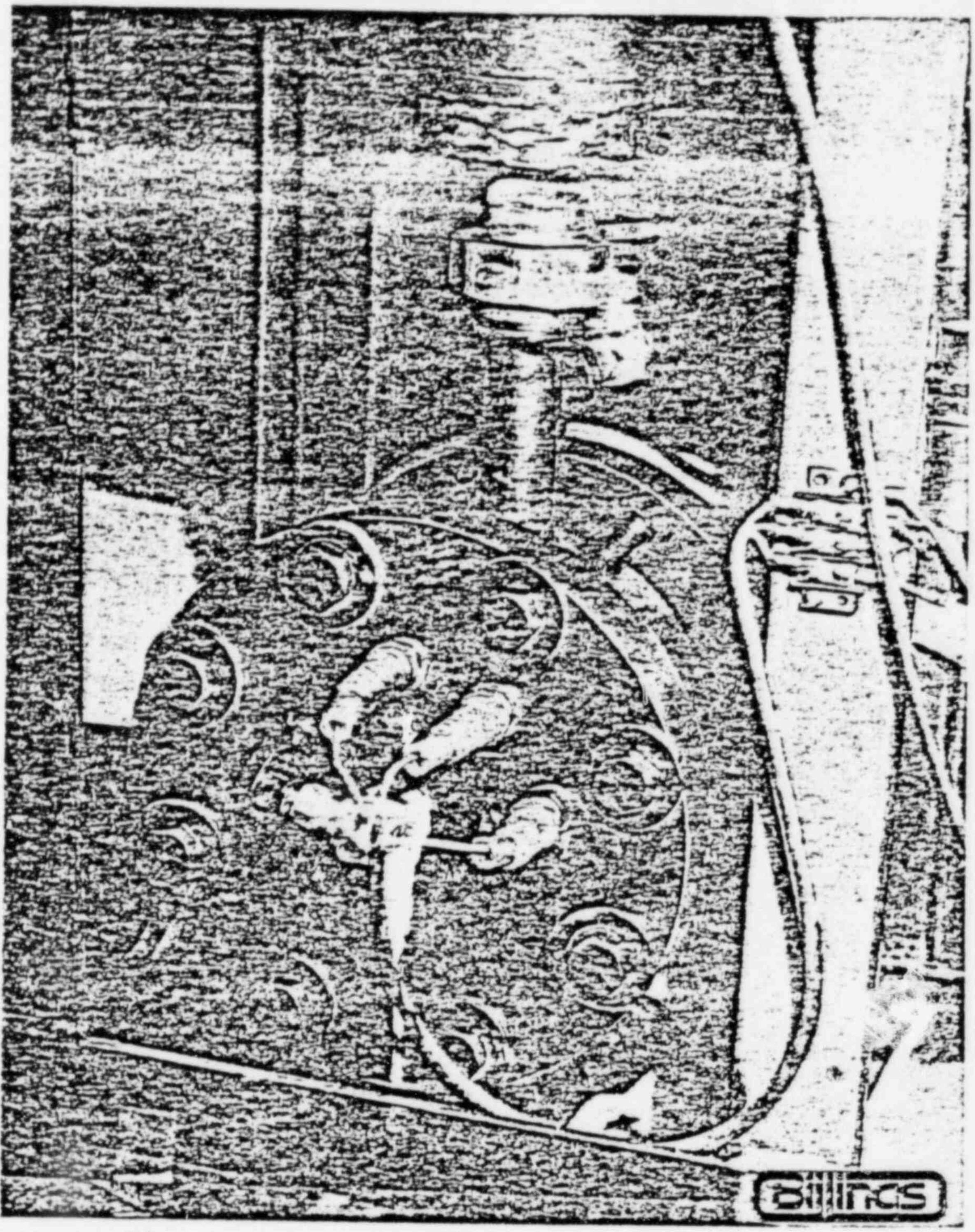


Figure 19 Photograph of the Simulated Reactor High Pressure Pump

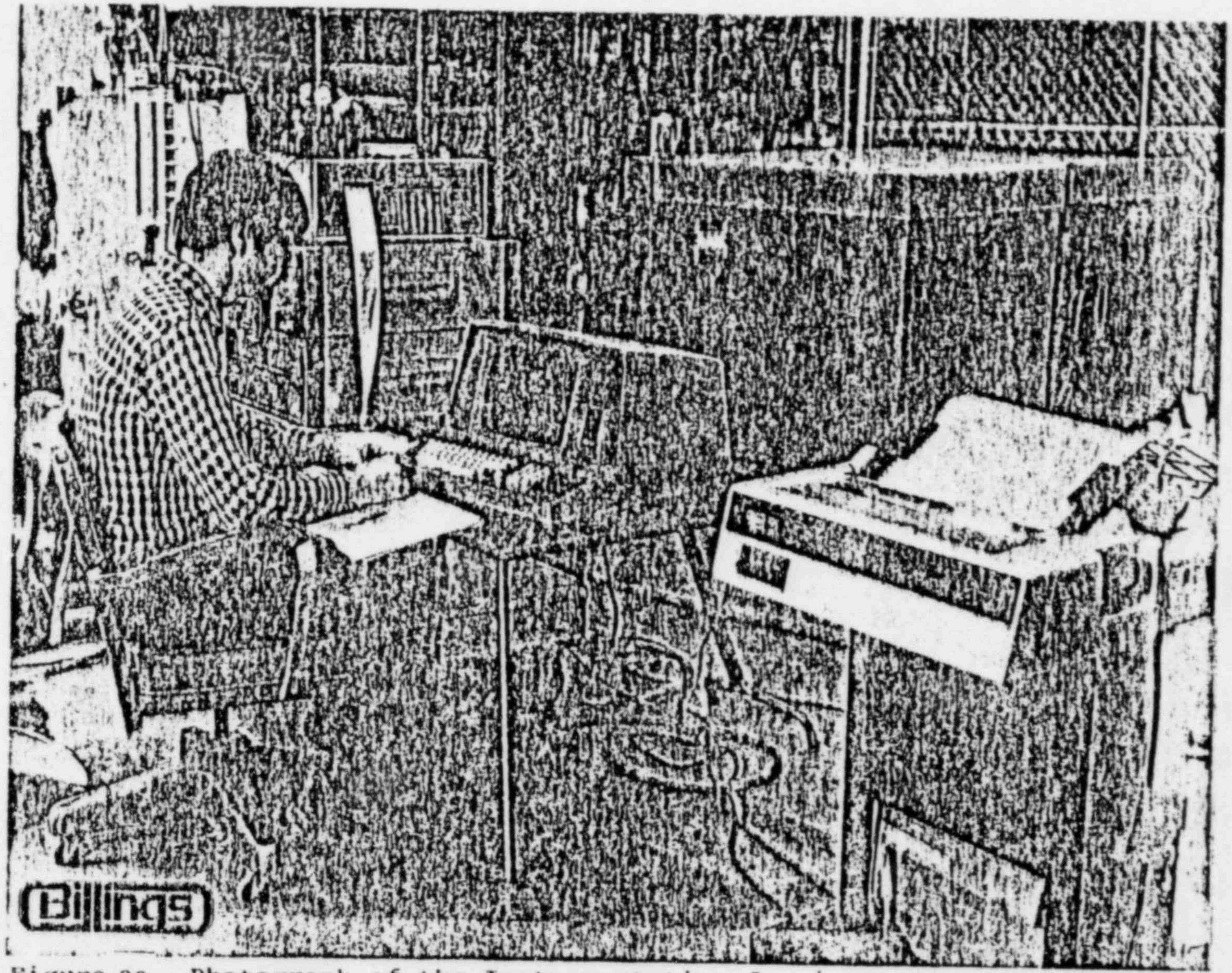


Figure 20 Photograph of the Instrumentation for the Simulated Reactor System

8.4.2 Test A - April 6, 1979

The system was pressurized to 1000 psig (nominal) and heated to 280°F using a primary heating element simulating the core and a secondary heating element around the pipe leg. A band heater on the steam generator was also used.

During test, the secondary heater was disconnected. The primary heater was used to maintain 280°F. This heating element was controlled manually in an on/off fashion. The data plot shows pressure ripples that are coincident with the temperature variation associated with the heating cycle.

Water was drawn from the base of the reactor vessel in an amount that produced approximately 100 psi pressure drops. The water sample passed through a heat exchanger in an ice bath to cool prior to measurement. The mean temperature of the water exiting in the heat exchanger was 86°F. The volume of water was measured directly with graduated glassware.

The plot of Test A (Figure 21) shows graphically that the water was not saturated with hydrogen until a pressure of approximately 300 psig was obtained. At this point a definite pressure rebound, characteristic of saturation, was observed. The fact that the solution was not saturated at 1000 psig was due to some procedural difficulties experienced in setting up for this first test. The data show, however, that in accordance with the laboratory pressure drop tests, the pressure at which saturation occurs can be determined by watching for pressure rebound after an aliquot is extracted.

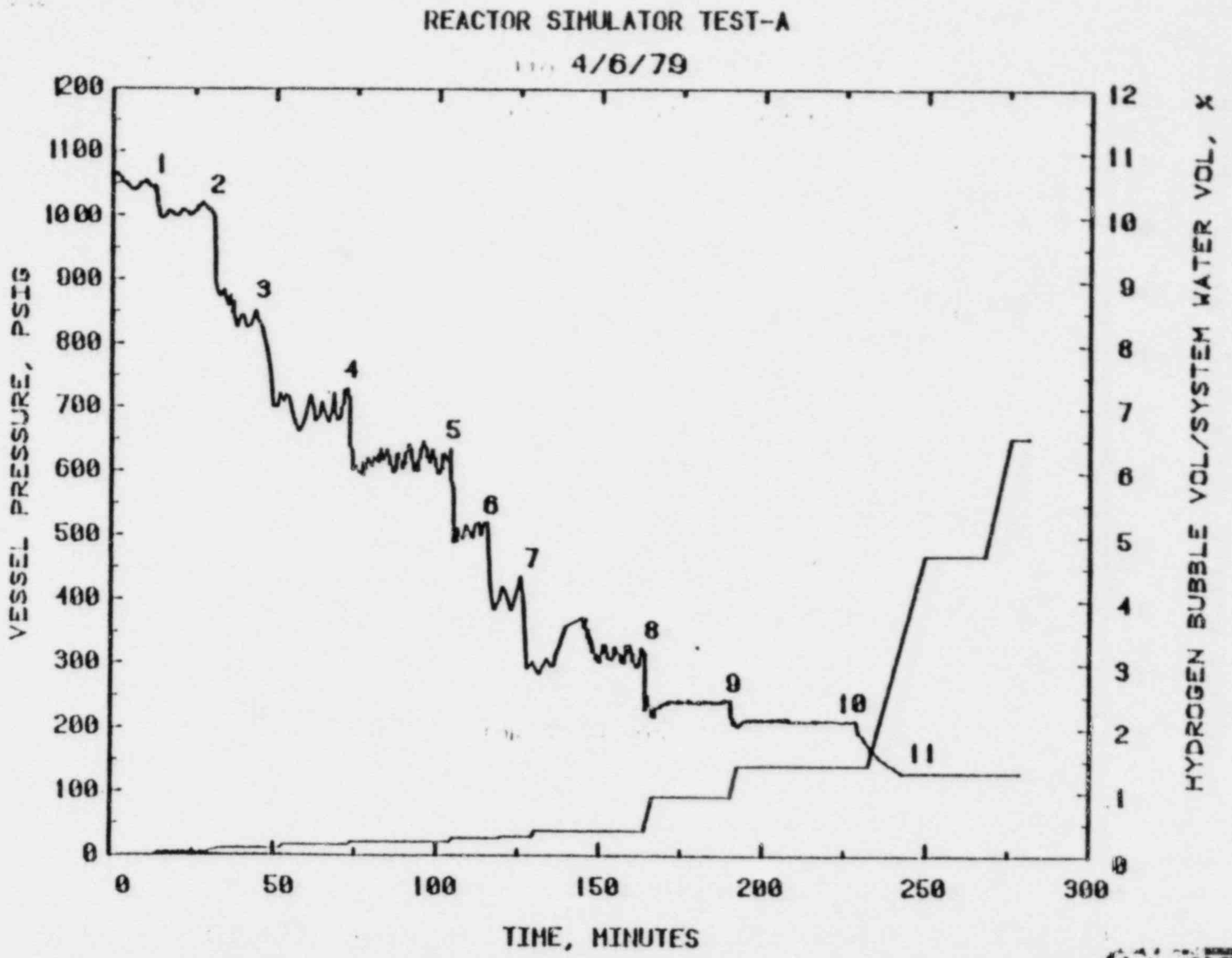


Figure 21 Plot of Bubble Growth as a Function of Pressure, Test A

The hydrogen bubble volume to system water volume ratio corresponded to 0.4 percent at 300 psig. By dropping the pressure further (to 100 psig) the bubble volume grew to 6.5%. (Note that hydrogen bubble volume is inferred from measurements of water removal). No correction has been made in the calculation for volume contraction of the pressure vessels as pressure is decreased. This effect will be examined in Test G.

