

Advanced Sulfur Control Concepts for Hot Gas Desulfurization Technology

**Quarterly Report
April - June 1995**

Douglas P. Harrison

July 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

MASTER

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By
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EXECUTIVE SUMMARY

Delivery of the Antek R-6000 total sulfur analyzer and modifications of the Shimadzu GC-14A gas chromatograph are scheduled for early July. Installation and calibration of these instruments will follow shortly.

The atmospheric pressure electrobalance was used during the quarter for studies of the regeneration of FeS with O_2/N_2 gas mixtures. Some anomalies in the data initially obtained required adjustment of balance sensitivity, reduction of sample size, and recalibration of the air rotameter. We are now confident that we can routinely obtain accurate and reproducible data with this unit. Definitive tests of effects of temperature, O_2 concentration, and gas flow rate will be done next quarter.

The high pressure electrobalance was put into service, and calibration experiments were started. Decomposition of $CuSO_4 \cdot 5H_2O$ produced agreement with expected results. Heating of FeS in an O_2/N_2 gas stream gave results in qualitative agreement with experiments using the atmospheric pressure electrobalance. Initial tests on effects of temperature, O_2 concentration, and gas flow rate on the regeneration of FeS were done. Results were generally in agreement with expectations and with previous experiments on the atmospheric apparatus. Possible problems arose when the lowest range of the air mass flow controller was used. Fluctuation of the electrobalance signal in the early part of the regeneration experiment was an additional problem. Effort during the next quarter will focus on these problems and on definitive tests for FeS regeneration at elevated pressure.

The Alonized fixed bed reactor pressure vessel was successfully leak tested early in the quarter. Other components of the fixed bed reactor system continued to arrive. Construction will begin in July along with installation of the analytical instruments.

GAS ANALYSIS

An Antek R-6000 fluorescence analyzer for determining total sulfur and a modification of the Shimadzu GC-14A gas chromatograph for H_2S and SO_2 determination were ordered during the previous quarter. Delivery is promised for early July. Installation and calibration of these instruments are planned during the last two weeks of July.

ATMOSPHERIC PRESSURE ELECTROBALANCE

The electrobalances are to be used to study the rate of regeneration of metal sulfides with O_2/N_2 gas mixtures. Effects of temperature, pressure, gas composition, and gas flow rate will be studied in an effort to determine optimum conditions for elemental sulfur formation.

Our effort during this quarter focussed on FeS regeneration using O₂/N₂ gas mixtures. The objective of the studies was to develop operating procedures that will routinely produce reliable, reproducible data. Several problems were discovered and corrected during the quarter.

The first problem involved erratic values of total weight loss of FeS in regeneration tests with O₂/N₂ mixtures. The theoretical value of W_f/W_o for complete regeneration to Fe₂O₃ is 0.908. Figure 1 shows the results of 22 tests completed during May. There is considerable variation in W_f/W_o and in 20 of the tests the final value is less than the theoretical minimum.

Several possible causes of this problem were identified and remedied insofar as possible.

(1) Balance sensitivity.

Increasing the electrobalance sensitivity helped but did not completely solve the problem.

(2) Trace quantities of O₂ present during the time when the FeS is exposed to a supposedly inert N₂ atmosphere.

This causes slow oxidation prior to the start of the regeneration experiment and a low loss of weight during the experiment. This slow oxidation was demonstrated by a long duration test in N₂ at 700°C. There was a slow, steady loss of weight. After twelve hours the value of W/W_o indicated an 80% conversion of FeS to Fe₂O₃. We now minimize the time of exposure of FeS to N₂ and have ordered an O₂ purifier to be installed in the N₂ feed line.

(3) Rapid oxidation at the start of the regeneration experiment.

When high concentrations of O₂ are first admitted to the balance there is an initial rapid oxidation. This produces a rapid rise in the solid temperature and a sudden rapid evolution of SO₂. A severe temporary weight increase in the electrobalance reading is seen at this time. In some tests this upset was severe enough to dislodge a small portion of solid from the balance pan. Small quantities of a black substance were seen inside the quartz hangdown tube in some tests. Clearly the loss of FeS from the sample pan would cause W_f/W_o to be low. This effect has been minimized by reducing the initial sample size from 7 to 8 mg to about 2 to 3 mg.

(4) FeS purity.

Several references indicate variability in the purity of FeS. Many give the formula as FeS_{1+x} with x values reported as large as 0.1. The analysis provided for our sample of FeS was 61.78% Fe, significantly less than the expected value of 63.53% Fe for pure FeS. The total concentration of other metals such as Cu, Mn, Al, Ca was reported to be less than 0.09%. Any excess sulfur in our FeS would lead to values of W_f/W_o less than the theoretical 0.908. For example, for FeS_{1.02}, corresponding to a 2% excess of sulfur, W_f/W_o = 0.902. Because of the expected variability in composition of FeS, there appears that little can be done to correct this problem. However, it provides an explanation for somewhat low values of W_f/W_o.

