DOE/MC/30012 -- 4078
(DE95009724)

Advanced Sulfur Control Concepts for Hot Gas Desulfurization Technology

Quarterly Report
January - March 1995

Douglas P. Harrison

April 1995

Work Performed Under Contract No.: DE-AC21-94MC30012

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Louisiana State University
Baton Rouge, Louisiana

DISCLAIMER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DOE/MC/30012 -- 4078
(DE95009724)
Distribution Category UC-106

Advanced Sulfur Control Concepts for Hot Gas Desulfurization Technology

Quarterly Report
January - March 1995

Douglas P. Harrison

Work Performed Under Contract No.: DE-AC21-94MC30012

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
P.O. Box 880
Morgantown, West Virginia 26507-0880

By
Louisiana State University
Department of Chemical Engineering
Baton Rouge, Louisiana 70803

April 1995

EXECUTIVE SUMMARY

Antek Instruments reported success in the use of a quartz capillary tube having a diameter of about 0.005 inches and a length of 6 inches to reduce the pressure of a 600°C gas stream from 15 atm to 1 atm. This capillary tube will be incorporated into the Antek R-6000 elemental sulfur analyzer; an order was placed for the modified instrument during the latter stages of the quarter. SO_2 and H_2S analysis will be accomplished by modifying an existing Shimadzu GC-14A gas chromatograph. A purchase order for the necessary modifications was issued during the quarter.

The atmospheric pressure electrobalance, which had not been used for approximately four years was brought out of mothballs in January. Repairs to both the electrobalance and the furnace temperature controller were accomplished and a manifold system capable of feeding N_2, O_2, H_2, and H_2O was constructed. A number of calibration and scoping tests were completed, and atmospheric pressure testing of the regeneration of FeS with O_2/N_2, H_2O/N_2 and $O_2/H_2O/N_2$ atmosphere is scheduled to get underway early in the next quarter.

The high pressure electrobalance had not been used for approximately 2½ years. Key components of the reactor system, including the data acquisition computer, furnace and temperature controller, gas feed manifold, high pressure syringe pump, and back pressure regulators, were last used in a fixed-bed reactor study. Primary effort during the quarter was devoted to correcting problems with the data acquisition system and reassembling the components for the high pressure electrobalance. Scoping and calibration testing of this unit is scheduled to get underway early in the following quarter.

Most activities associated with the design and construction of the fixed-bed reactor were put on hold pending resolution of the gas analysis problem. The reactor pressure vessels to be used with both the high pressure electrobalance and the fixed-bed reactor were Alonized during the quarter. Problems associated with the Alonizing process are described below. Once the product gas analysis method was defined, we proceeded to order key components of the reactor system including the high pressure syringe pump, high pressure mass flow controllers, etc. Construction of the reactor system will get underway as the major components are delivered. In addition, the analytical instruments should be delivered during the forthcoming quarter, and their calibration will commence.

GAS ANALYSIS

Previous research in which elemental sulfur was produced during sorbent regeneration used a condenser to determine the cumulative amount of sulfur produced during the test. However, because a fixed-bed gas-solid reactor must operate in an unsteady-state mode, we expect both the production rate of total sulfur and the distribution of sulfur species to vary with time. An important component of our test program, therefore, is the development of an analytical method to provide effectively real time analysis of the product gas composition.

Our original plan was to split the product stream with one portion fed to a total oxidizer where all sulfur would be converted to SO_2, which would then be analyzed using IR spectroscopy. Sulphur would be condensed from the other portion of the product stream and individual concentrations of H_2S and SO_2 would be determined spectroscopically. This approach, which involved the determination of elemental sulfur by difference, was judged to be acceptable since the objective was to produce large quantities of elemental sulfur. This technique was abandoned when we learned that IR cells capable of operating at the temperature and pressure of interest would cost about $5,000 each with no guarantee that the cells windows would not react with the sulfur compounds.

Antek Instruments, a leader in sulfur analysis in the petroleum refining and petrochemicals industries, was then contacted. Existing Antek instruments could accomplish the analysis except that they were limited to atmospheric pressure. Antek took an active interest in the project and suggested the use of a thick-walled quartz capillary tube to reduce the pressure of the hot product gas from 15 atm to 1 atm. Antek experimentally determined that a capillary having a diameter of 0.005 inches and a length of 6 inches would be structurally stable, and would produce an appropriate gas volumetric flow rate for analysis. Antek subsequently integrated this capillary tube into an existing pyrotube to oxidize all sulfur species to SO_2. The SO_2 concentration will then be determined using an Antek R-6000 sulfur analyzer. This instrument was ordered during March. The remainder of the regeneration product gas will be passed through an elemental sulfur condenser after which the concentrations of H_2S and SO_2 will be determined by gas chromatography. A schematic flow diagram of the current design of the analytical train is shown in Figure 1. We plan to modify an existing Shimadzu GC-14A gas chromatograph to accomplish the H_2S and SO_2 analysis. A purchase order was issued during March to Shimadzu for the necessary modifications. This approach also involves the determination of elemental sulfur by difference and is justified, as with the original plan, on the expected high elemental sulfur concentrations.

ATMOSPHERIC PRESSURE ELECTROBALANCE

The atmospheric pressure electrobalance is to be used to study the regeneration of FeS in atmospheres consisting of O_2/N_2, H_2O/N_2, and $O_2/H_2O/N_2$. The primary objective will be to determine reaction temperatures and gas compositions such that the concentration of SO_2 formed by the reaction of FeS and O_2, and the concentration of H_2S formed by the reaction of FeS and H_2O will be suitable for the Claus reaction to produce elemental sulfur.

This instrument, which had not been used for about four years, was removed from mothballs during the quarter. The inevitable instrument problems were identified and have been corrected. An electronic board associated with the temperature controller had to be replaced before the furnace would work, and minor problems with the electronic recorder were also found and corrected. The gas feed manifold was constructed, and calibration and scoping tests were completed during the quarter.