8.4.3 Test B - April 6, 1979

Test B was performed similarly to Test A with the exception that the core simulation heater was controlled via a variable power transformer rather than an on-off switch. As a result, the pressure ripple due to heating variation was no longer in evidence.

Step changes in vessel pressure were again caused by taking incremental volumes of water from the base of the reactor.

The plot of Test B (Figure 22) shows pressure rebound after the first increment of water was removed. This indicates that hydrogen saturation was achieved at a pressure in excess of 1000 psig. Accordingly, the fraction of bubble volume to water system volume was much greater than in Test A. At 300 psig, for instance, the bubble volume comprised 9.55% of the total system as compared with 0.4% at the same pressure in Test A.

At the conclusion of the test, the size of the bubble in the steam generator was measured by exhausting the gas through a heat exchanger and measuring the volume by displacement of water. At room temperature and atmospheric pressure, reabsorption of

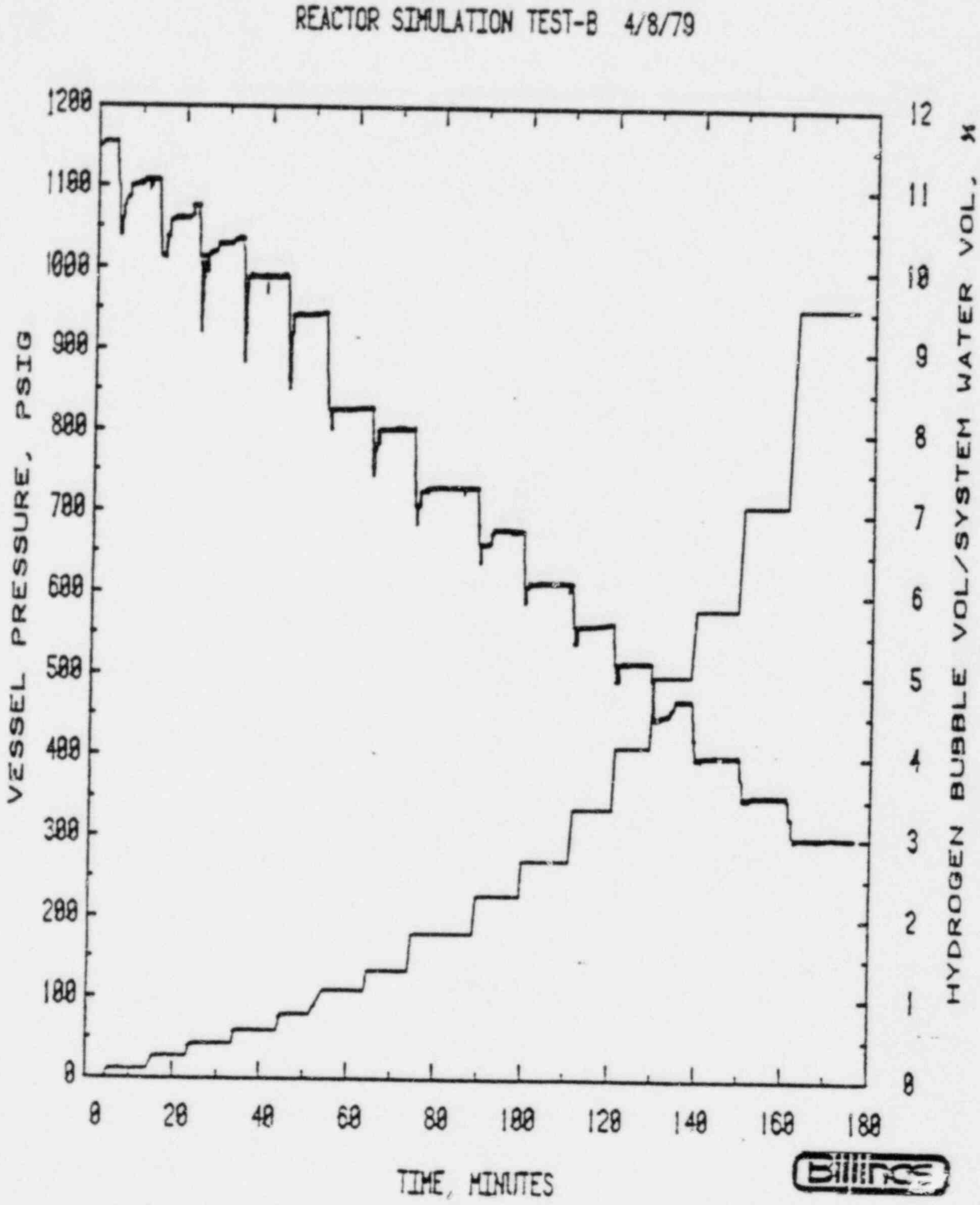


Figure 22 Plot of Hydrogen Bubble Growth vs. Pressure, Test B

hydrogen in the displacement water was assumed minimal. The bubble at the top of the steam generator was obtained by maintaining the final pressure with the pressurizer valved into the system. The valve at the top of the steam generator was then opened slightly and the fluid passed through the heat exchanger. When liquid was obtained, sampling was discountinued. The gas volume in the steam generator adjusted to 280°F and 300 psig, conditions which existed at the end of the test, was very small compared to the hydrogen bubble contained in the total system. Of the total hydrogen bubble, 96% was in the reactor and 4% in the steam generator.

Although the steam generator is physically higher than the reactor, there are three effects that may contribute to the placement of the major portion of the bubble in the reactor. These effects are related to (1) localized pressure drop in the reactor, (2) preferential removal of hydrogen in the reactor due to heat effects at the core simulator heater, and (3) sweeping action of the water flow which convects hydrogen bubbles from the steam generator to the reactor where they collect in the upper half volume above the exit port.

Figure 23 shows the relationship of the pressure rebound verses the target pressure for water saturated with hydrogen. This figure compares to Figure 12 in section 5.0. During a depressurization period, if the water is saturated, as the pressure is reduced an increased amount of hydrogen will evolve thus resulting in a pressure rebound.

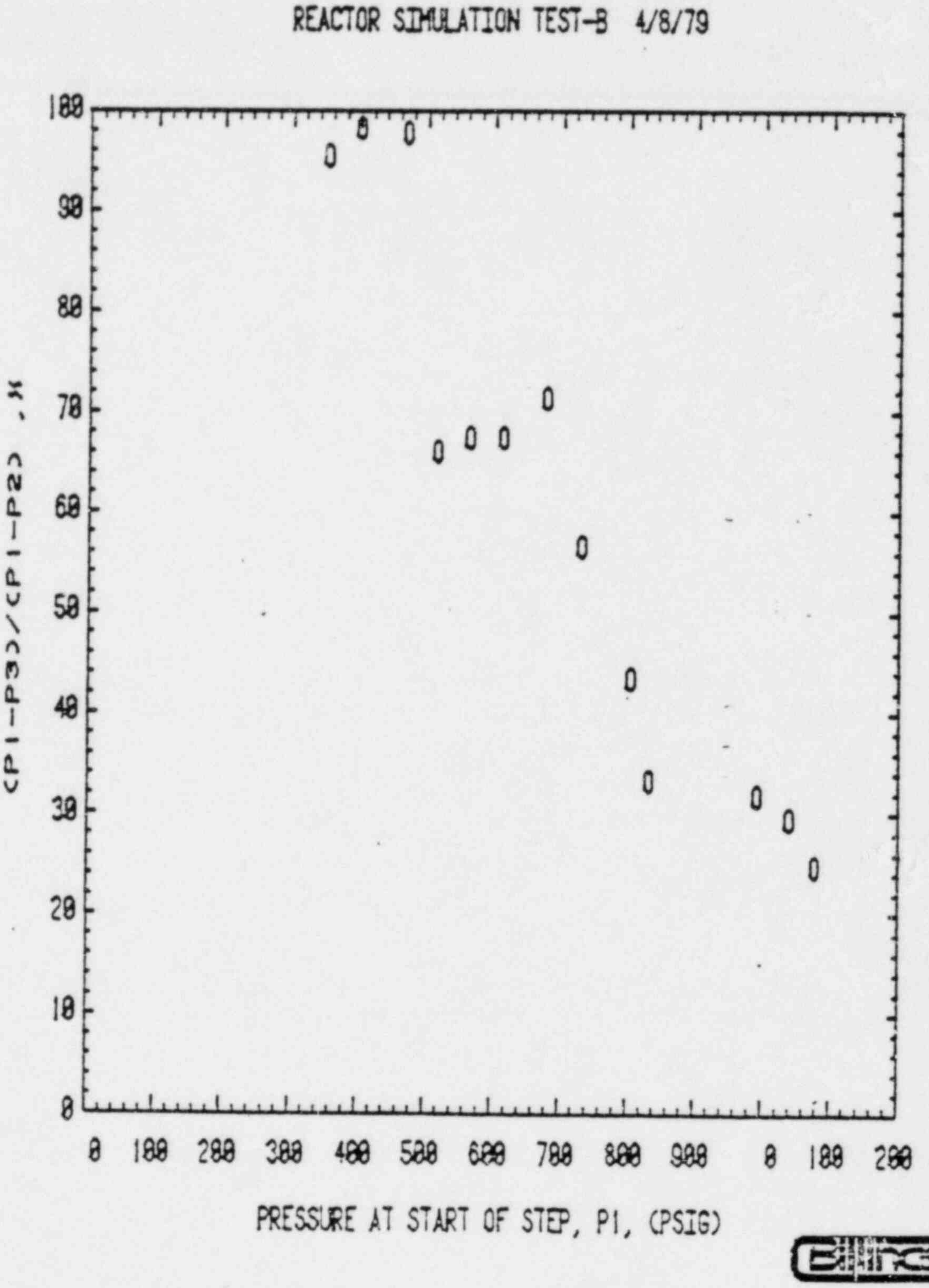


Figure 23 Relationship of Pressure Rebound vs. Target Pressure for Water Saturated with Hydrogen

8.4.4 Test C

A delta P meter was supplied by E.G.&G. with the intent of measuring the change in pressure differential as additional data for ensuing tests. The meter supplied was identical to the meter used in the Harrisburg, Three Mile Island Reactor, and was therefore oversized for the simulated reactor system.

Measurements taken for the purpose of calibration of the meter revealed that the meter would not meet the requirements of the simulator tests and the calibration test was terminated.

8.4.5 Test D - April 9, 1979

Test D was similar to test B with the exception that the water withdrawal rate was continuous instead of periodic. Although the water had been previously saturated with hydrogen, the hydrogen saturation pressure had decreased prior to start of test, as is evidenced by the data plot (see Figure 24). Bubble growth was only 3% of the system water volume.

8.4.6 Test E - April 9, 1979

The continuous sample method of Test D was repeated in Test E after re-establishing hydrogen saturation at 1000 psig. Figure 25 shows a much more dramatic growth of bubble size with pressure decrease.

As in all previous tests, the water temperature was held at 280°F during depressurization.