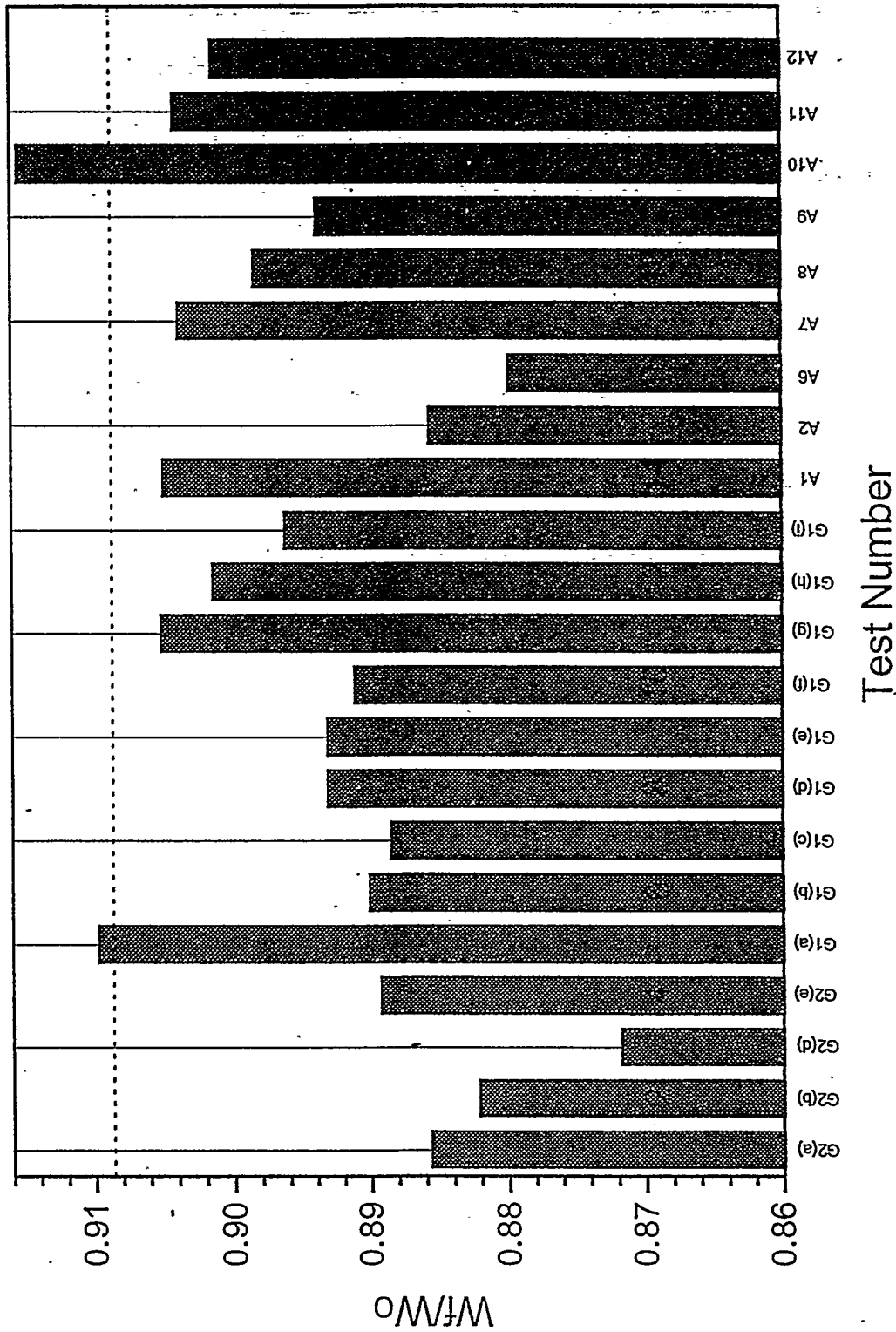


Figure 1. Variation in the Final Value of W_f/W_o in FeS Regeneration (before corrective measures)

(5) Incomplete oxidation.

The W_f/W_o for conversion of FeS to Fe_3O_4 is 0.878. Therefore, incomplete oxidation of part of the sample, yielding Fe_3O_4 , would explain a low value of W_f/W_o .

In summary, we now feel that values of W_f/W_o somewhat less than 0.908 are to be expected and are acceptable. We have taken steps, where possible, to correct the problems noted above. Figure 2 shows W_f/W_o for 21 experiments performed after corrective measures were taken. The results are more consistent. Though many values are still below the theoretical, none are lower than 0.89.

Preliminary experiments were now started determining reproducibility and examining effects of such parameters as temperature and O_2 concentration. Temperature had relatively little effect, indicating the importance of mass transfer resistances. Reproducibility of duplicate runs was not as good as expected. Observed effects of O_2 were anomalous. For example, the initial reaction rate for two tests at $600^\circ C$, 3% O_2/N_2 , and 130 sccm gas flow rate differed by approximately 30%. Even more troubling, test B1 with 1% O_2 produced a faster rate than test B4 with 1.13% O_2 , while the reaction rates from test B2 at 3.75% O_2 and test B3 using 4.08% O_2 were effectively equal.

The problems derived from an improperly sized and wrongly calibrated rotameter which made it difficult to set the O_2 concentration accurately. The rotameter was replaced, and the new rotameter was carefully calibrated. Figure 3 shows results of reproducibility tests B10 and B11, carried out at $600^\circ C$ with 3% O_2 and 130 sccm gas flow rate. The dimensionless weight versus time curves are essentially the same until near the end of the test. Figure 4 shows the effect of O_2 concentration at $600^\circ C$ and a gas flow rate of 130 sccm. The rates behave qualitatively as expected, increasing with increasing O_2 concentration. Quantitatively they are consistent with a global rate which is first order in O_2 concentration. Figure 5 shows the results of linear regression of initial rate versus mol fraction O_2 . The initial rate was measured by $-\Delta(W/W_o)/\Delta t$, taken between $t=0$ and $t=1$ minute. The slope, equal to the reaction order with respect to O_2 , is 1.03. The correlation coefficient is 0.994. The intercept is 0.002, effectively zero considering the error involved in measuring initial rates.

These experiments give us confidence that we will now be able to routinely and consistently produce reliable data. During the next quarter we plan to proceed with the investigation of effects of temperature, gas composition, and gas flow rate.

HIGH PRESSURE ELECTROBALANCE

Early in the quarter final construction and leak detection on the high pressure electrobalance system were completed. Various repairs to valves, thermocouples, and furnace were done. Operation of the high pressure syringe pump at 250 psig was demonstrated. Preliminary calibration tests were then started.