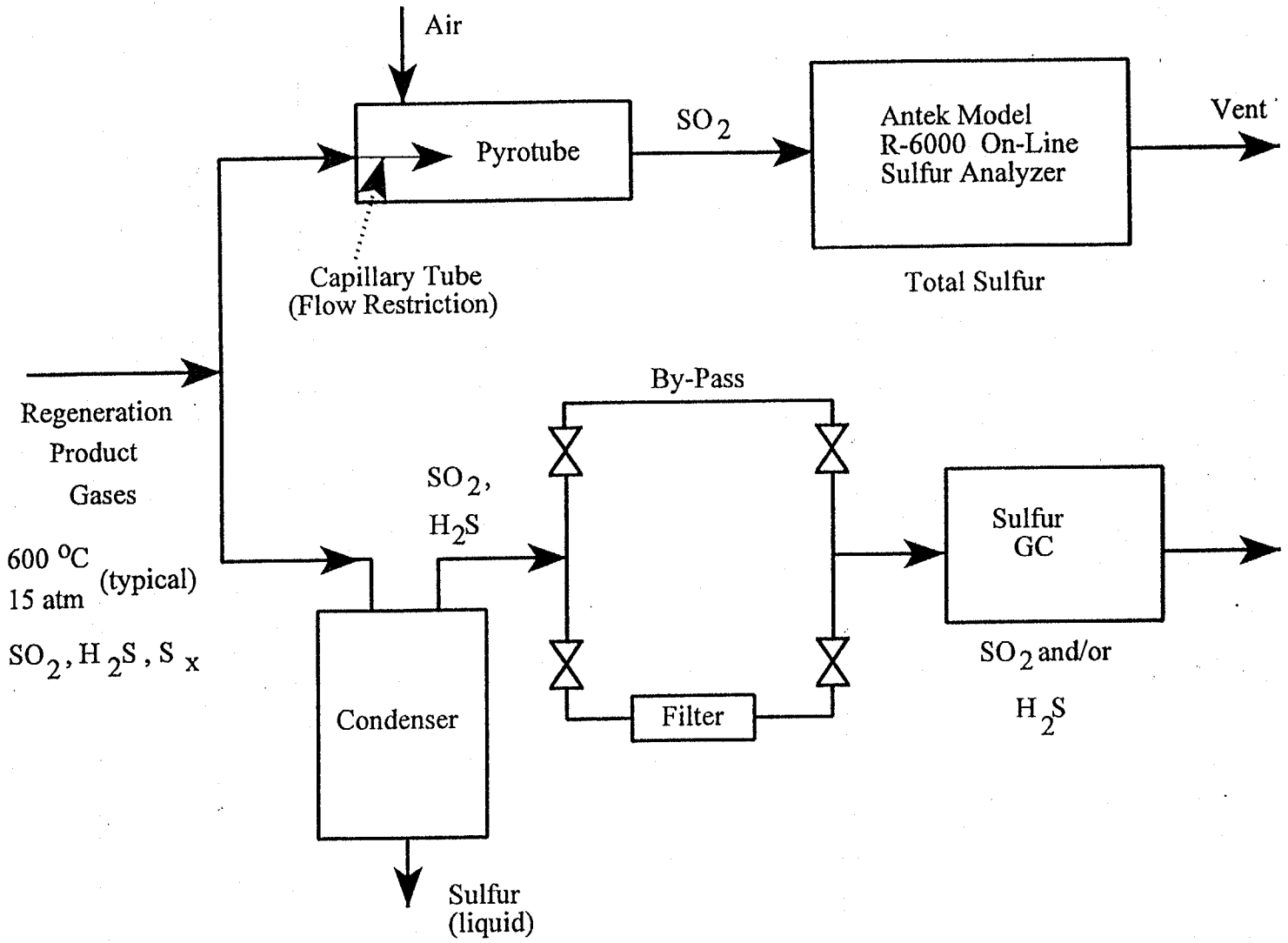

Figure 1. Revised Schematic of the Regeneration Product Gas Analytical Train

A schematic diagram of the feed manifold coupled to the electrobalance is shown in Figure 2. Nitrogen, hydrogen, oxygen (air), and water may be fed to the reactor. Gases are obtained from high-pressure cylinders and flow rates are controlled by calibrated rotameters and needle valves. H_2O is fed as a liquid from a vessel maintained under slight positive N_2 pressure through a calibrated rotameter and needle valve for flow control. Inert N_2 is fed into the top of the electrobalance to protect the electronics from corrosive reactive gases. The reactive gases, which in this configuration may contain O_2, H_2, H_2O and N_2 (no O_2 and H_2 are to be fed simultaneously), enter through the side-arm of the hang-down tube where they mix with additional N_2 blanketing the electronics and the combined gases flow downward over the reacting solid. Appropriate feed lines are heat traced to insure that the H_2O is completely vaporized. The three-way valve in the reactive gas feed line permits reactive gas flow rates to be established and to by-pass the reactor while the solid is exposed to inert gas. When desired operating conditions are established the three-way valve is switched and the solid is exposed to the full reactive gas flow with minimum upset.

Sample temperature is monitored using the thermocouple placed just below the sample pan. The thermocouple signal is fed to a Micricon temperature controller, which can be programmed for a number of linear heating and cooling rates as well as for isothermal operation. Signals from both the thermocouple and the electrobalance, which provides a continuous record of the weight of the reactive solid, are transmitted to a Bascom-Turner electronic recorder for storage, processing, and plotting.

Once the system was operating properly, calibration tests involving the decomposition of hydrated copper sulfate were carried out. Temperature problems were identified which required us to establish a thermocouple calibration curve. Figure 3 compares our decomposition curve from test 13 to a standard hydrated copper sulfate decomposition curve. Initial weight loss from $W/W_o = 1.0$ to $W/W_o \sim 0.72$ corresponded to the loss of $4H_2O$ from the original $CuSO_4 \cdot 5H_2O$. The second weight loss corresponded to loss of the final H_2O and the final weight loss corresponded to the decomposition of copper sulfate to copper oxide. All of the experimental W/W_o plateaus were quite close to those of the standard decomposition curves. However, the experimental temperature at which each decomposition occurred was always less than suggested by the standard curve. In particular, in the temperature range of primary interest ($\geq 600°C$), our temperature measurements were approximately 30 to 40°C lower than indicated by the standard.