8.4.7 Test F - April 9, 1979

Test F was a repeat of test E with continuous water removal. The only change made was that the water was drawn

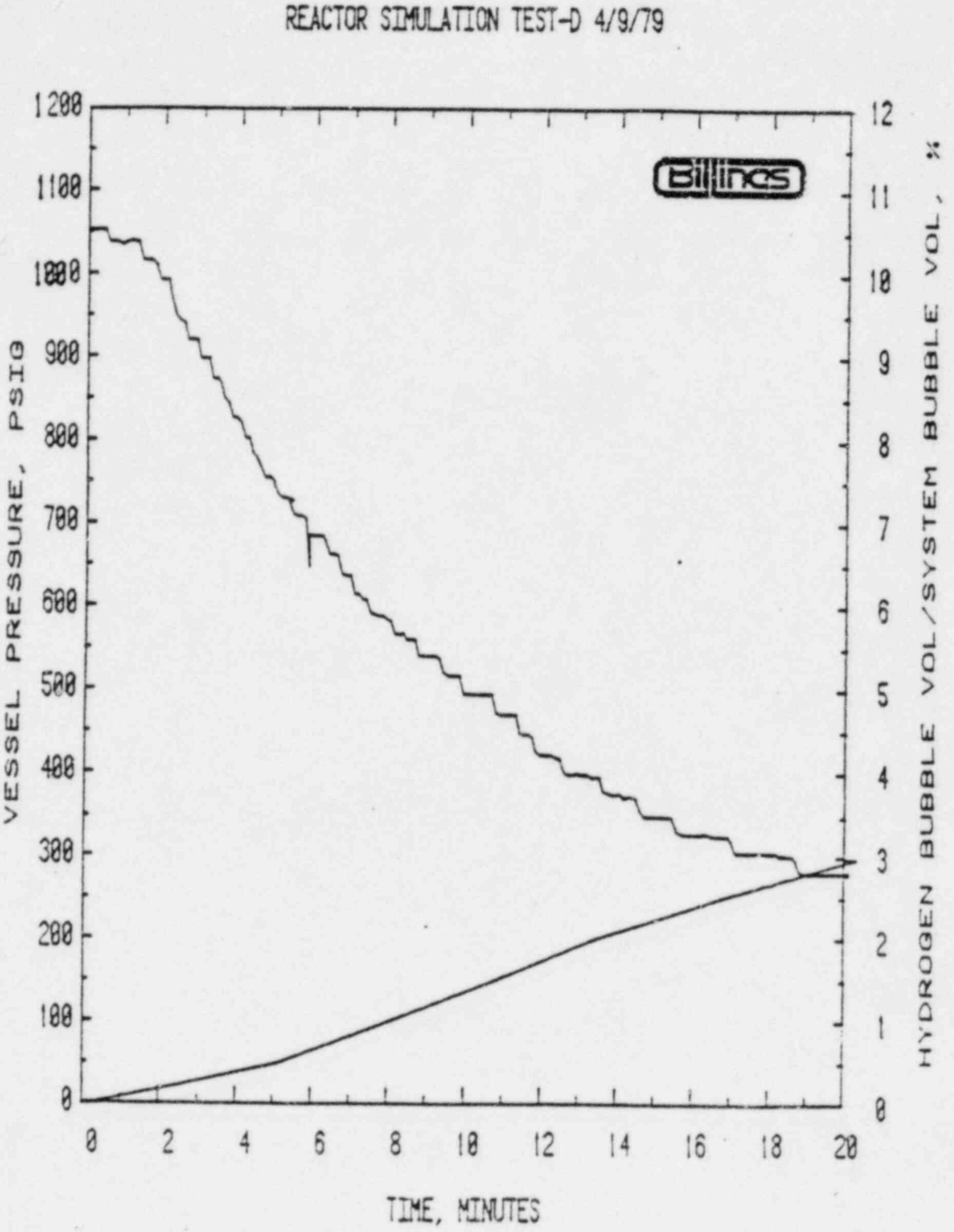


Figure 24 Hydrogen Bubble Volume as a Function of Pressure, Test D

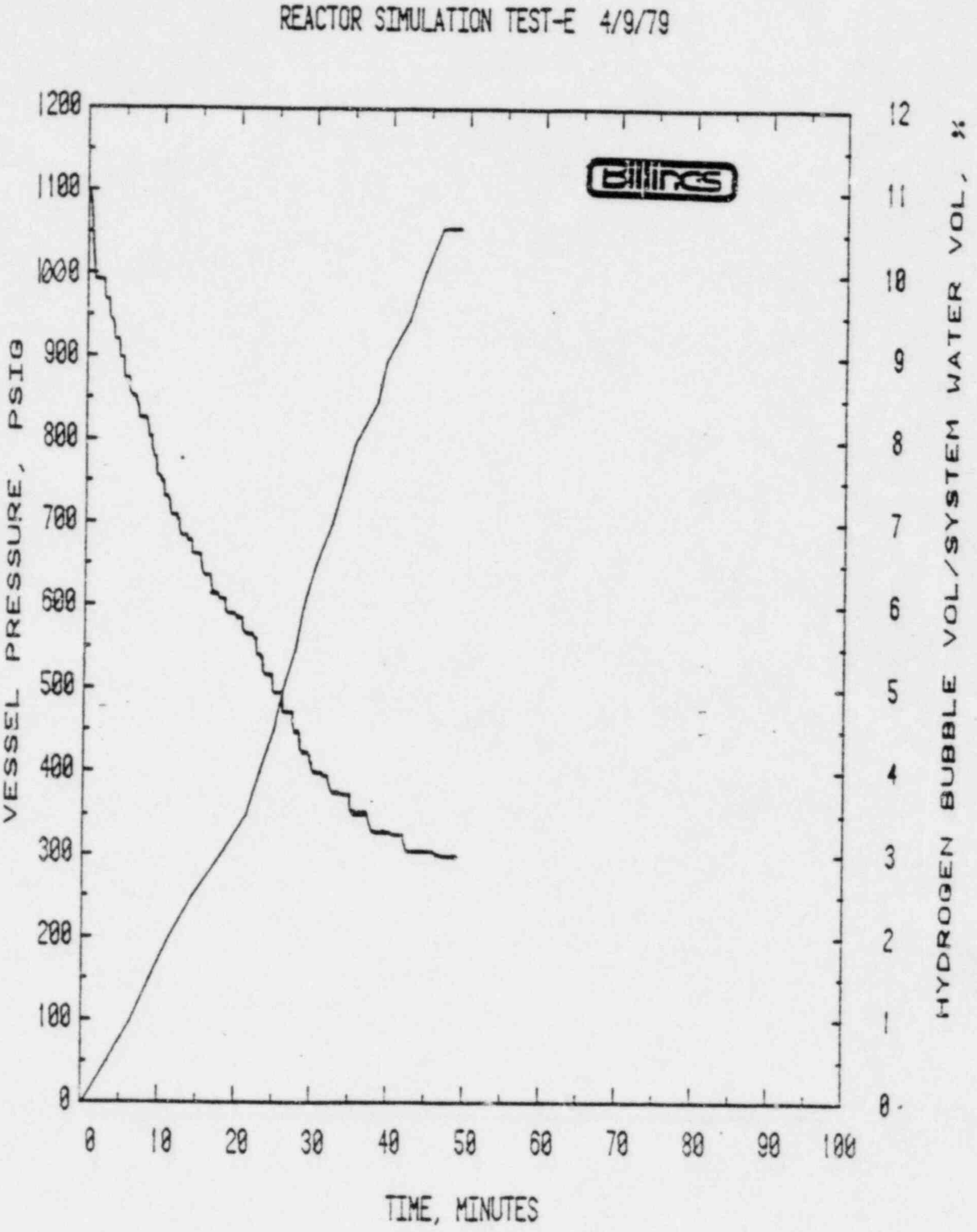


Figure 25 Hydrogen Bubble Volume vs. Pressure, Test E

from a tap at the base of the pressurizer instead of at the base of the reactor vessel. This change was made to more closely simulate the withdrawal of water from the pressurizer and also to see if a greater percentage of the hydrogen bubble would form in the steam generator.

Results were similar to test I. A slightly greater hydrogen bubble was created in the system at 300 psig in test E than in test F (See Figure 26). The amount of hydrogen volume present in the steam generator was still small in comparison to the total bubble size indicating that the location of the water withdrawal tap was not a significant factor.

8.4.8 Test G

Part 1: Using unsaturated water the system was brought up to temperature while measuring delta p. Pressurization above the boiling point was accomplished by applying hydrogen to the pressurizer. It was assumed that the surface area of contact would be sufficiently small and the volume flow from the pressurizer sufficiently low that the amount of hydrogen going into solution would be slight.

Part 2: The system was depressurized as in Tests D, E, and F. This run established the system volume decrease with pressure reduction as the vessels contract. Results of test G are plotted in Figure 30, in which the relationship of tests A, B, E, F, G, and I is shown.

Measurement of delta p was taken in both parts. The peak to peak noise level of the delta p signal was noted on a strip chart recorder. No difference in noise level was observed.