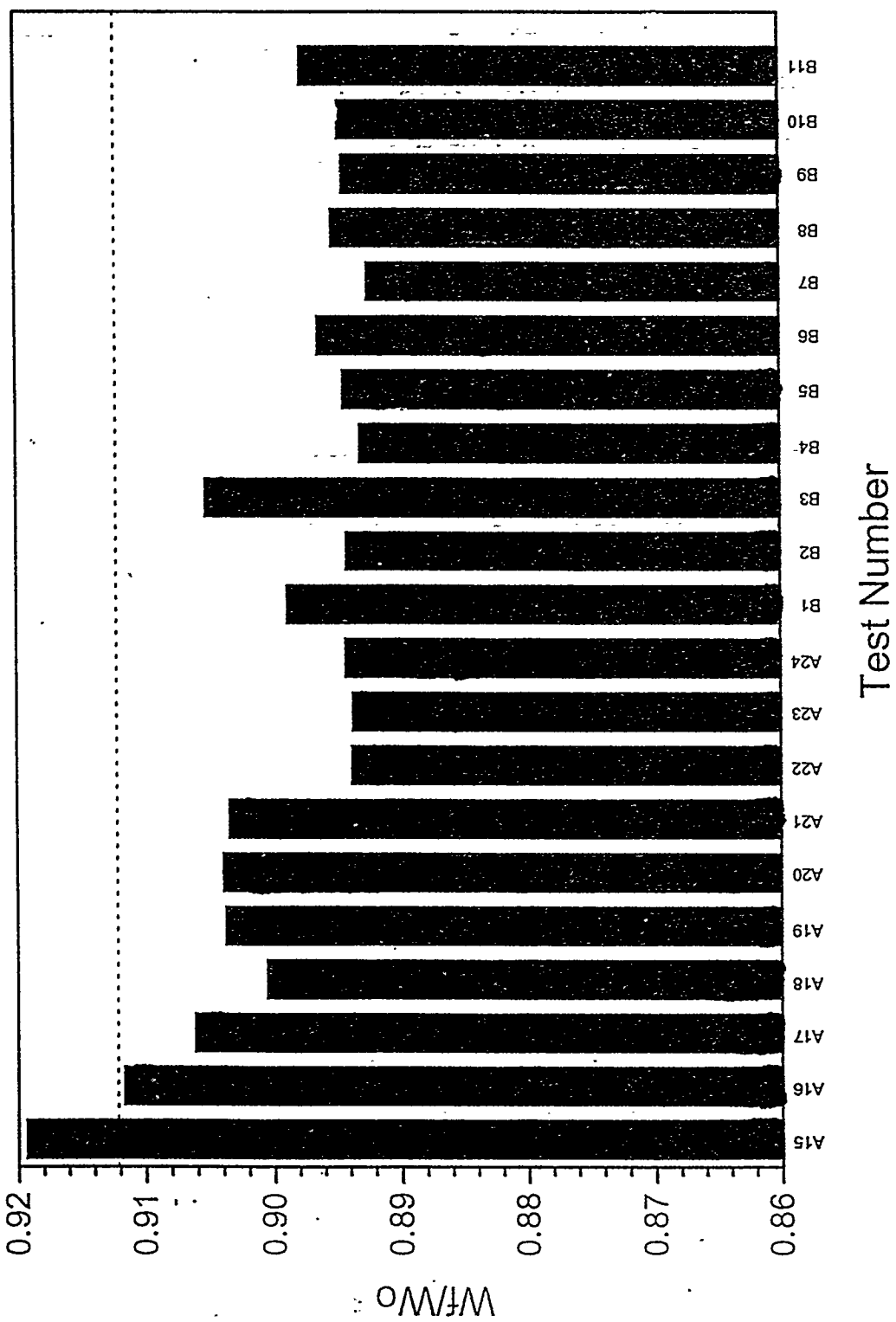


Figure 2. Variation in the Final Value of W_f/W_o in FeS Regeneration (after corrective measures)