As a result, the electrobalance thermocouple and temperature indicator were calibrated against a second thermocouple connected to a standard potentiometer. Significant errors were identified and the temperature calibration curve shown in Figure 4 was developed. The difference between the electrobalance set-point temperature and the actual temperature increased as the temperature increased and was in the 20°C range at the temperatures of primary interest. When the temperature correction was applied to our experimental copper sulfate decomposition data, there was much better agreement with the standard results. Figure 5 compares the results of three duplicate experimental tests using the corrected temperature to the standard decomposition curve. The reproducibility between the three tests was quite good, and the difference between the experimental and standard temperatures was reduced to what we consider

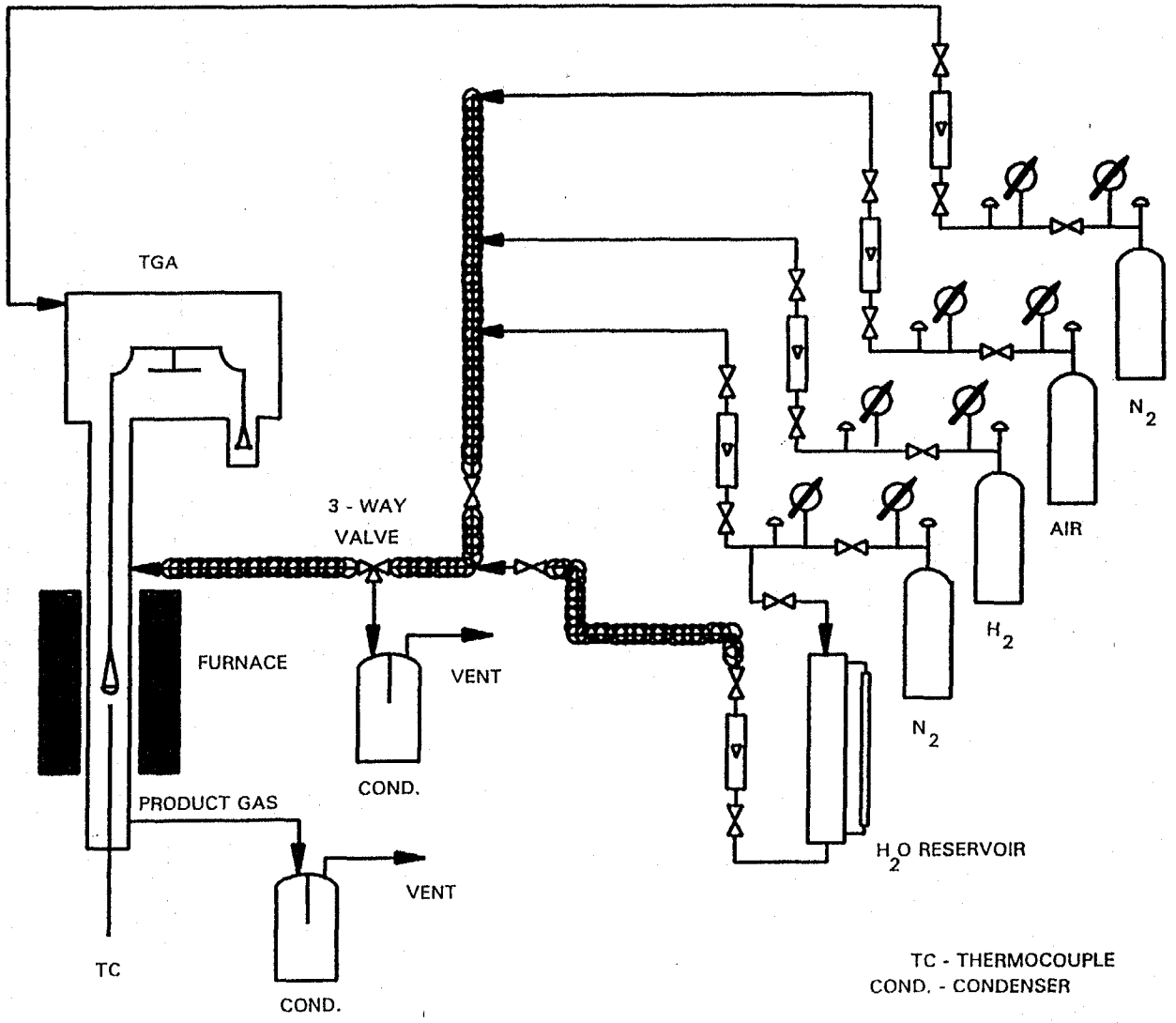

Figure 2. The Atmospheric Pressure Electrobalance Reactor

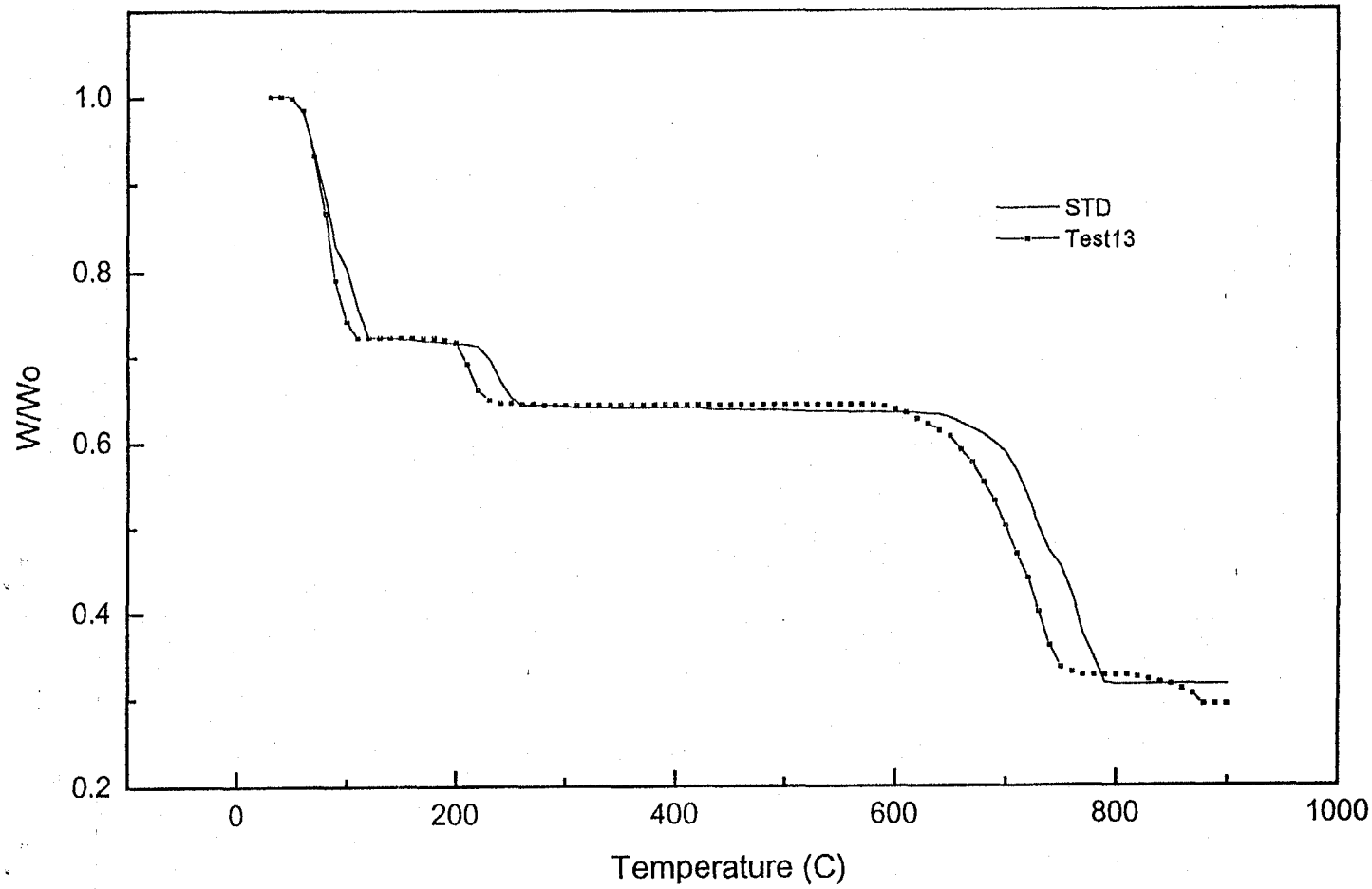

Figure 3. Comparison of the Atmospheric Pressure Electrobalance Response for the Decomposition of Hydrated Copper Sulfate With a Standard Decomposition Curve

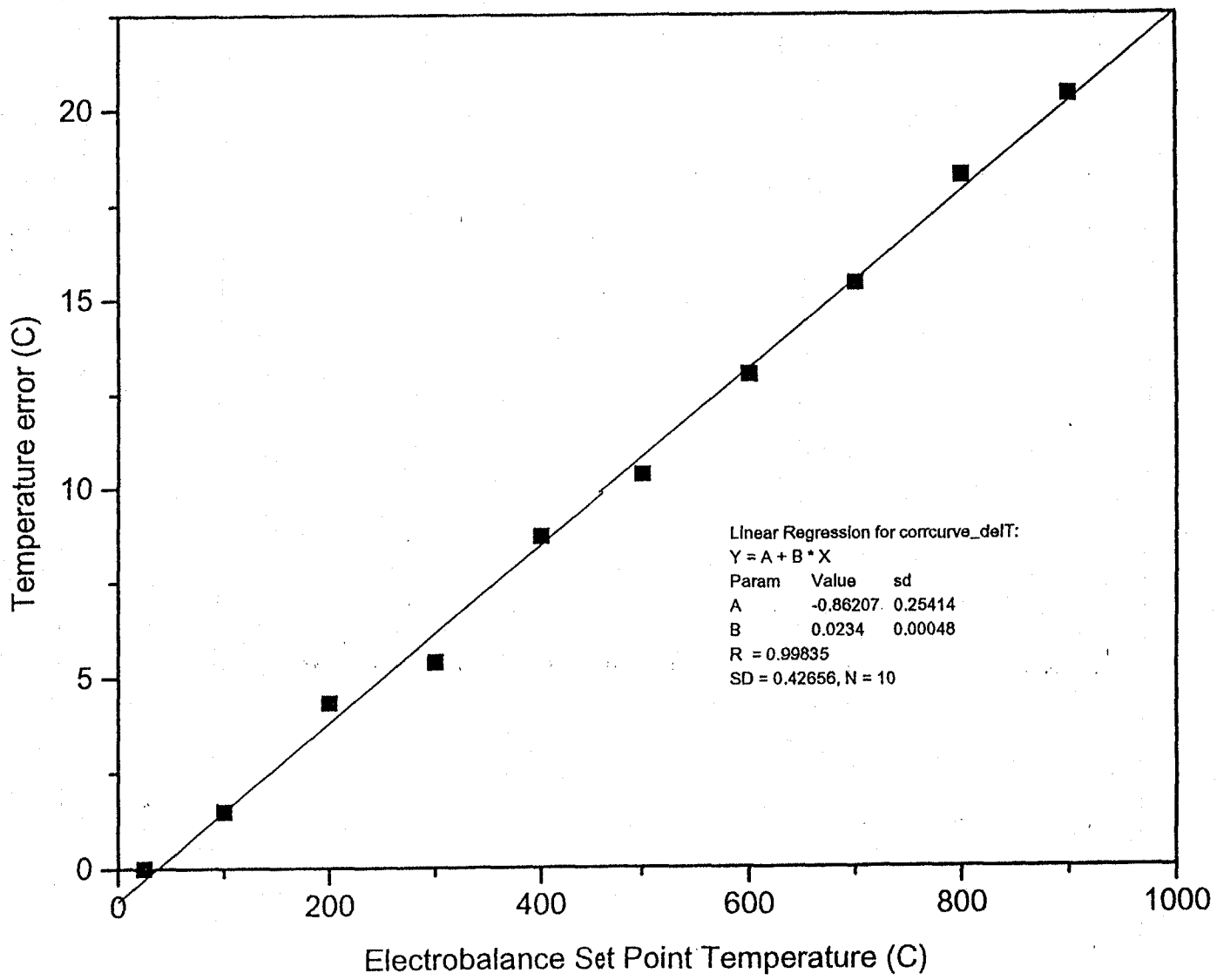

Figure 4. Calibration Curve for the Atmospheric Pressure Electrobalance Thermocouple and Temperature Indicator