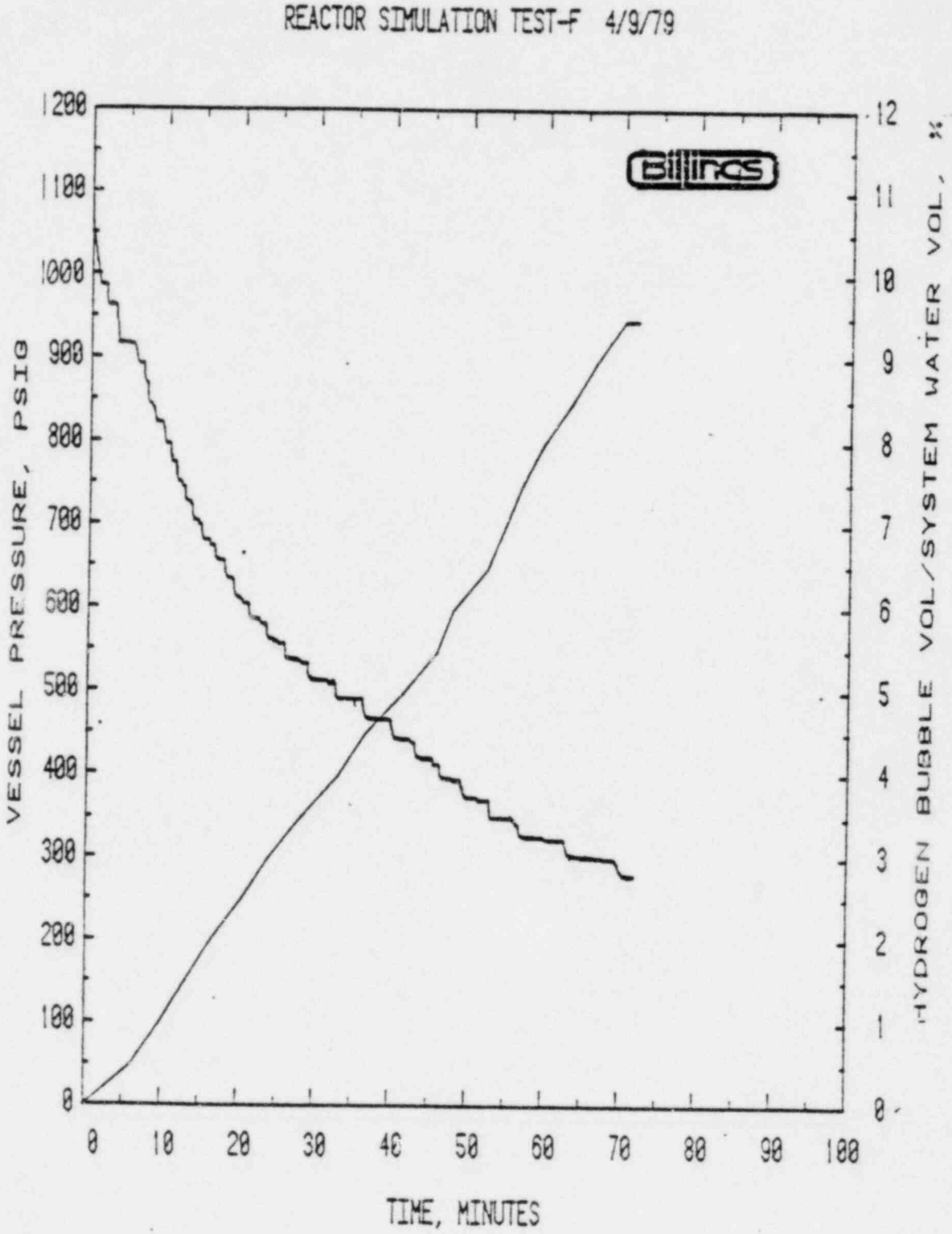


Figure 26 Hydrogen Bubble Volume vs. Pressure, Test F

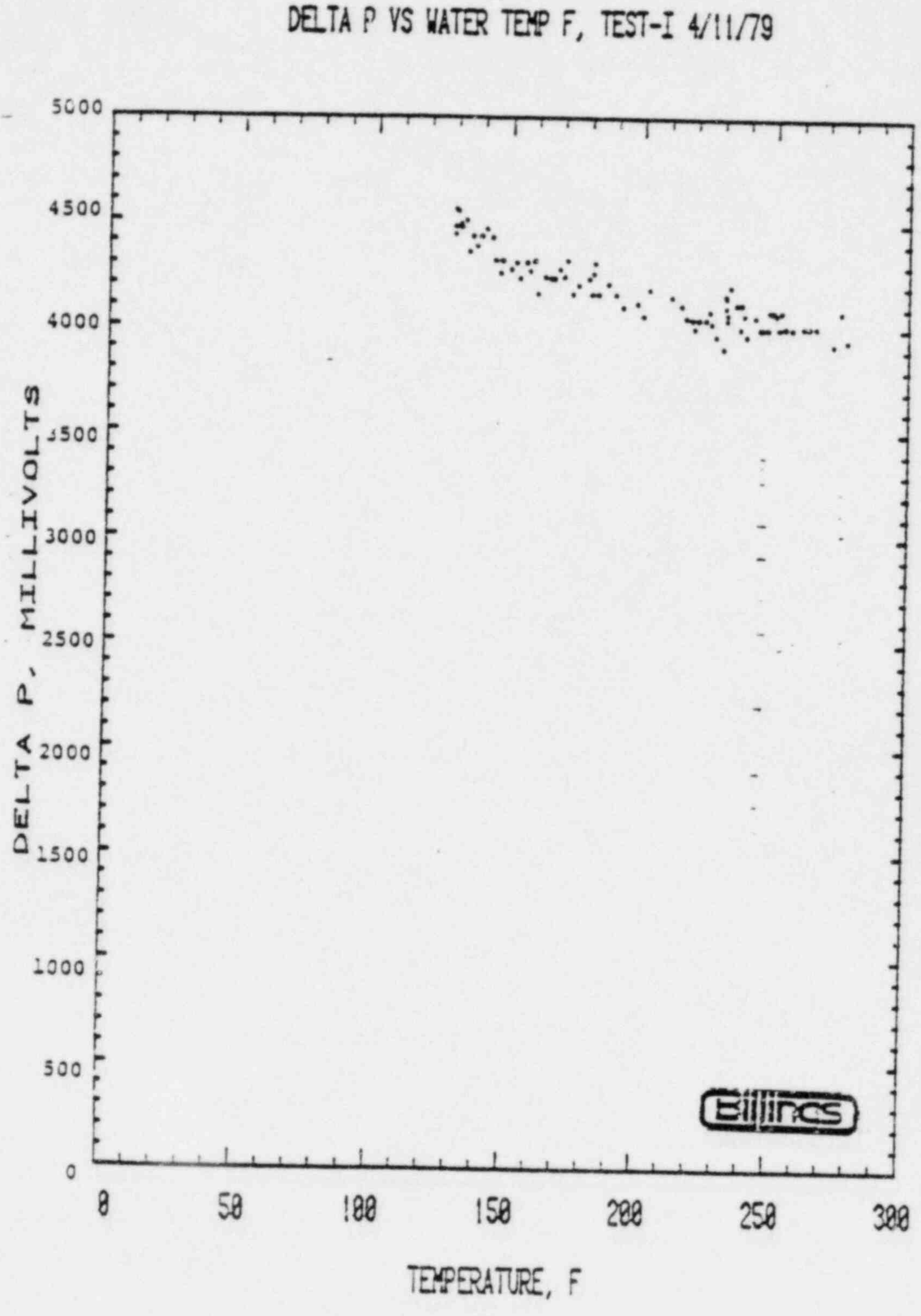


Figure 27 Differential Pressure as a Function of Temperature, Test F

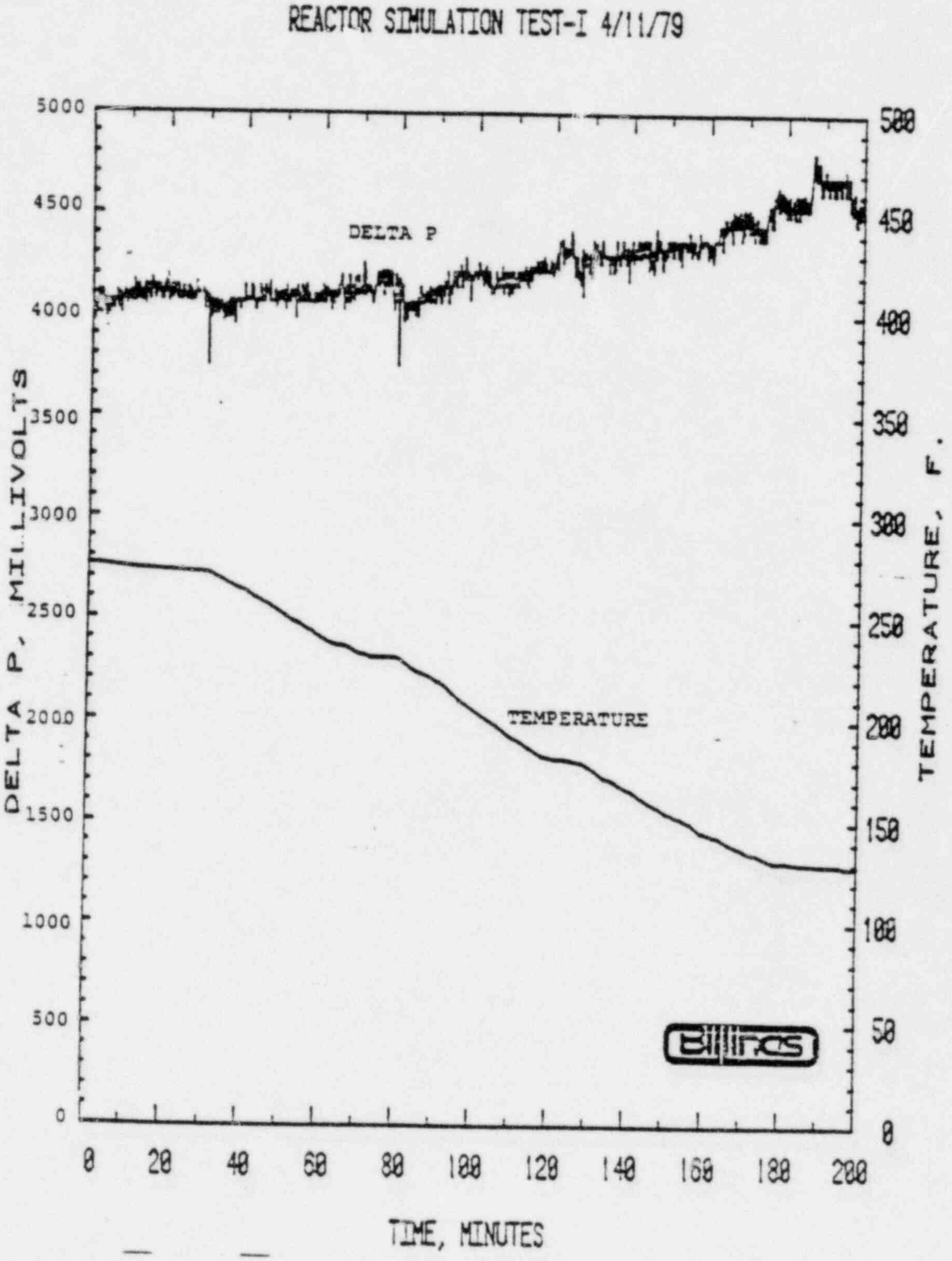


Figure 28 Differential Pressure as a Function of Temperature and Time, Test I

REACTOR SIMULATION TEST-I 4/11/79

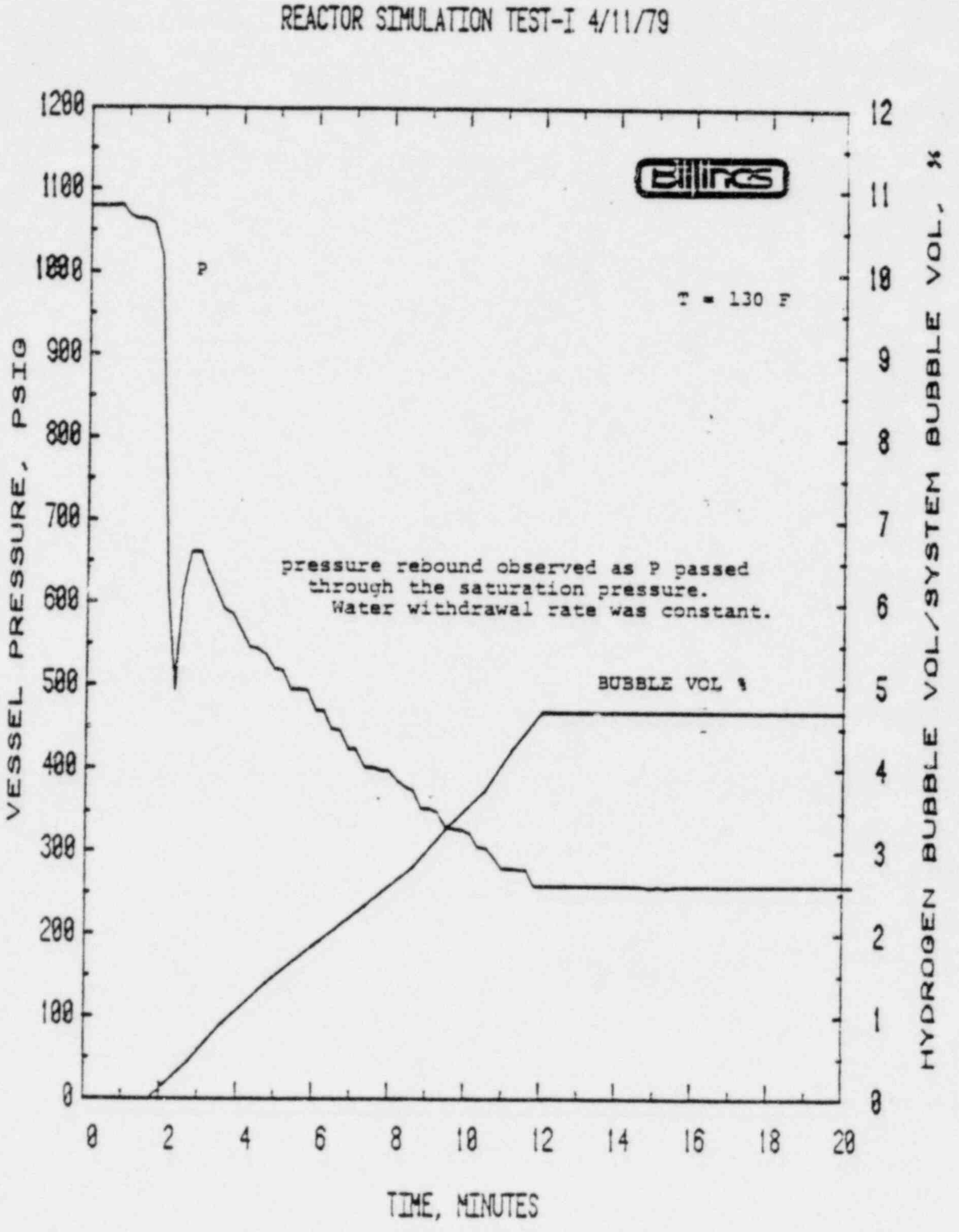


Figure 29 Hydrogen Bubble Volume as a Function of Pressure, Test I

8.5 Interrelationship of Tests A, B, E, F, G and I

Figure 30 shows the pressure vs. bubble volume relationship for tests A, B, E, F, and I. Test G is also shown, which indicates volume correction to be made for vessel system contraction with pressure reduction.

Figure 31 presents a semi-logarithmic plot of vessel pressure drop versus hydrogen bubble size for tests A, B, E and F. The slope of each line is representative of the rate of bubble growth with pressure drop. The intercept at the ordinate roughly estimates the hydrogen saturation pressure.

The bubble for test I is obviously smaller than would be expected in comparison with tests B, E, and F and the rate of bubble growth is lesser. The reasons for this include the following:

(a) The starting saturation pressure was less than for tests B, E, and F.

(b) Decreasing the temperature while holding the pressure constant required that approximately 6% additional water be added to the system from the pressurizer to compensate for the water volume decrease with temperature decrease. The additional water was unsaturated and therefore decreased the saturation pressure of the system.