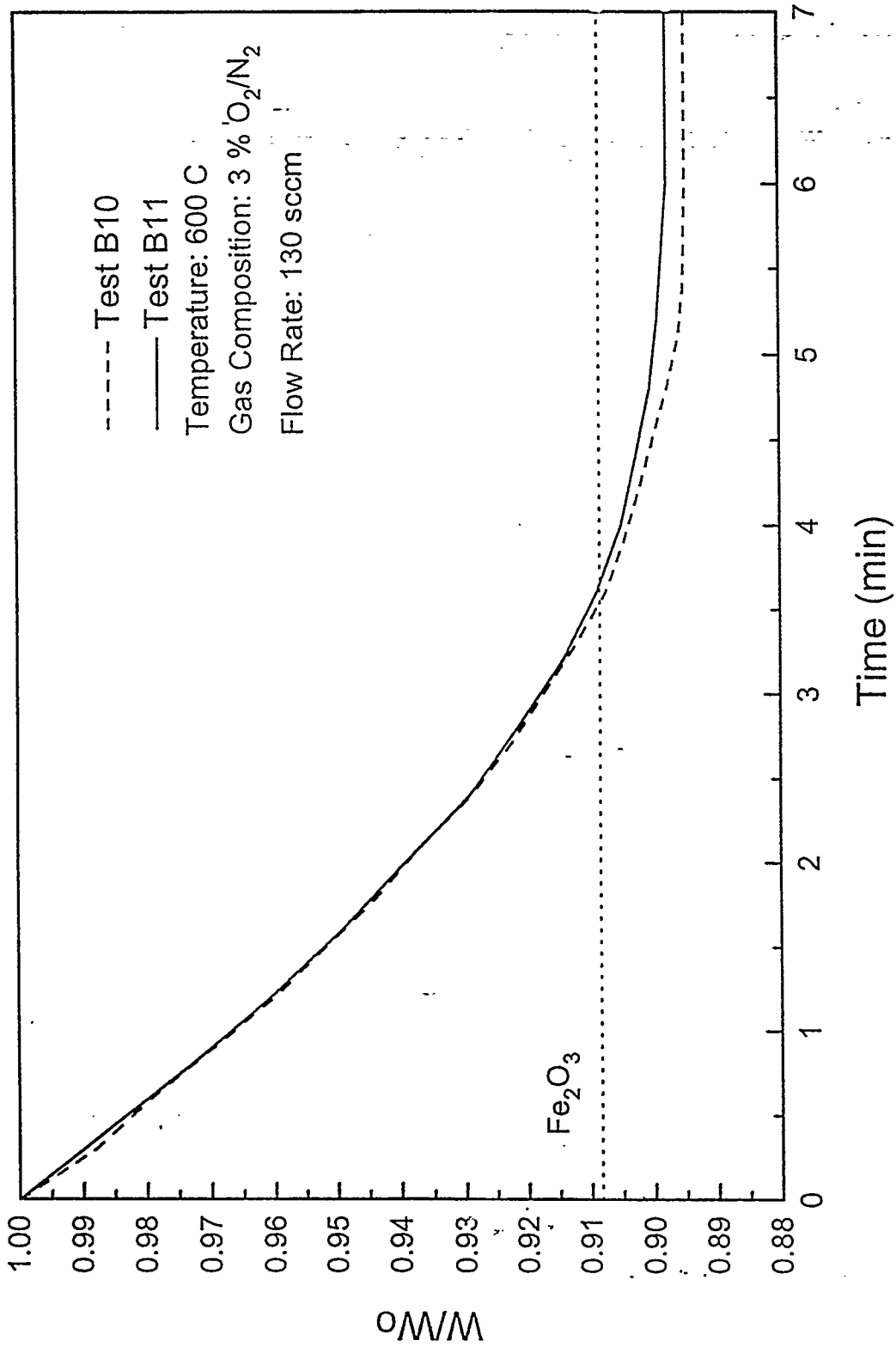


Figure 3. Reproducibility of Duplicate Tests Following Replacement of the Improperly Sized Rotameter

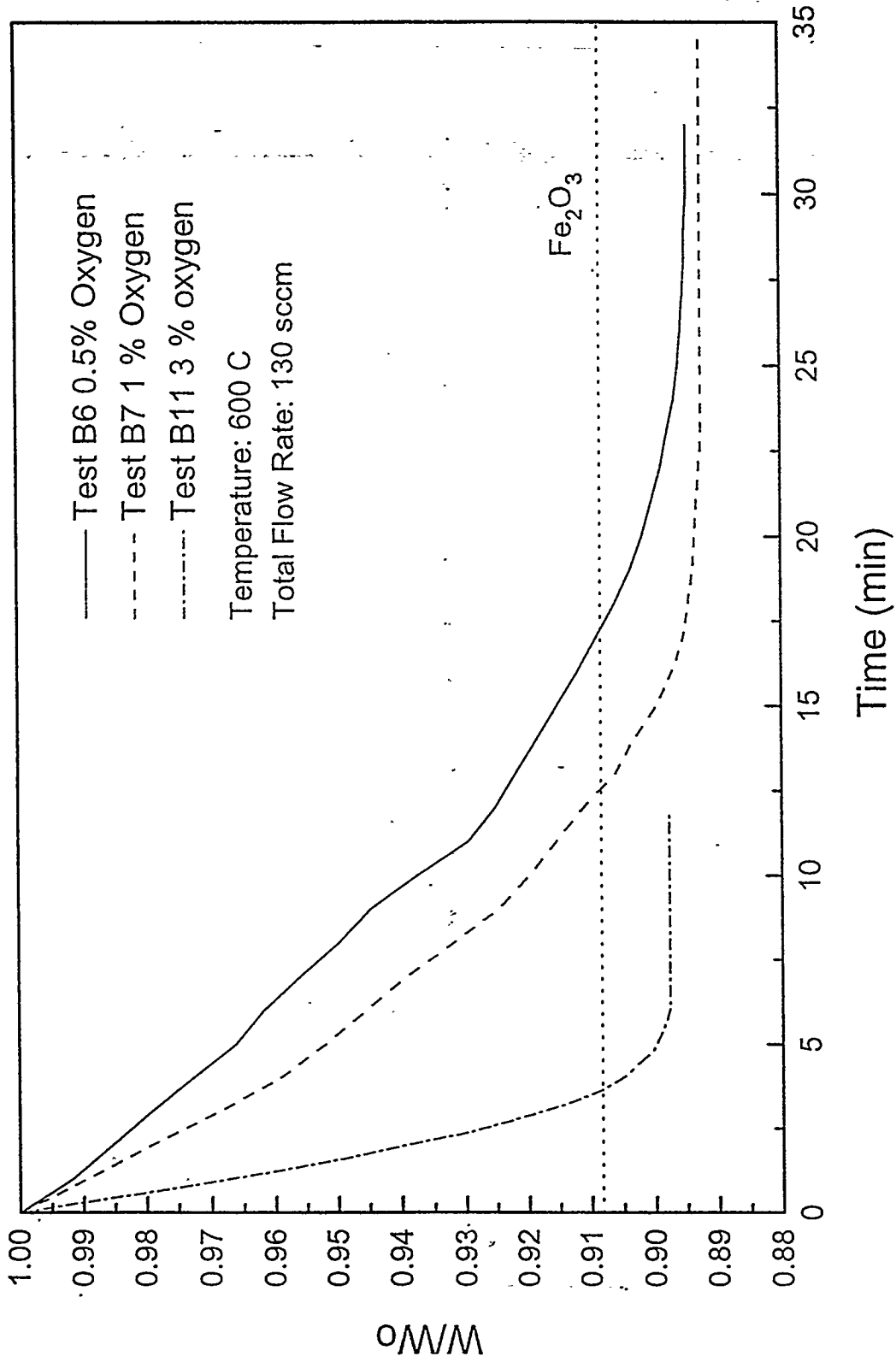


Figure 4. Effect of O₂ Concentration
(using new rotameter)