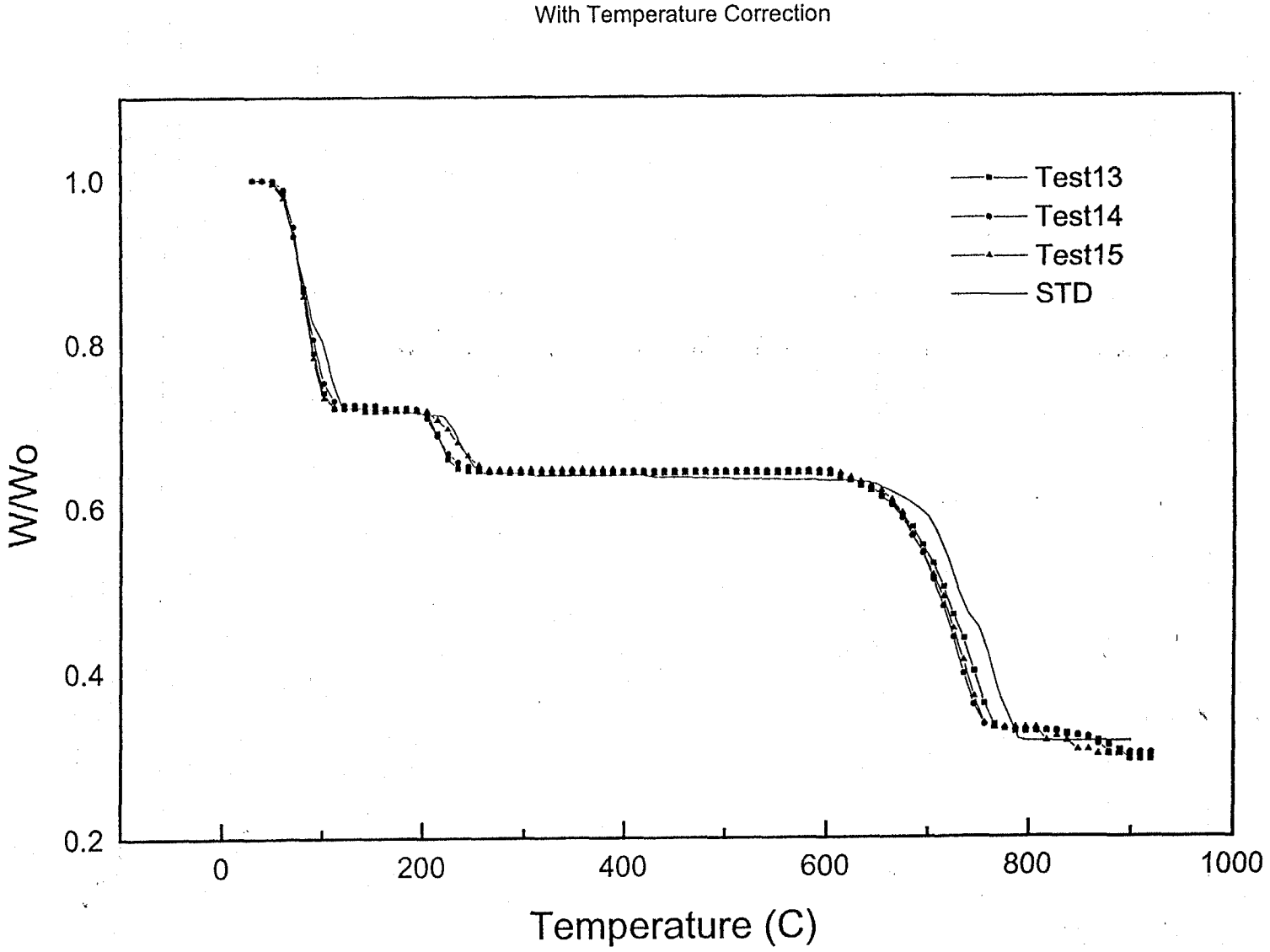

Figure 5. Comparison of the Reproducibility of Three Duplicate Copper Sulfate Decomposition Tests With a Standard Decomposition Cruve (With Temperature Correction)

to be permissible levels. Henceforth, corrected temperatures will be used when reporting all results.

We had hoped to begin preliminary FeS regeneration tests once the temperature problems were resolved. There was, however, an unforeseen delay in the receipt of FeS from the supplier. In the interim, a number of Fe_2O_3 reduction tests were carried out to gain familiarity with the operation of the reactor system and to learn more about the characteristics of iron oxide reduction. Under the appropriate combination of reducing gas concentration and temperature, iron oxide will undergo step-wise reduction according to the following approximate stoichiometry

	W/W_o
$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$	0.967
$2Fe_3O_4 + 2H_2 \rightarrow 6FeO + 2H_2O$	0.900
$6FeO + 6H_2 \rightarrow 6Fe + 6H_2O$	0.699

The values of W/W_o at the end of the equations represent the ratio of the weights of the final solid product to the initial Fe_2O_3 assuming complete reaction according to the indicated stoichiometry.

Figure 6 compares the results of two reduction tests in which approximately 9mg of Fe_2O_3 was heated from room temperature to 600°C in an atmosphere of 10% H_2/N_2. In test 1 the heating rate was a nominal 5°C/min while test 4 used a nominal heating rate of 2°C/min. The electrobalance responses were similar. Reduction of Fe_2O_3 to Fe_3O_4 occurred in the 340 - 370°C temperature range in each test. The rate of Fe_3O_4 reduction became appreciable at about 420°C. No plateau corresponding to FeO was observed. Instead, the weight loss was continuous from Fe_3O_4 to the final weight corresponding to Fe, which was reached at approximately 590°C. One would expect the results of test 4 (2°C/min) to be more "correct" as the slower heating rate would permit equilibrium to be more closely approached at each temperature. The only unexpected feature of the experimental results was the small difference in the final values of W/W_o.

Vertical dashed lines in Figure 6 represent the results of a CHEMQ thermodynamic analysis using the experimental gas composition over the experimental range of temperature. Fe_2O_3 is not thermodynamically stable at any of the temperatures shown. Complete reduction of Fe_2O_3 to Fe_3O_4 is favored at temperatures up to about 200°C. FeO formation is favored beginning about 200°C and all Fe_3O_4 should be reduced to FeO by about 230°C. FeO is the only stable solid in the 230°C to 350°C range, with reduction of FeO to Fe predicted to begin at 350°C and to be complete by 575°C.