(c) When the pressure was dropped it was at a constant temperature of 130°F. The size of the hydrogen bubble formed was smaller for a given amount of hydrogen leaving the solution because of the lowered

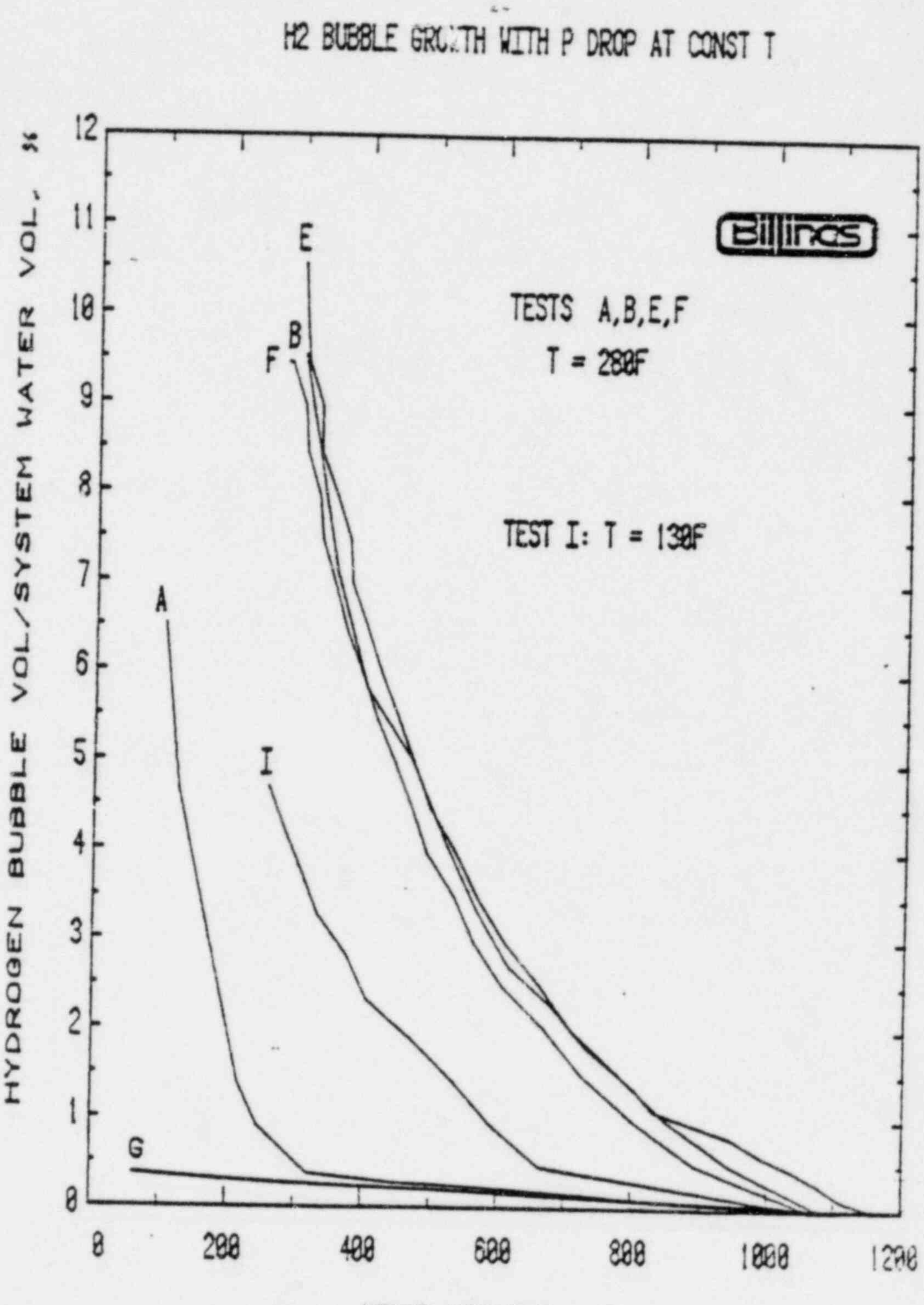


Figure 30 Composite Plot of Tests A, B, E, F, G, I Showing Bubble Growth as a Function of Pressure

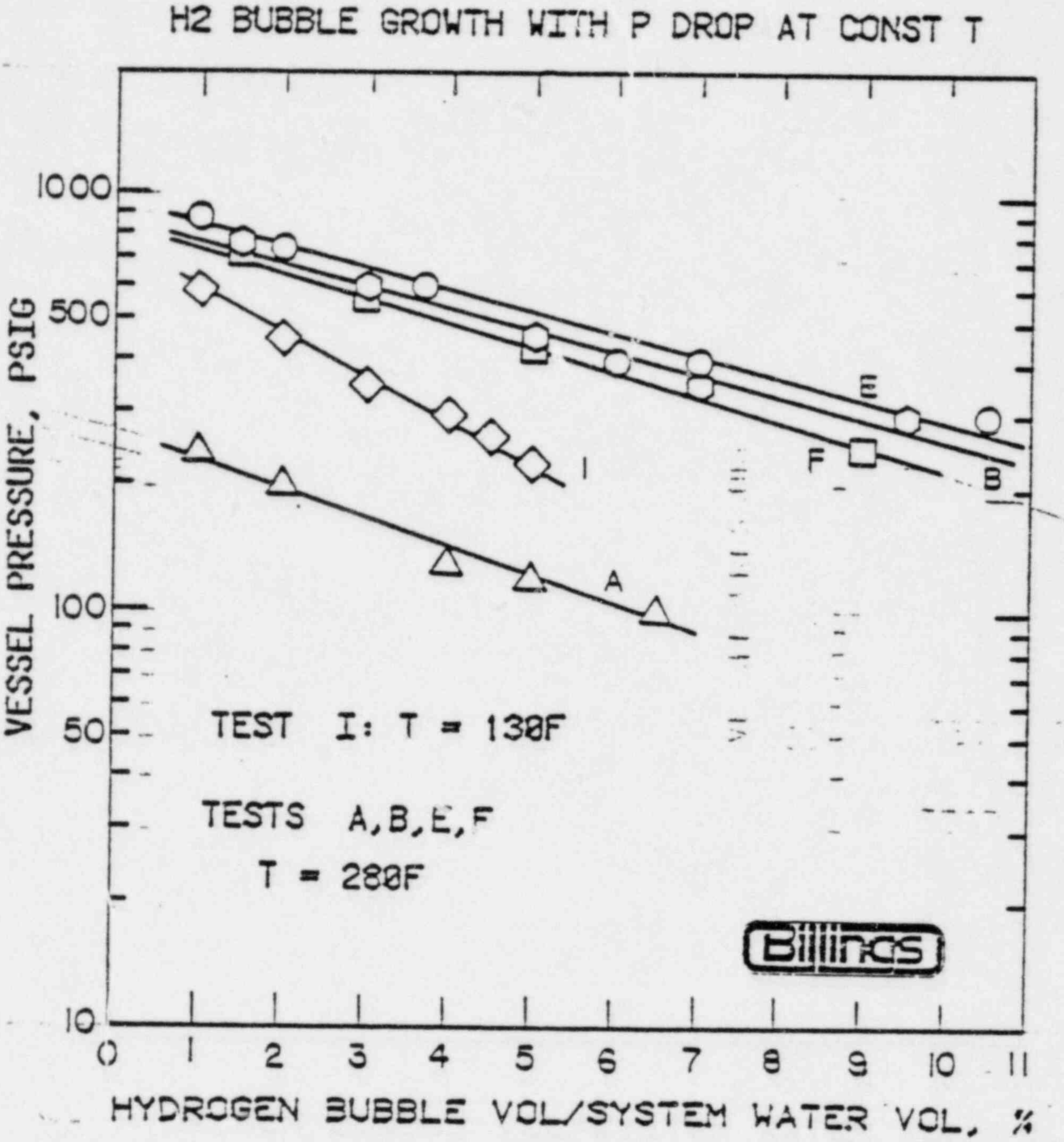


Figure 31 Composite Plot on Semi Log Paper of Bubble Growth as a Function of Pressure, Tests A, B, E, F, I

temperature of the gas bubble.

Figure 30 shows that tests B, E, and F had roughly the same saturation pressure and that even though B was a stepwise depressurization test while E and F were continuous, the rate and extent of bubble formation was comparable. Water was withdrawn from the system from the base of the reactor simulator in tests B and E, whereas water withdrawal was from a connection below the pressurizer in test F. The difference in withdrawal ports apparently has little effect upon bubble formation.

Test A had a beginning saturation pressure of approximately 300 psig at 280°F, yet exhibited the same rate of hydrogen bubble growth as tests B, E, and F. Test I had a saturation pressure of approximately 700 psig at 130°F and demonstrated a significantly lower rate of bubble growth with depressurization. The difference of bubble growth rate can be attributed to the difference in depressurization temperatures. The advisability of first reducing temperature and then reducing pressure for minimum bubble growth is demonstrated.

Test G (See Figure 30) shows the extent of apparent hydrogen bubble growth for the system upon depressurization. This apparent bubble growth is in actuality the volume decrease of the system seen as a volume of water that is taken from the system as the vessel contracts with decreasing pressure. Points along line G in figure 29, for any given pressure, should be subtracted from the indicated bubble growth for a given test as compensation for vessel contraction.

Delta P measurements revealed changes with temperature but no change in either level or peak to peak noise with change in hydrogen content.

8.6 Observation During Set-up and Procedures

During the final procedural steps before beginning Test A, a fortuitous "accident" occurred. The information obtained is important enough to be included here.

The sequence of events is recounted below. No data were being taken at the time.

1. Hydrogen was being bled through the system from below and bled out the top of the reactor vessel.
2. The pressure was near 1100 psig and the temperature was in the range of 110 to 115°C and increasing preparatory to test.
3. The pressurizer was connected to the system so that the system was "soft" with a gas volume in the pressurizer. No gas volume was being maintained in the reactor simulator.
4. Workmen were installing another heating element on the outside of the water circulation leg (HC in figure 15) when the system pressure began to rise out of control. The hydrogen supply was turned off.
5. Pressure continued to rise and the sight gauge showed the appearance of a hydrogen bubble in the reactor vessel that was growing in size. System pressure had reached 1400 psig and the liquid level indicator was falling rapidly.

6. The vent was opened at the top of the steam generator. This caused the bubble to grow more rapidly, and the pressure would rebound whenever venting was stopped.

7. The heater was turned off. This permitted a stable pressure to be reached at about 1416 psig, but the bubble remained.

8. Some venting from the top of the bubble was tried. The pressure dropped during venting but rebounded when the valve was shut.

9. A workman noticed that he had no power to his drill and it was found that the power plug to the circulation pump had been inadvertently pulled from the wall.

10. Water circulation was reestablished.

11. As the system temperature was observed to be falling, the heater was again turned on. When the auxilliary heater was ready, it too was turned on.

12. Venting continued periodically to hold the pressure in the 1100 and 1200 psig range.

13. Heating with circulation caused the bubble to stabilize. Continued rise in temperature caused the bubble to decrease in size and to disappear eventually.

14. Hydrogen flow through the system was reestablished.

15. Bleed flow of hydrogen continued for approximately another two hours at which time the test temperature was obtained. The test was then carried out under the false assumption that saturation had been reachieved.

8.7 Appendix

INSTRUMENTATION LIST

1. Bailey Differential Pressure Transducer - Type BQ

   Accuracy: 0.25% of span + 0.01% of upper range limit per °F.
   Less than .005% per volt change of power supply.

2. Sargent Welch Strip Chart Recorder - Model XKR

   Accuracy: 0.5% of full scale.

3. Billings A to D board

   Accuracy: ± LSB, approx. 0.025% of full scale reading.

4. Monitor Labs Data Logger - Model 9300

   Accuracy: For temperature measurement - .1° ± 0.54°F or 0.3°C compensation error assuming no temperature gradient on the iso-thermal block (connection block).
   For voltage measurements - 0.055% total error.

5. Bourns Indicating Pressure Transducer - Model 2053126050

   Accuracy: ± 3.0% of full scale.

6. Bourns PSIA Transmitter - Model 2900

   Accuracy: 0.5% of full scale (total non-linearity & hysteresis).