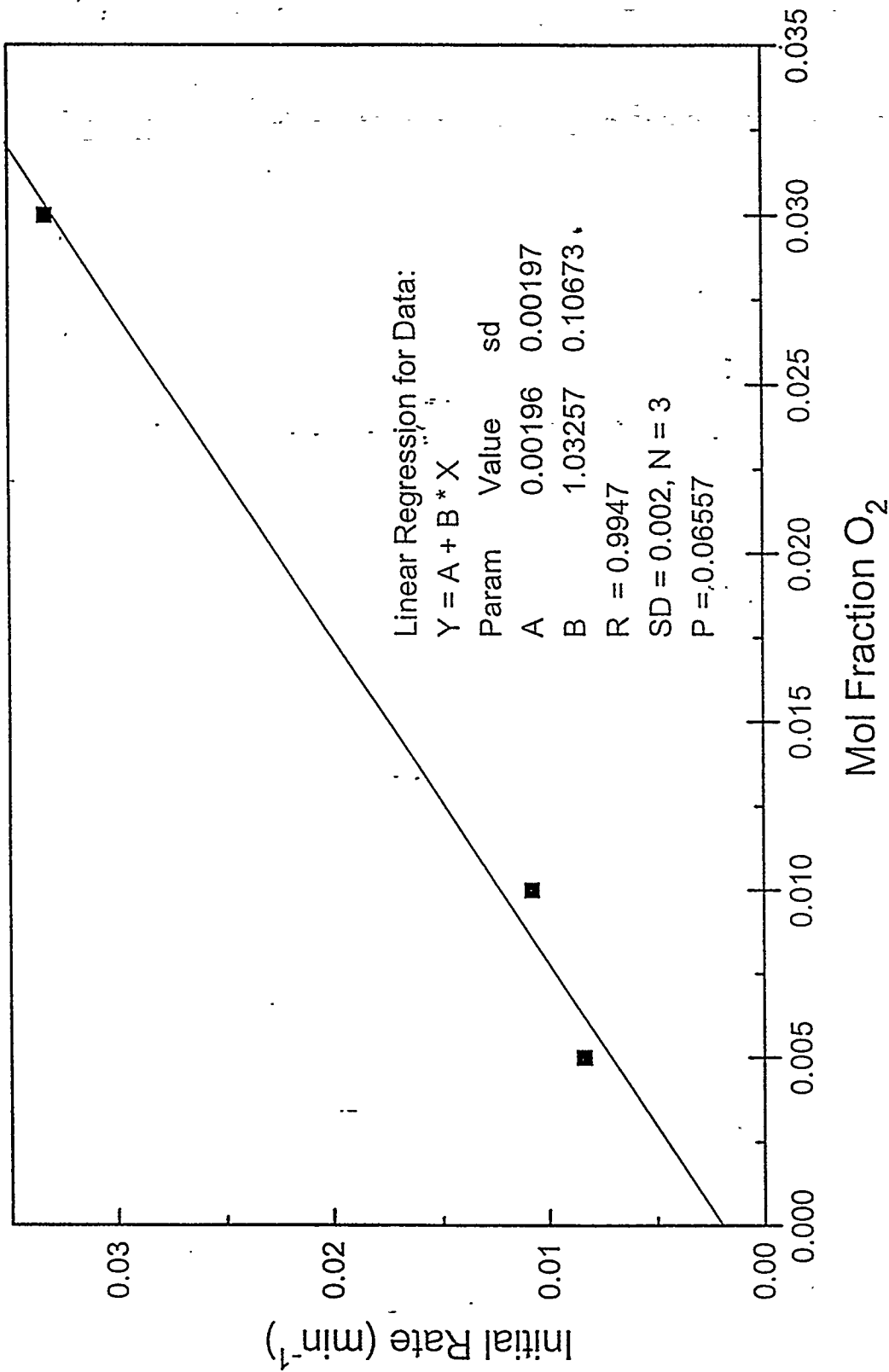
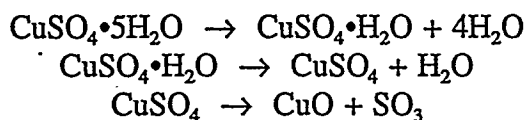


Figure 5. First-Order Dependence of Initial Reaction Rate on Oxygen Concentration

The first test was a control test on decomposition of hydrated copper sulfate. Figure 6 compares results at 1 atm and 5 atm for this compound heated in a stream of N₂. Horizontal dashed lines are drawn at theoretical values of W/W₀ corresponding to the steps in the decomposition.



Experimental weight plateaus were close to these expected values. Somewhat higher decomposition temperatures were required at each step for the higher pressure, in agreement with expectations.

In the next test FeS was heated from ambient temperature to 800°C in a 3% O₂/N₂ stream at the nominal rate of 10°C/min. Figure 7 shows the resulting W/W₀ versus temperature. We attribute the initial slow weight increase, which occurred between ambient and 300°C, to increased drag as the temperature increased. The more rapid increase, between 300°C and 500°C, derives from drag supplemented by formation of Fe₂(SO₄)₃. Above 500°C sulfate decomposition begins and W/W₀ rapidly falls to ~ 0.900, close to the theoretical 0.908. These results are qualitatively the same as those observed previously with the atmospheric pressure electrobalance. At this point the apparatus was deemed ready for preliminary experiments on effects of temperature, pressure, gas composition, and gas flow rate on FeS regeneration kinetics.