Although Fe_3O_4 was thermodynamically favored at lower temperatures, initial Fe_2O_3 reduction did not begin until about 320°C. This deviation from equilibrium is due to the slow

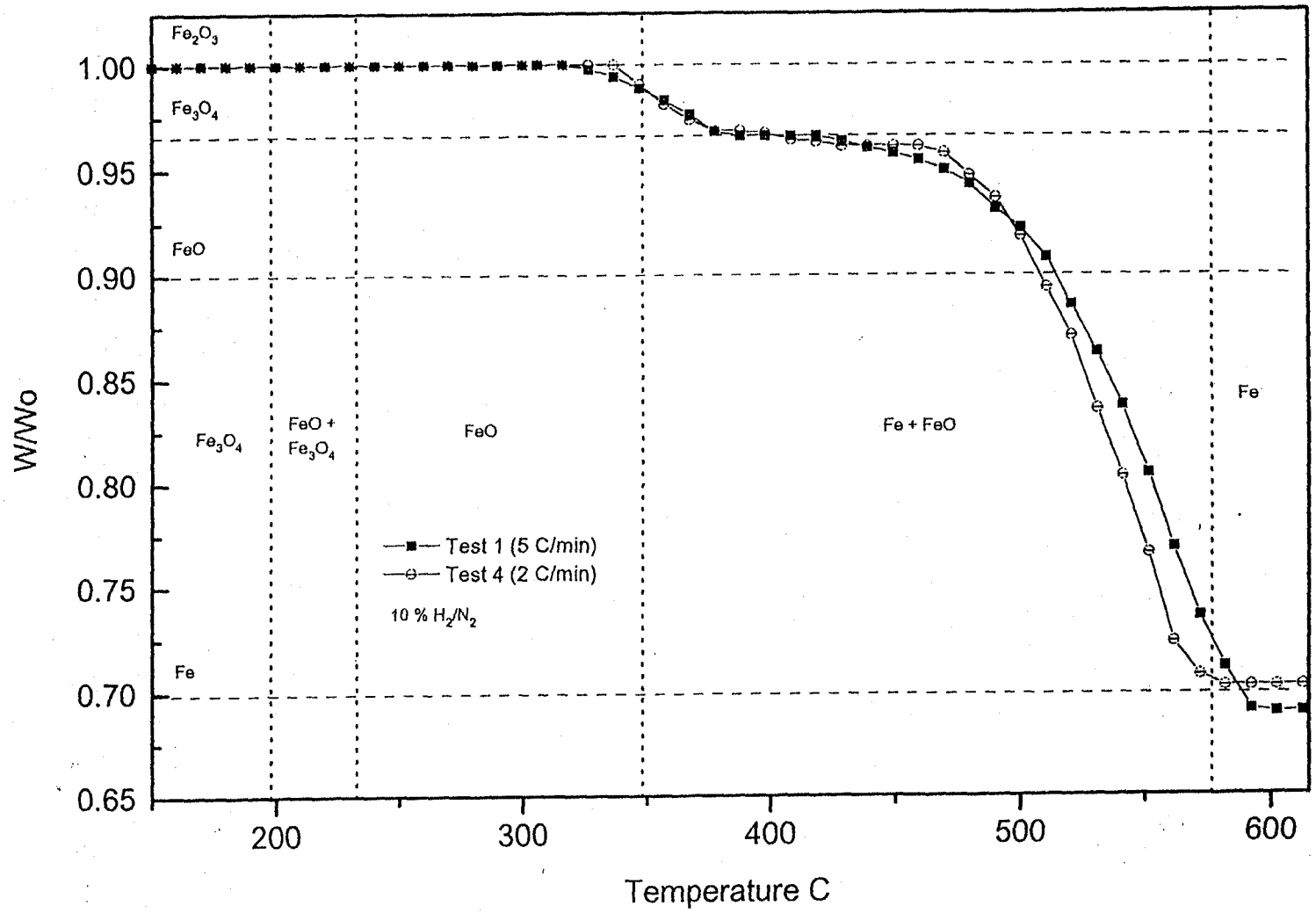

Figure 6. Iron Oxide Reduction in 10% H_2 /N_2 at Two Heating Rates

kinetics of the reduction reaction at low temperature. The experimental weight plateau for Fe_3O_4 occurred over the approximate temperature range of 380 to 430°C which, at equilibrium, should correspond to a mixture of FeO and Fe. No FeO weight plateau was observed. However, complete reduction to Fe occurred at about the temperature where all FeO should disappear. The latter result suggests that kinetics are sufficiently fast to permit a close approach to equilibrium near 600°C.

Figure 7 shows the results of an isothermal test at 400°C in a 10% H_2/N_2 atmosphere. Fe_2O_3 was heated under flowing N_2 from room temperature to 400°C. Hydrogen was introduced at t ~ 25 minutes. Fe_2O_3 was quickly reduced and a brief W/W_o plateau corresponding approximately to Fe_3O_4 was observed. Further slow reduction began after 50 minutes and a continuous weight loss was observed until the test was terminated after 85 minutes at a value of $W/W_o \sim 0.89$. If we assume that all of the Fe_3O_4 had been reduced by the end of the test, the final value of W/W_o corresponds to a mixture of FeO and Fe in a molar ratio of about 20 to 1. Presumably, if the test had been extended for sufficient time, all of the FeO would be reduced to metallic Fe since the feed gas contained no H_2O.

The feed gas composition was altered in test 5 with the H_2 content increased to 30% and 10% H_2O added to the feed gas. Otherwise, reaction conditions in test 1 and 5 were identical. Results of the two tests are compared in Figure 8. The addition of H_2O delayed reduction of Fe_2O_3, with reduction beginning at about 360°C with steam compared to about 320°C without steam. The W/W_o plateau corresponding to Fe_3O_4 was also extended with Fe_3O_4 remaining stable to about 500°C in the presence of steam compared to about 430°C without steam. No weight plateau corresponding to FeO was apparent in either test and the entire solid was reduced to Fe by about 580°C in both tests.

HIGH PRESSURE ELECTROBALANCE

The high pressure electrobalance, which had not been used for approximately 2½ years, was brought out of mothballs during the quarter. Much of the peripheral equipment used for controlling temperature, gas flow rates, and water injection was last used in connection with a fixed-bed reactor study.

The reconstructed reactor system, shown schematically in Figure 9, is similar in operating principle to the atmospheric pressure electrobalance. However, in order to operate at high temperature and pressure, the entire electrobalance is housed in stainless steel. The hangdown tube, which will be exposed to corrosive gases, is constructed of Alonized stainless steel. Gas flows are controlled by high pressure mass flow controllers, and water injection is accomplished using a high pressure syringe pump. These units replace the rotameters and needle valves used on the atmospheric pressure system. Reactor temperature and solid weight data are collected, stored, and processed on a PC instead of the electronic recorder.