7. Omega J & K Type Thermocouples - ANSI Standard

   Accuracy: 4°F. conformity error in the range of 32 - 530°F

Instrumentation - Calibration

Prior to running any tests on the simulated reactor apparatus the various instruments were calibrated and checked for accuracy. Shown below is the calibration of the pressure transducers.

$$PSIG = A_g V_g + B_g$$

$A_g = 648.789$ psig/volt

$B_g = 85.0$ psig

$$PSIA = A_a V_a + B_a$$

$A_a = 612.595$ psia/volt

$B_a = +10.86$

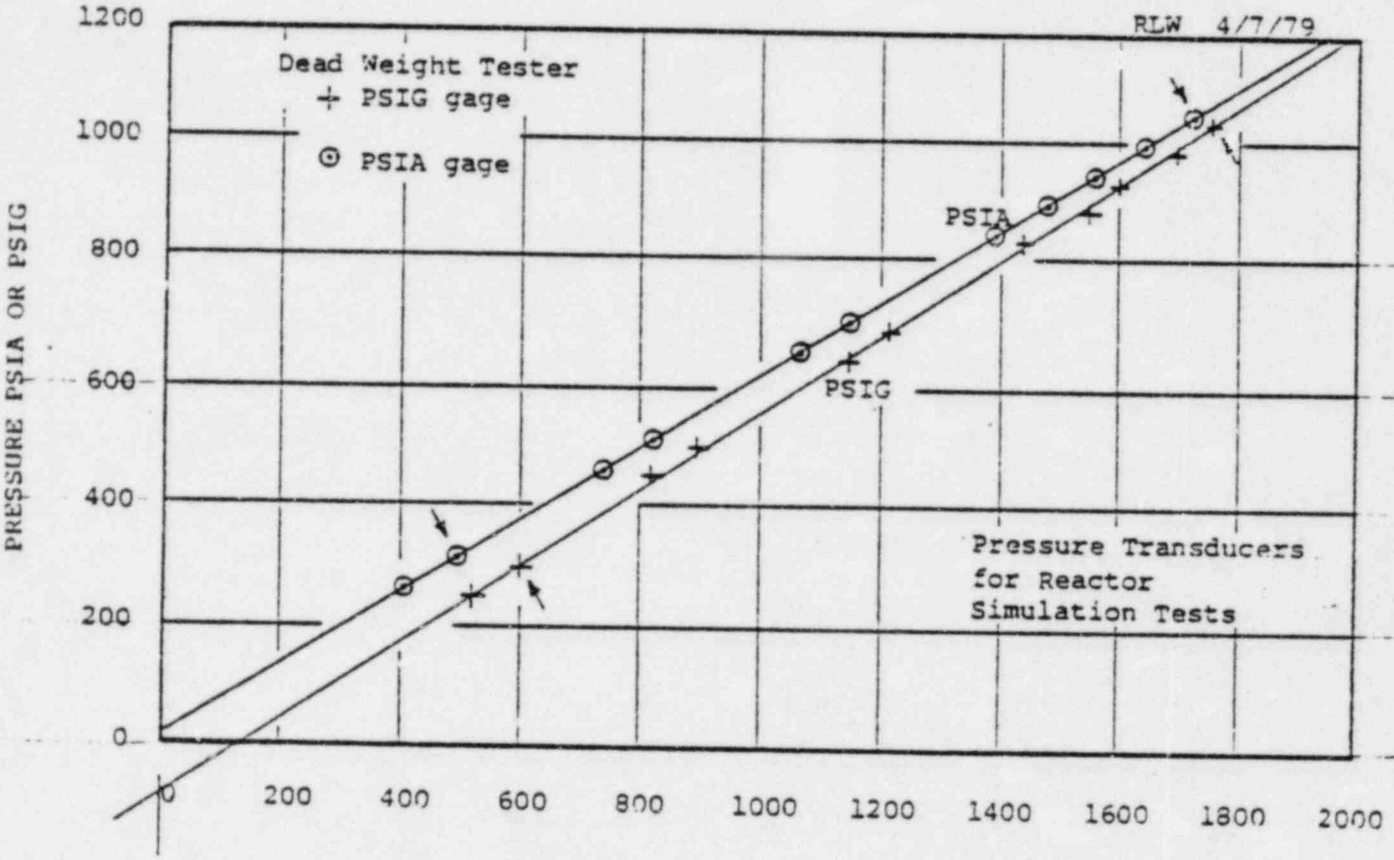
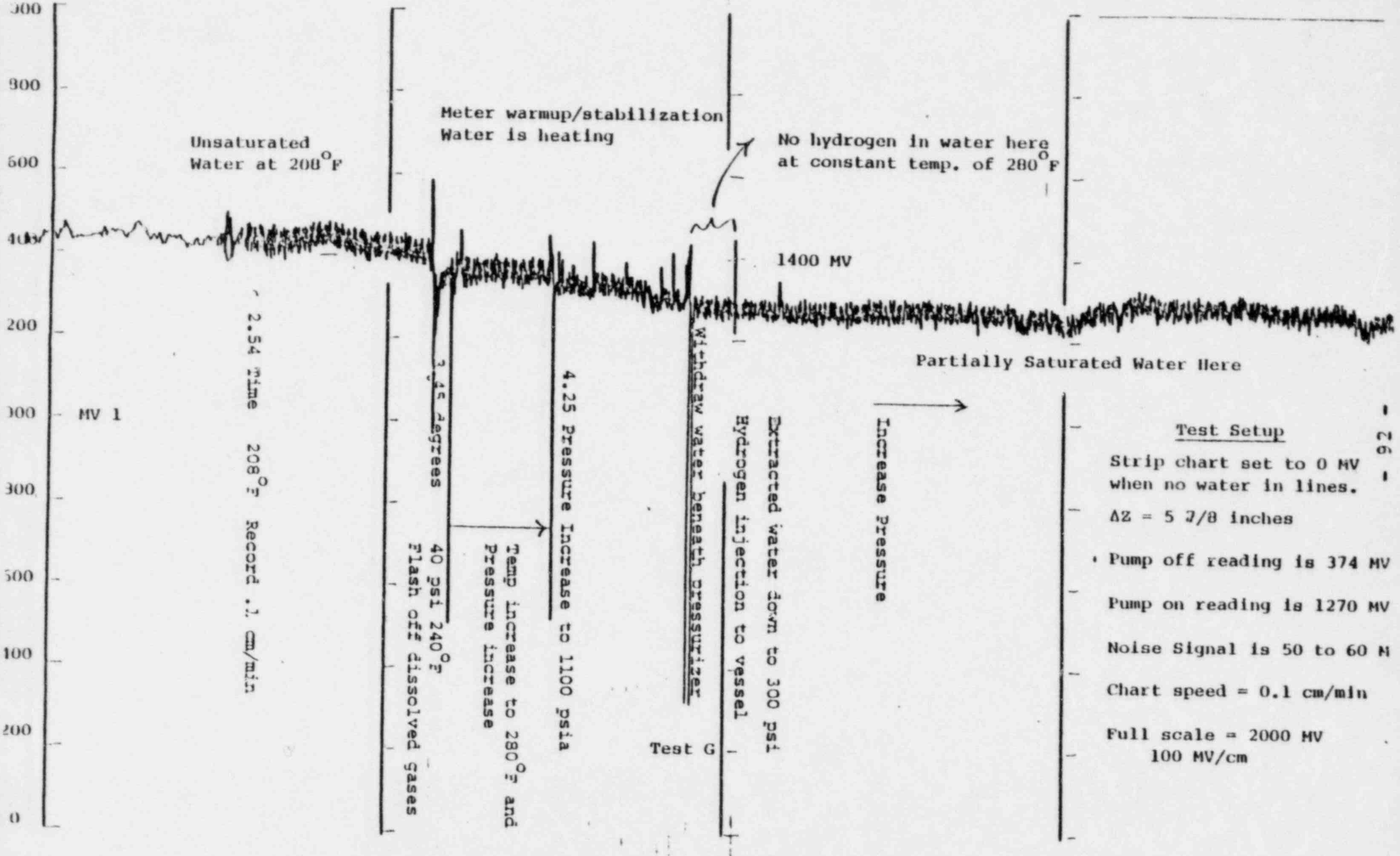


Figure 32 Calibration of Pressure Transducer



Test Setup

Strip chart set to 0 MV
when no water in lines.