Initial tests were done at one atmosphere for comparison with results from the atmospheric pressure balance. Figure 8 shows results at 600°C and 700°C for 3% O₂ concentration. The regeneration rate is only a weak function of temperature, indicating that the global rate is dominated by mass transfer resistances. Early results from the atmospheric pressure electrobalance showed a similar weak temperature dependence. Reaction conditions in the earlier atmospheric pressure experiments are not totally equivalent due to differences in the mass transfer characteristics. However, the initial global reaction rate from the high pressure system is within 10% of the initial rate measured with the atmospheric pressure electrobalance.

The next experiments investigated the effect of O₂ concentration. Figure 9 compares results from three tests at 600°C and 200 sccm gas flow rate with O₂ mol fraction varying from 0.0036 to 0.03. These data, like those from some of the earlier atmospheric pressure electrobalance experiments, are somewhat suspect at low O₂ concentrations. While the global rate clearly decreases, as expected, when O₂ mol fraction decreases from 0.03 to 0.01, there is little further decrease in rate when O₂ mole fraction goes to 0.0036. This inconsistent result at the lowest O₂ concentration may be due to operation below the accurate range of the mass flow controllers. It will be investigated further in the next quarter.

Figure 10 shows the effect of increasing the gas volumetric flow rate from 200 to 300 sccm. The higher flow rate produced an increase in global rate, indicating the importance of external mass transfer resistance. This was consistent with the earlier experiments on the effect

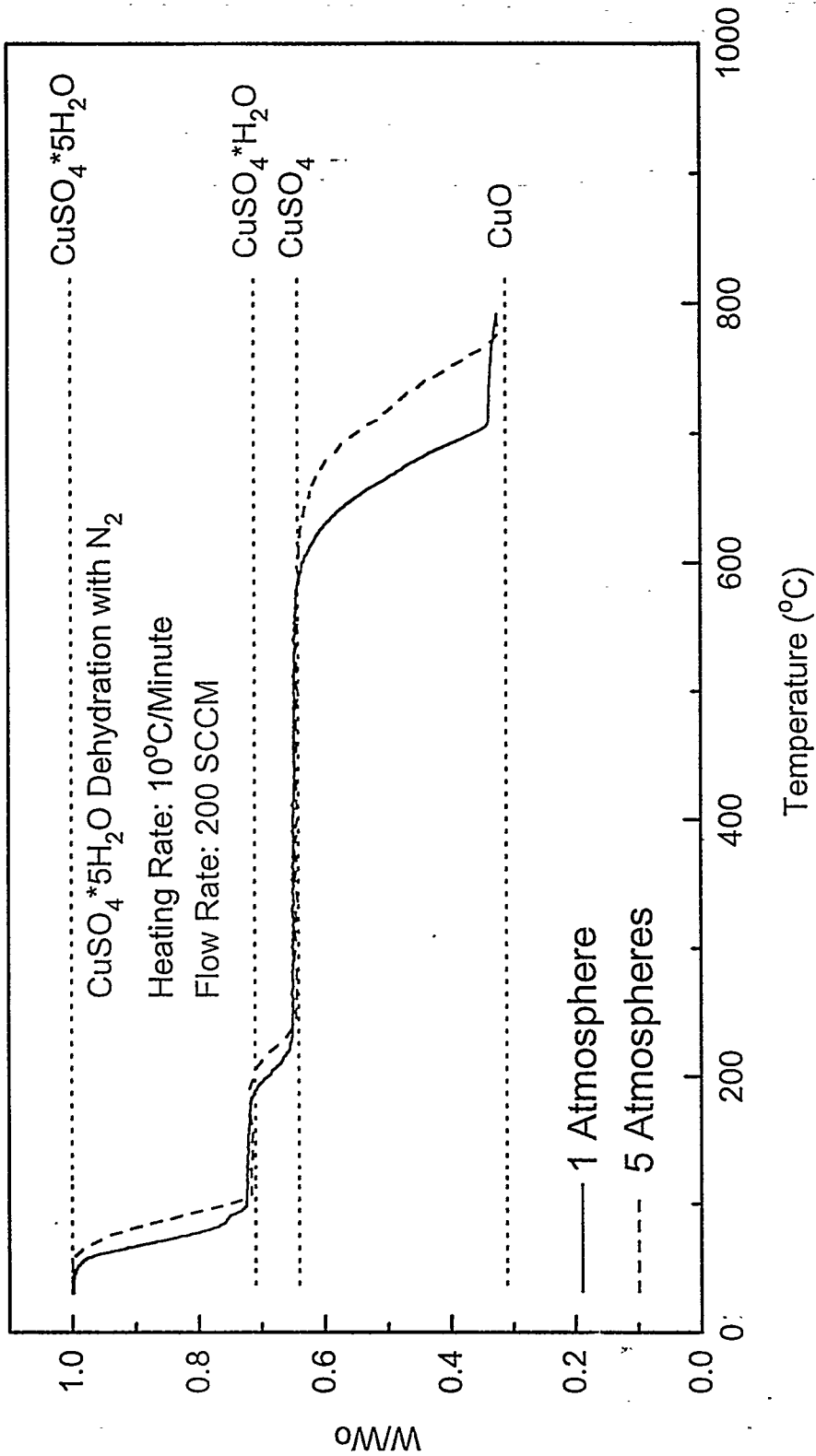


Figure 6. Nonisothermal Decomposition of Hydrated Copper Sulfate at 1 and 5 Atmosphere (High Pressure Electrobalance)