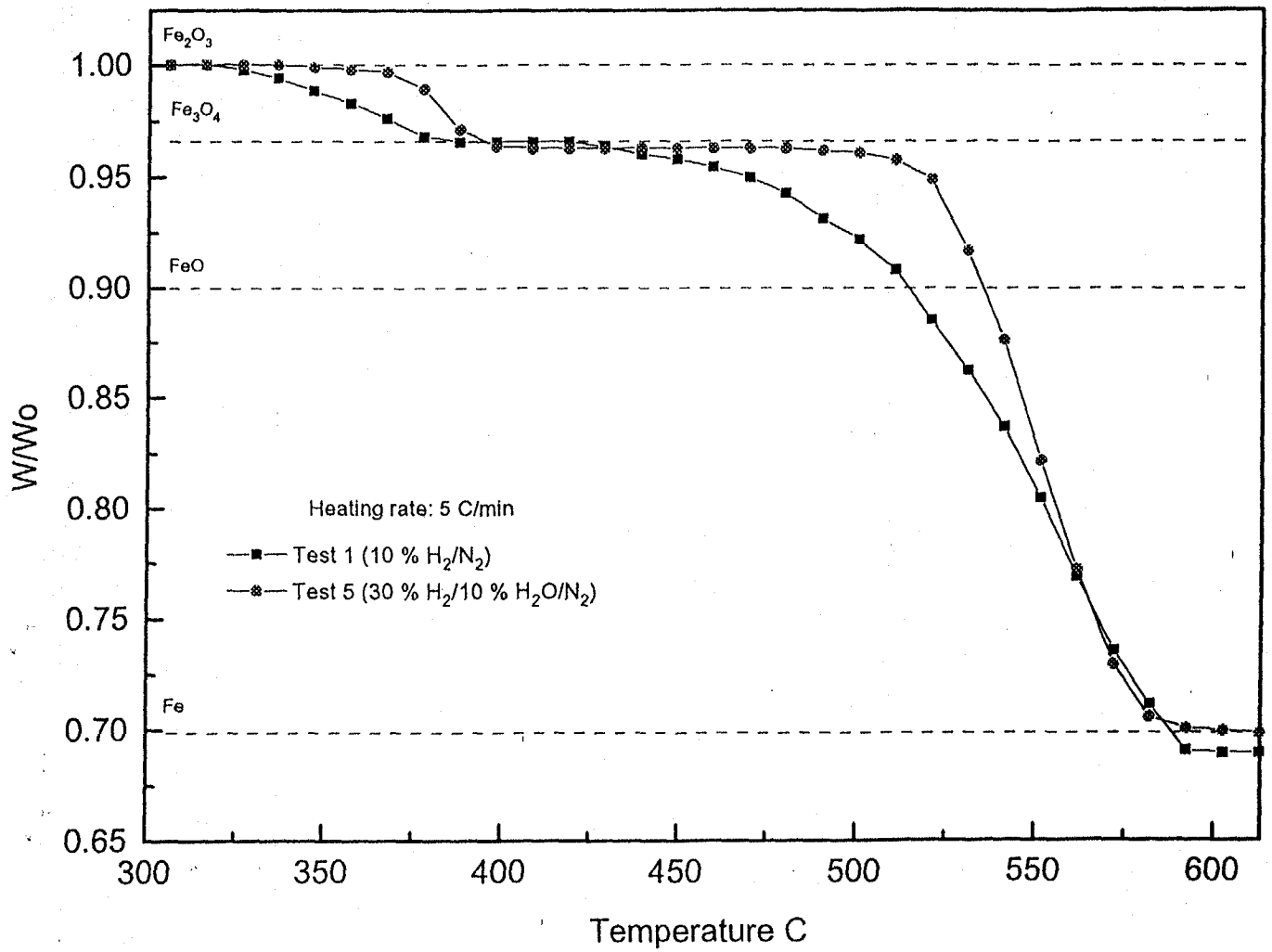

Figure 8. Iron Oxide Reduction as a Function of Temperature and Gas Composition

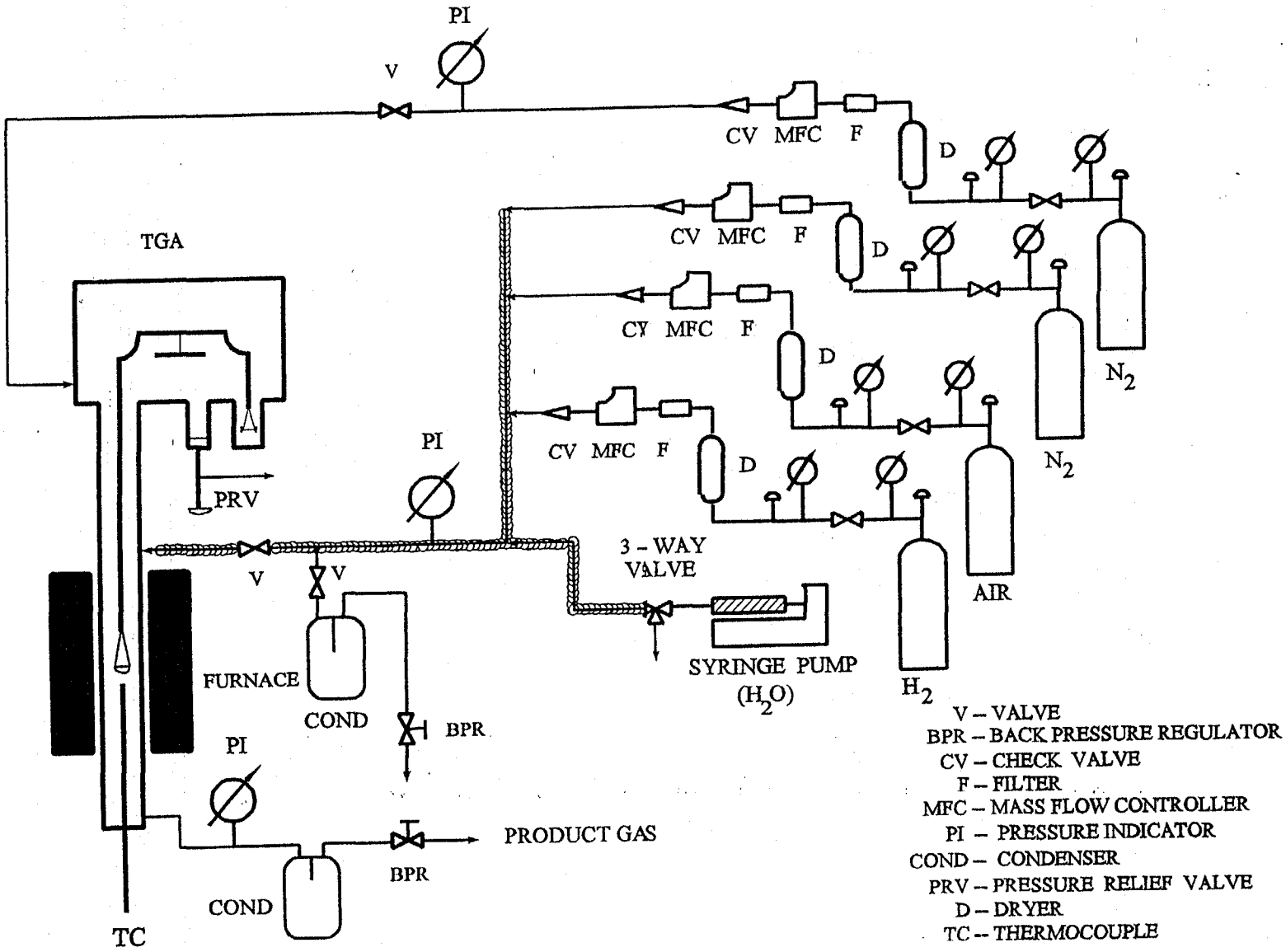

Figure 9. The High Pressure Electrobalance Reactor System

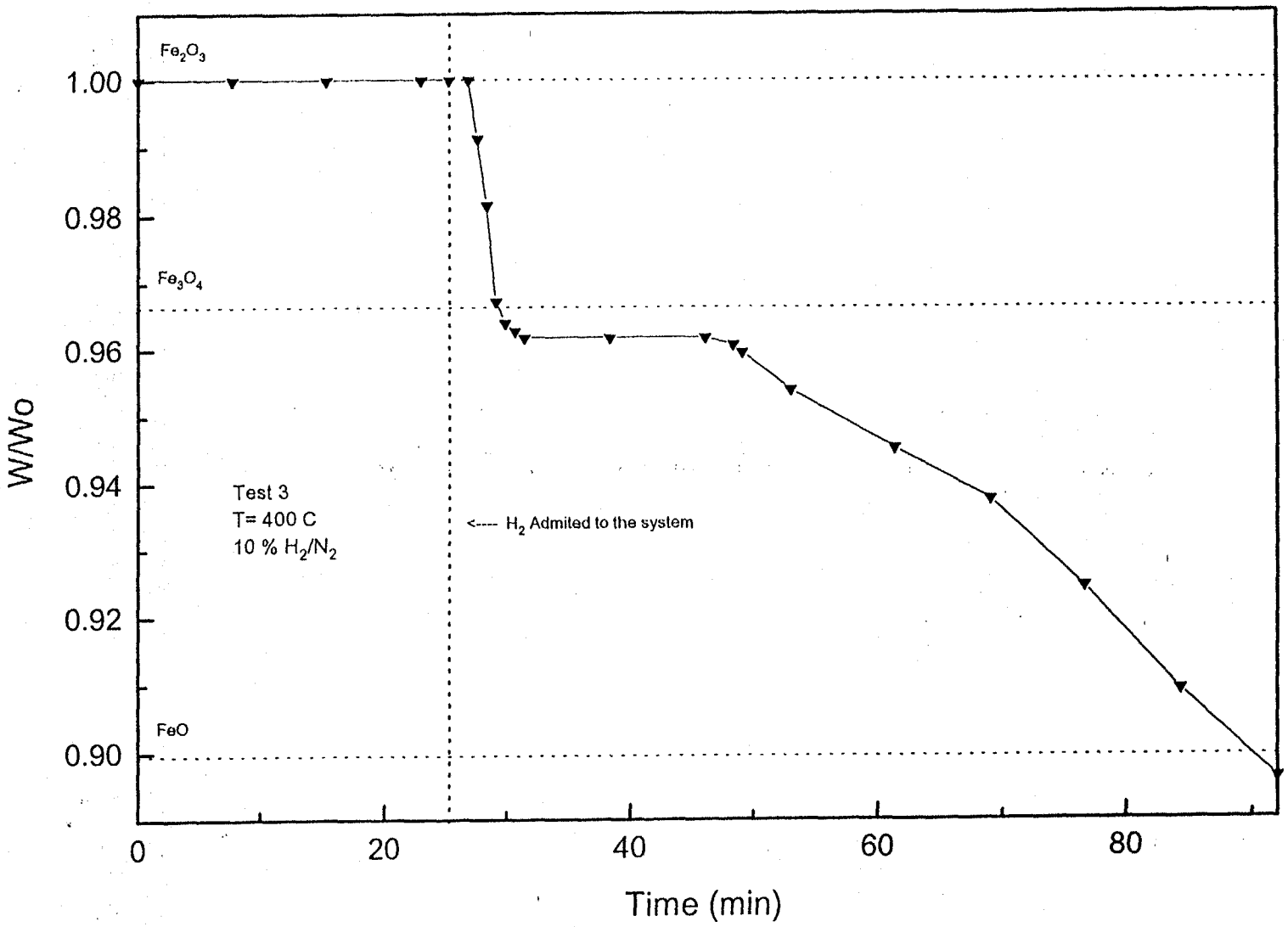

Figure 7. Iron Oxide Reduction at 400°C in 10% H_2/N_2

The typical problems associated with reassembly and debugging the peripheral equipment have been encountered. A software problem associated with data collection has, we believe, been solved. There is concern about the quality of the Alonizing process. Surfaces which were supposed to be masked off were Alonized. Some areas have had to be remachined which will potentially expose unprotected steel surfaces to corrosive gases. The severity of this problem, which is important for both the high pressure electrobalance and fixed-bed reactors, will have to be evaluated as the project proceeds.

At the end of the quarter, all major reassembly had been completed and the unit was being leak tested. The next step will be a series of calibration tests similar to those described for the atmospheric pressure electrobalance. We will then begin to study the kinetics of FeS regeneration at high pressure as a function of temperature and gas composition. O_2/N_2, H_2O/N_2, and $O_2/H_2O/N_2$ atmospheres will be studied with the objective of defining conditions such that the product gas will contain H_2S and SO_2 in the appropriate ratio for the Claus reaction to occur.

FIXED-BED REACTOR

Concentrated effort on the fixed-bed reactor was postponed pending resolution of the gas analysis problem. Once the method of analysis was defined, we began to move ahead in specifying and ordering supplementary equipment such as the mass flow controllers, syringe pump, furnace and temperature controller, and back pressure regulators.

All wetted surfaces within the high pressure reactor were Alonized, and the problems with this process were described in the previous section. The new high pressure syringe pump has been received and mass flow controllers should arrive in April. Construction of the fixed-bed system will receive high priority during the next quarter.