ΔZ = 5 7/8 inches

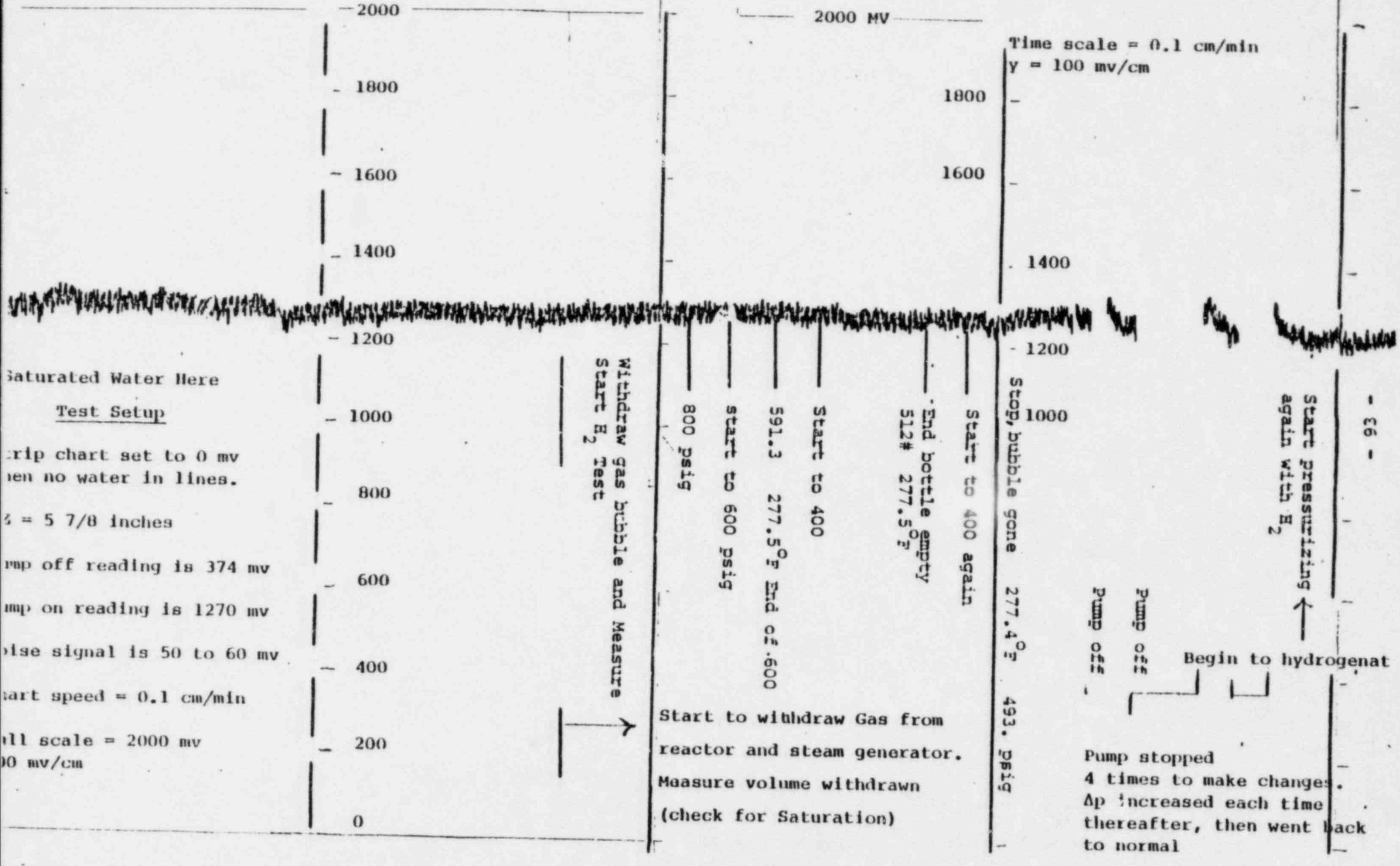
Pump off reading is 374 MV

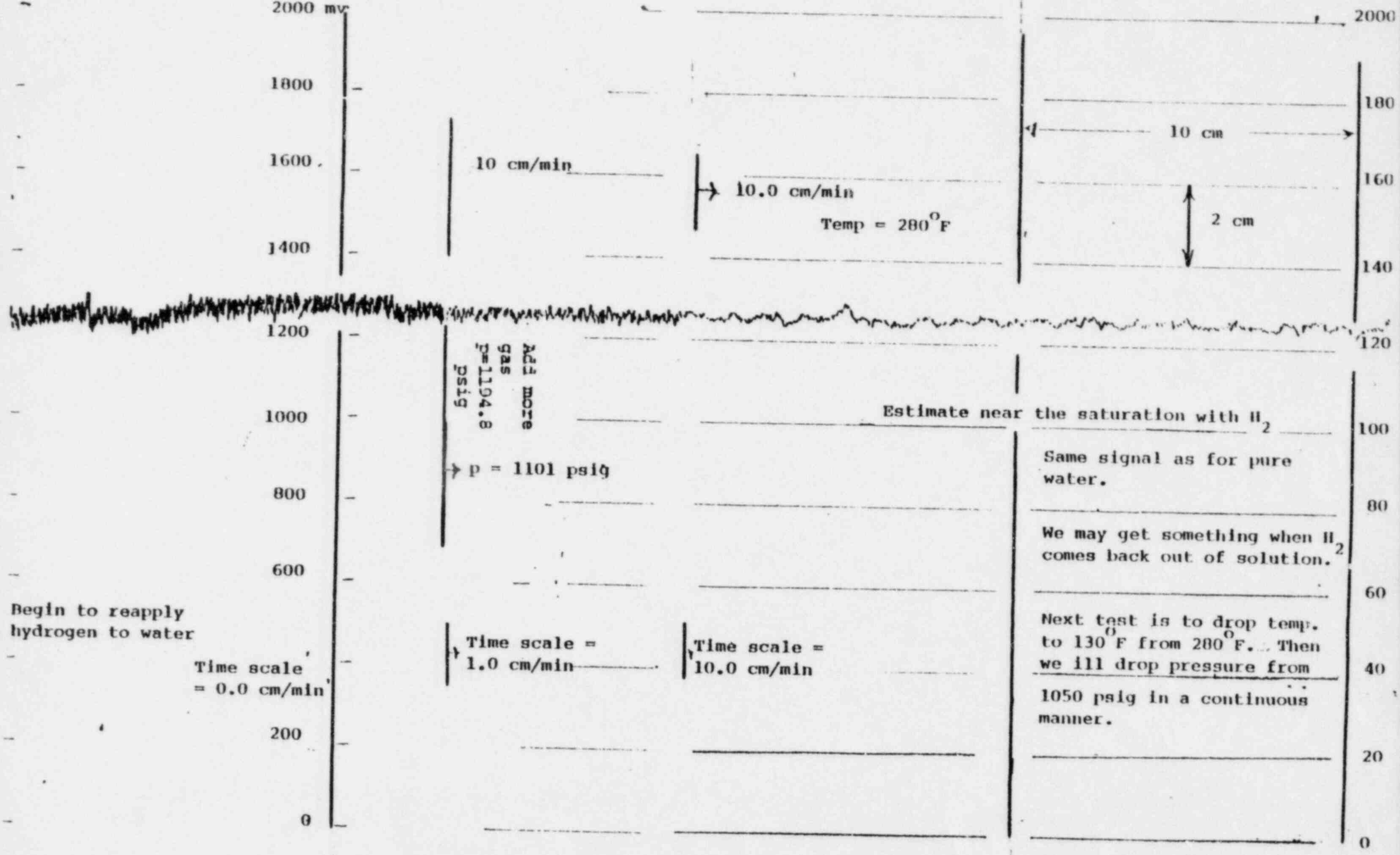
Pump on reading is 1270 MV

Noise Signal is 50 to 60 M

Chart speed = 0.1 cm/min

Full scale = 2000 MV
100 MV/cm


2000 MV
Time scale = 0.1 cm/min
y = 100 mv/cm
2000
1800
1600
1400
1200
1000
800
600
400
200
0
Saturated Water Here
Test Setup
rip chart set to 0 mv
ien no water in lines.
= 5 7/8 inches
mp off reading is 374 mv
mp on reading is 1270 mv
ise signal is 50 to 60 mv
art speed = 0.1 cm/min
ll scale = 2000 mv
0 mv/cm
Withdraw gas bubble and Measure
Start H2 Test
800 psig
start to 600 psig
591.3 277.5°F End of 600
Start to 400
End bottle empty
512# 277.5°F
Start to 400 again
Stop, bubble gone 277.4°F 493. psig
Start to withdraw Gas from
reactor and steam generator.
Measure volume withdrawn
(check for Saturation)
Pump off
Pump off
Begin to hydrogenat
Start pressurizing
again with H2
Pump stopped
4 times to make changes.
Δp increased each time
thereafter, then went back
to normal



Begin to reapply hydrogen to water

Time scale = 0.0 cm/min

10 cm/min

Add more gas p=1194.8 psig

p = 1101 psig

Time scale = 1.0 cm/min

10.0 cm/min

Temp = 280°F

Time scale = 10.0 cm/min

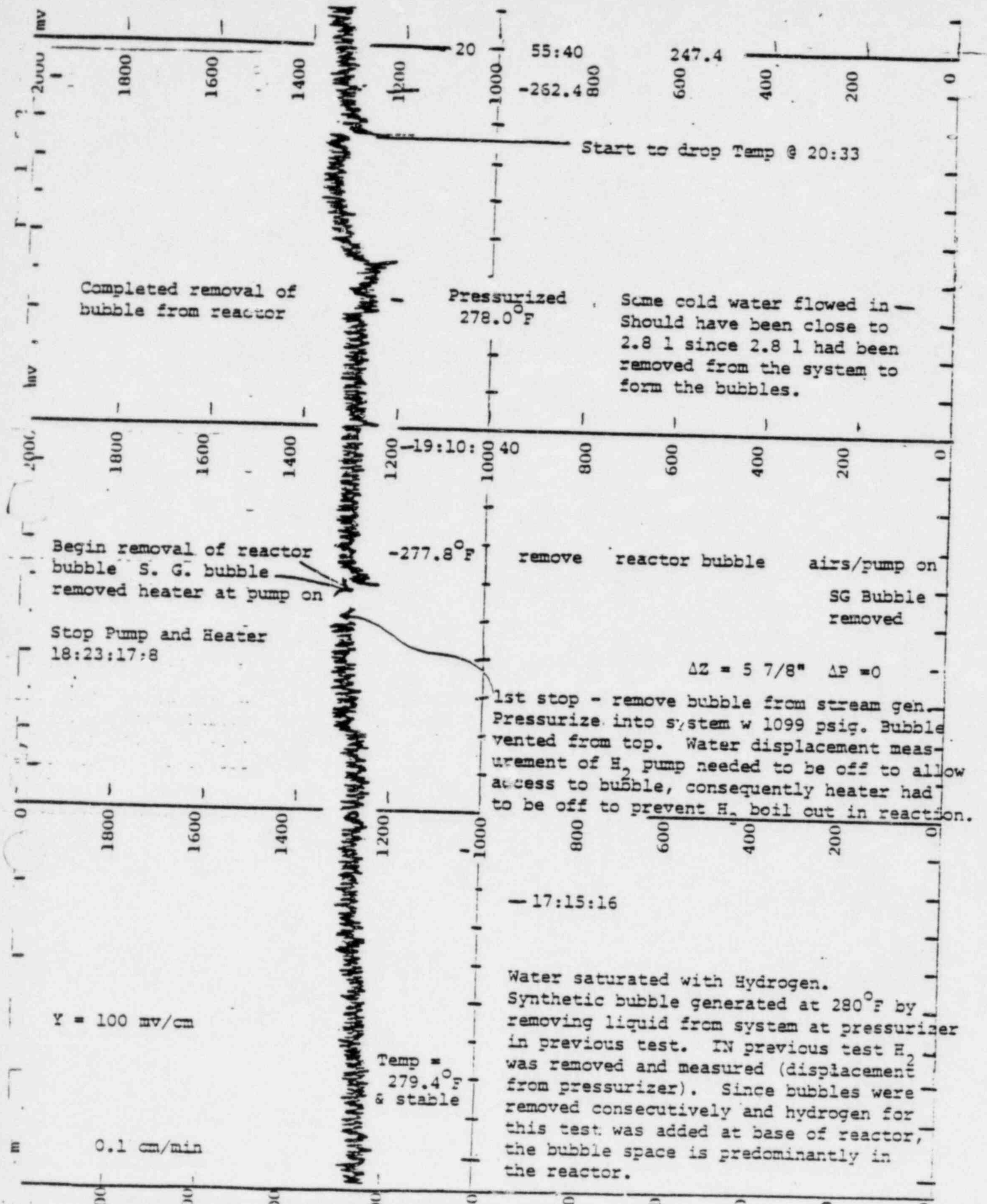
Estimate near the saturation with H_2

Same signal as for pure water.

We may get something when H_2 comes back out of solution.

Next test is to drop temp. to 130°F from 280°F. Then we ill drop pressure from 1050 psig in a continuous manner.

April 11, 1978
7:30 pm MST



Start to drop Temp @ 20:33

Completed removal of bubble from reactor

Pressurized 278.0°F

Some cold water flowed in — Should have been close to 2.8 l since 2.8 l had been removed from the system to form the bubbles.

-19:10:40

Begin removal of reactor bubble S. G. bubble removed heater at pump on

-277.8°F remove reactor bubble airs/pump on

SG Bubble removed

Stop Pump and Heater 18:23:17:8

ΔZ = 5 7/8" ΔP =0

1st stop - remove bubble from stream gen. Pressurize into system w 1099 psig. Bubble vented from top. Water displacement measurement of H_2 pump needed to be off to allow access to bubble, consequently heater had to be off to prevent H_2 boil out in reaction.

— 17:15:16

Water saturated with Hydrogen. Synthetic bubble generated at 280°F by removing liquid from system at pressurizer in previous test. IN previous test H_2 was removed and measured (displacement from pressurizer). Since bubbles were removed consecutively and hydrogen for this test was added at base of reactor, the bubble space is predominantly in the reactor.

Y = 100 mv/cm

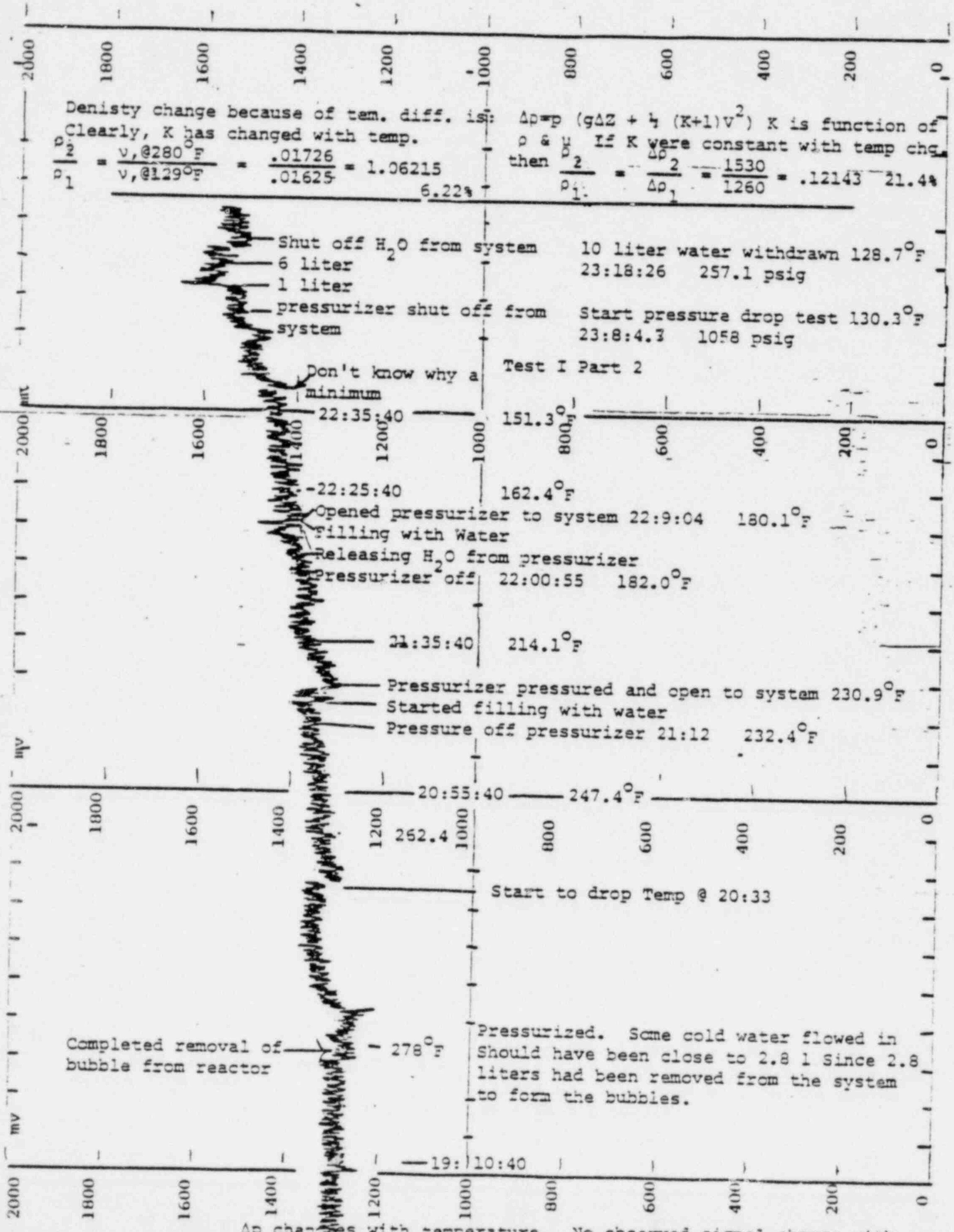
Temp = 279.4°F & stable

0.1 cm/min

15:57:54.0

10 cm/min

April 11, 1979
Test I
Temp drop test Part 1.