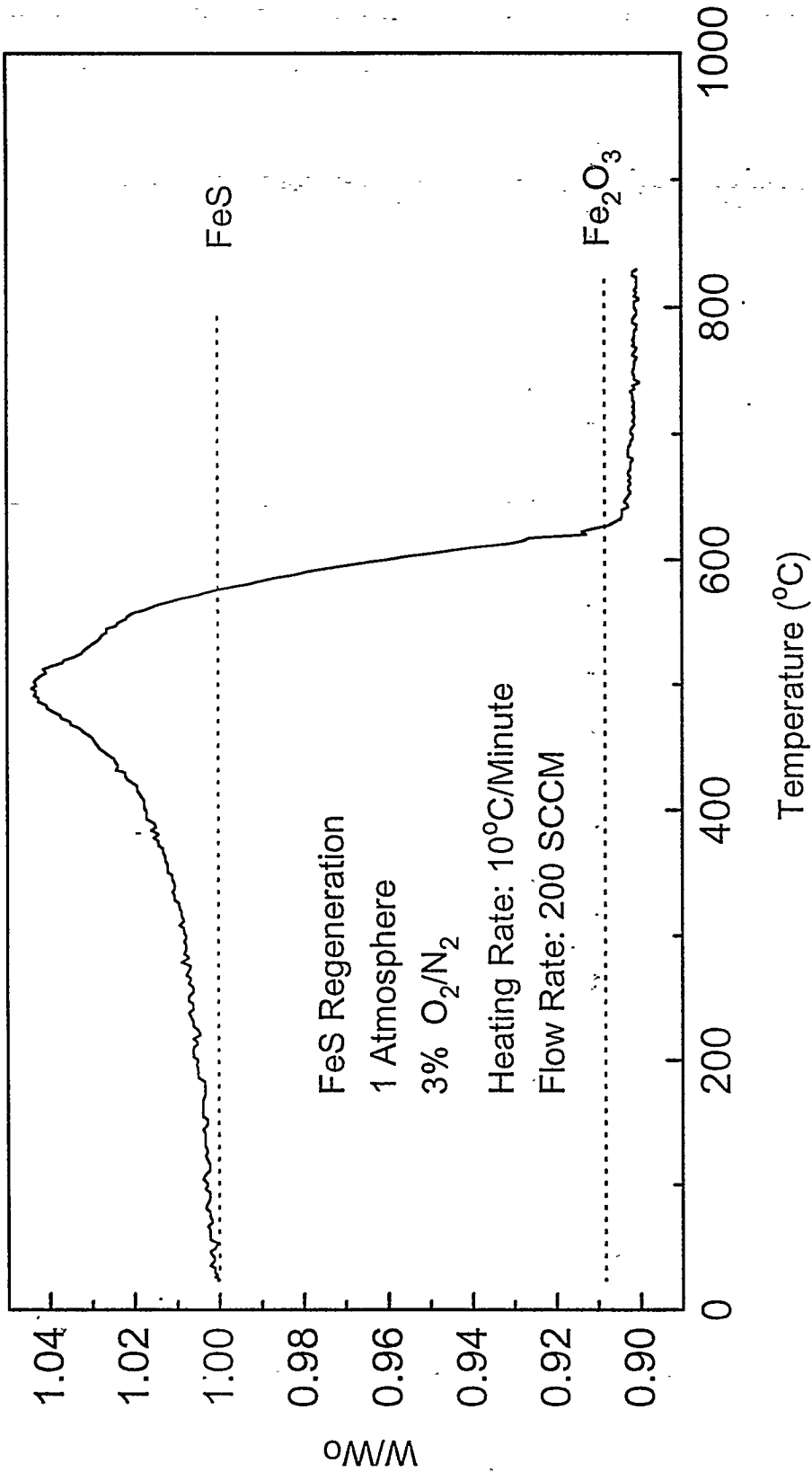


Figure 7. Nonisothermal Regeneration of FeS (High Pressure Electrobalance)