Denisty change because of tem. diff. is: $\Delta\rho = \rho\,(g\Delta Z + \frac{1}{2}(K+1)v^2)$ K is function of ρ & μ If K were constant with temp chg.

Clearly, K has changed with temp.

$\frac{\rho_2}{\rho_1} = \frac{v,@280^\circ F}{v,@129^\circ F} = \frac{.01726}{.01625} = 1.06215$ 6.22%

then $\frac{\rho_2}{\rho_1} = \frac{\Delta\rho_2}{\Delta\rho_1} = \frac{1530}{1260} = .12143$ 21.4%

Shut off H_2O from system

6 liter

1 liter

pressurizer shut off from system

10 liter water withdrawn 128.7°F
23:18:26 257.1 psig

Start pressure drop test 130.3°F
23:8:4.3 1058 psig

Test I Part 2

Don't know why a minimum

22:35:40 151.3°F

22:25:40 162.4°F

Opened pressurizer to system 22:9:04 180.1°F

Filling with Water

Releasing H_2O from pressurizer

Pressurizer off 22:00:55 182.0°F

21:35:40 214.1°F

Pressurizer pressured and open to system 230.9°F

Started filling with water

Pressure off pressurizer 21:12 232.4°F

20:55:40 247.4°F

262.4

Start to drop Temp @ 20:33

Completed removal of bubble from reactor

278°F

Pressurized. Some cold water flowed in Should have been close to 2.8 l Since 2.8 liters had been removed from the system to form the bubbles.

19:10:40

Δp changes with temperature. No observed signal change with

9.0 HYDROGEN PEROXIDE TESTS

9.1 Objective

The objective of this experiment was to examine the feasibility of introducing hydrogen peroxide into an experimental apparatus which, upon decomposition, would react with the hydrogen in the test cell and thus reduce the pressure of the system.

9.2 Introduction

Tests were performed by introducing hydrogen peroxide into hydrogen saturated water at 1000 psig and 280°F. It was felt that the oxygen resulting from the decomposition of the peroxide would possibly react with the hydrogen to produce water, thus reducing the reactor pressure. Theoretically this reaction may proceed without the use of a catalyst, but a catalyst may increase the rate at which reaction occurs.

Two tests were performed (noted as Test A and Test B in the text). In Test A, no catalyst was used, and in Test B a platinum catalyst was used (5 grams of catalytic pellets impregnated with Pt DNS plating solution and heated at 600°F).

9.3 Experimental Apparatus

The experimental apparatus used for the hydrogen peroxide test is illustrated in Figure 33. The instrumentation and data system used is shown in Figure 34. The Billings Energy Corporation's Autohydrider was used because of its heat controlled, instrumented sample chamber.

9.3 Experimental Apparatus

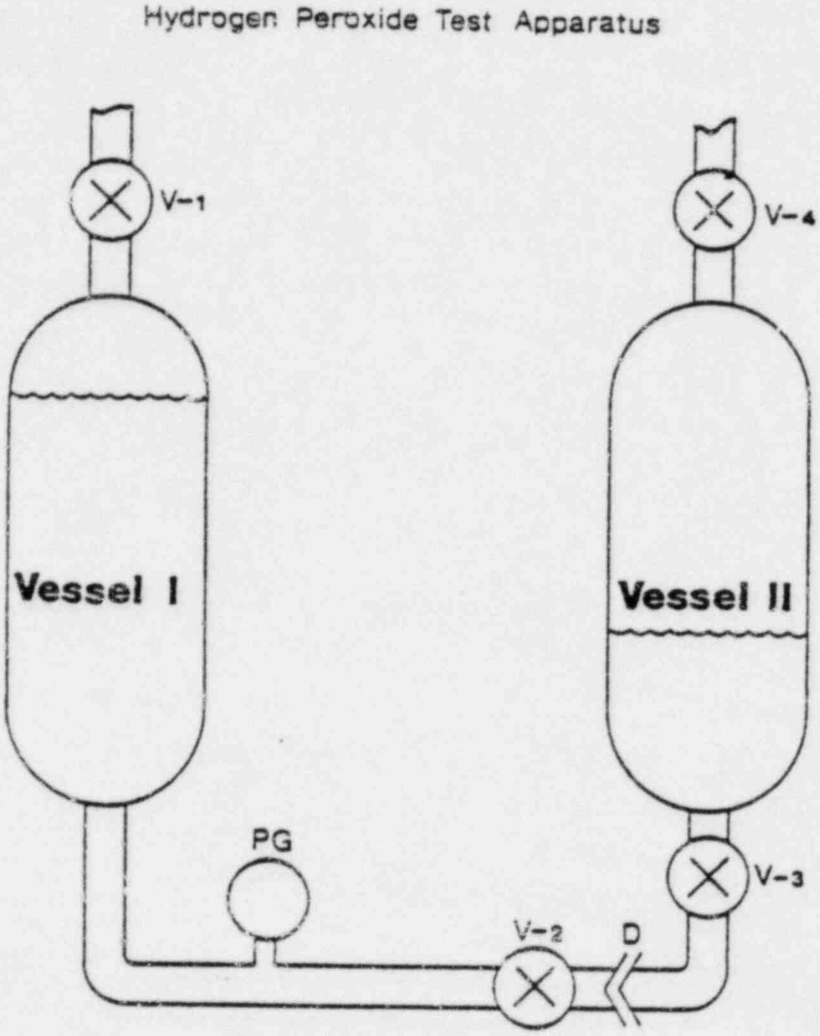


Figure 33 Hydrogen Peroxide Test Apparatus

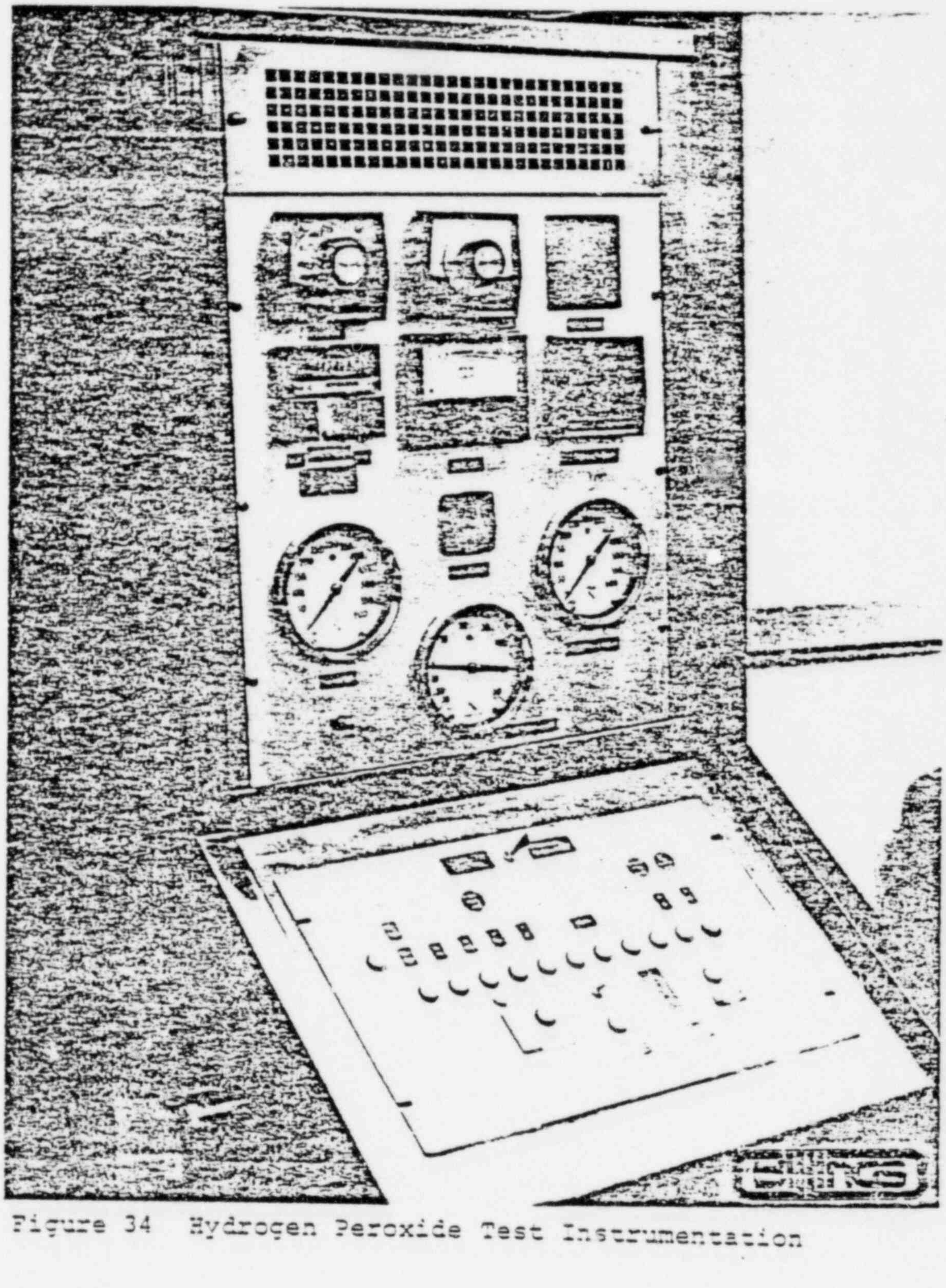


Figure 34 Hydrogen Peroxide Test Instrumentation

9.4 Experimental Procedure

9.4.1 Test A

The uncatalyzed hydrogen peroxide test was performed according to the following procedure:

1. Fill Vessel I with boiled, deionized water.
2. Pressurize Vessel I to 1000 psig with hydrogen.
3. Remove 50 ml of water through Valve 2.
4. Pressurize to ≈750 psig with hydrogen.
5. Periodically heat and shake Vessel I adding hydrogen to maintain pressure at 1000 psig and temperature at 280°F.
6. Place in insulated heated chamber with digital temperature readout. Heat to ≈ .80°F.
7. Add 100 ml ≈10% hydrogen peroxide to Vessel II and pressurize with argon.
8. Connect Vessel II to Vessel I as indicated in apparatus drawing.
9. Open Valves 2 and 3 with Valve 4 open and connected to argon at 1050 psig.
10. Reduce pressure in Vessel I to 925 psig by opening needle valve (Valve 1) thus allowing some peroxide solution to enter Vessel I through Valve 2.
11. Close all valves.
12. Record pressure and temperature measurements as a function of time beginning immediately after addition

of hydrogen peroxide.

13. At conclusion determine volume of unused peroxide solution.

9.4.2 Test B

The catalyzed hydrogen peroxide test was performed according to the following procedure:

1. Fill Vessel I with boiled, deionized water. Add 5 gm. Pt treated catalytic pellets.
2. Pressurize Vessel I to 1000 psig with hydrogen.
3. Remove 50 ml of water through Valve 2.
4. Pressurize to ≈750 psig with hydrogen.
5. Periodically heat and shake Vessel I adding hydrogen to maintain pressure at 1000 psig and temperature at 280°F.
6. Place in insulated heated chamber with digital temperature readout. Heat to ≈280°F.
7. Add 100 ml ≈10% hydrogen peroxide to Vessel II and pressurize with argon.
8. Connect Vessel II to Vessel I as indicated in apparatus drawing.
9. Open Valves 2 and 3 with Valve 4 open and connected to argon at 1050 psig.
10. Reduce pressure in Vessel I to 810 psig by opening needle valve (Valve 1) thus allowing some peroxide solution to enter Vessel I through Valve 2.