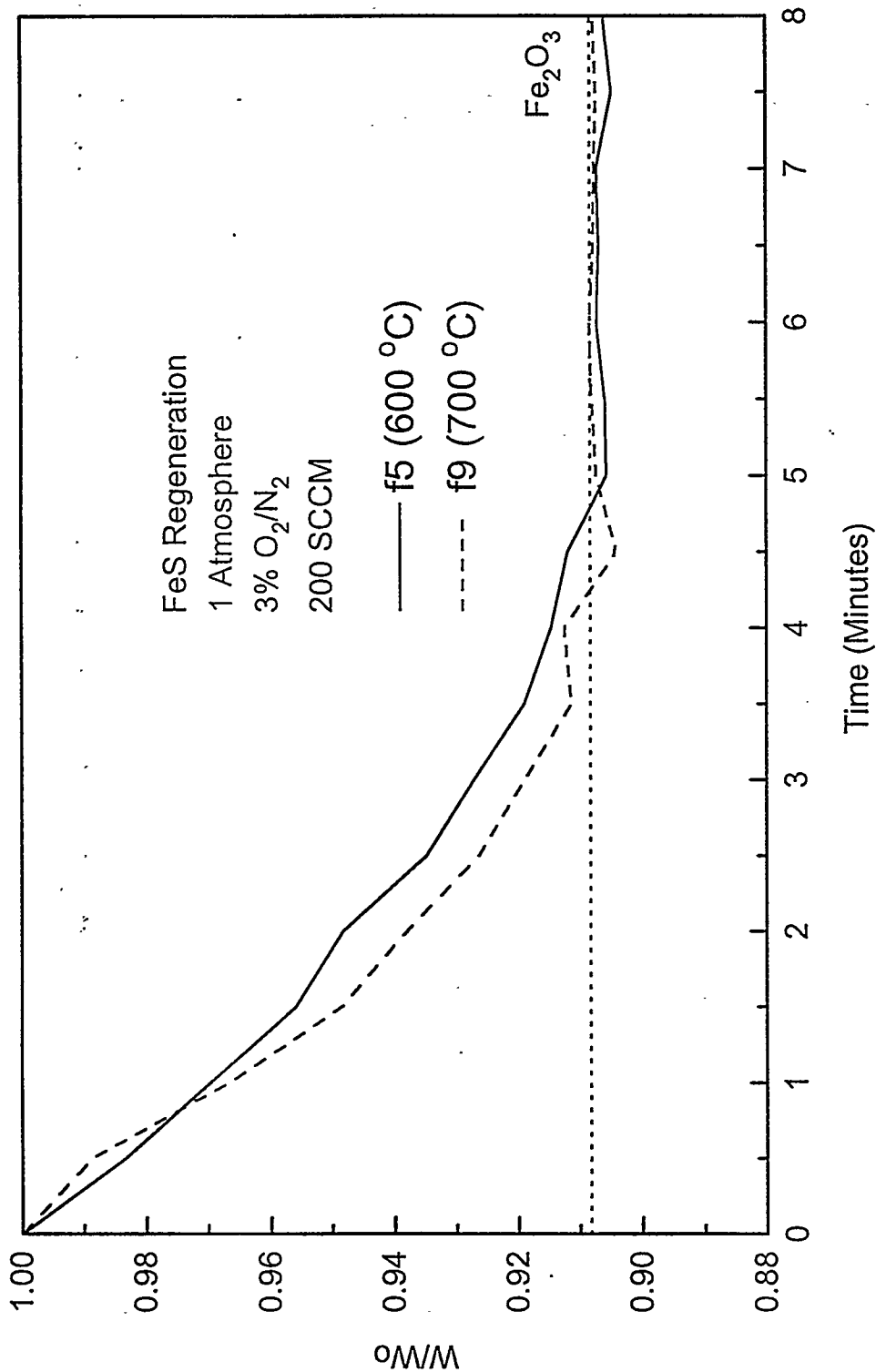


Figure 8. The Effect of Temperature on FeS Regeneration

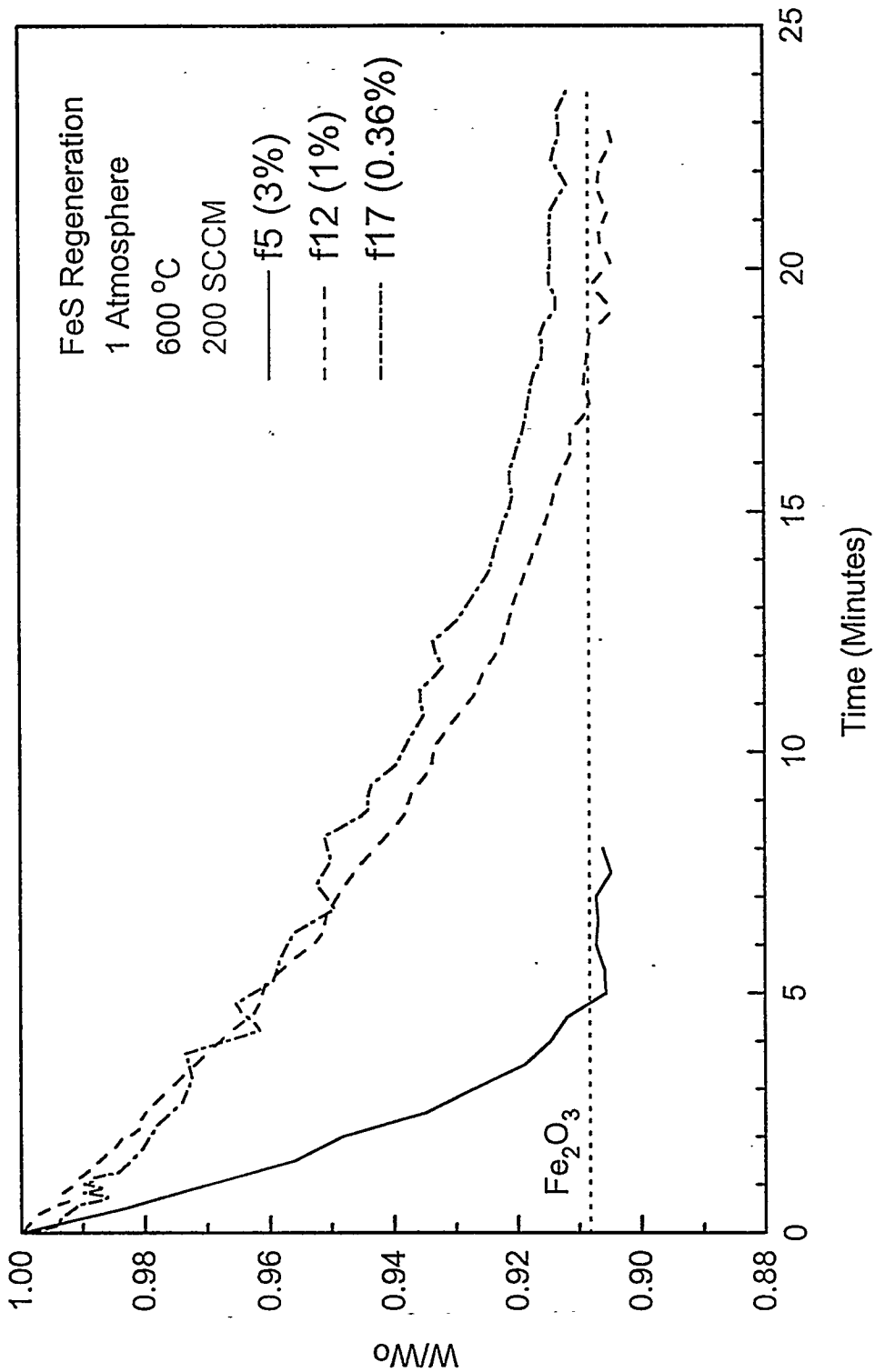


Figure 9. The Effect of O₂ Concentration on FeS Regeneration

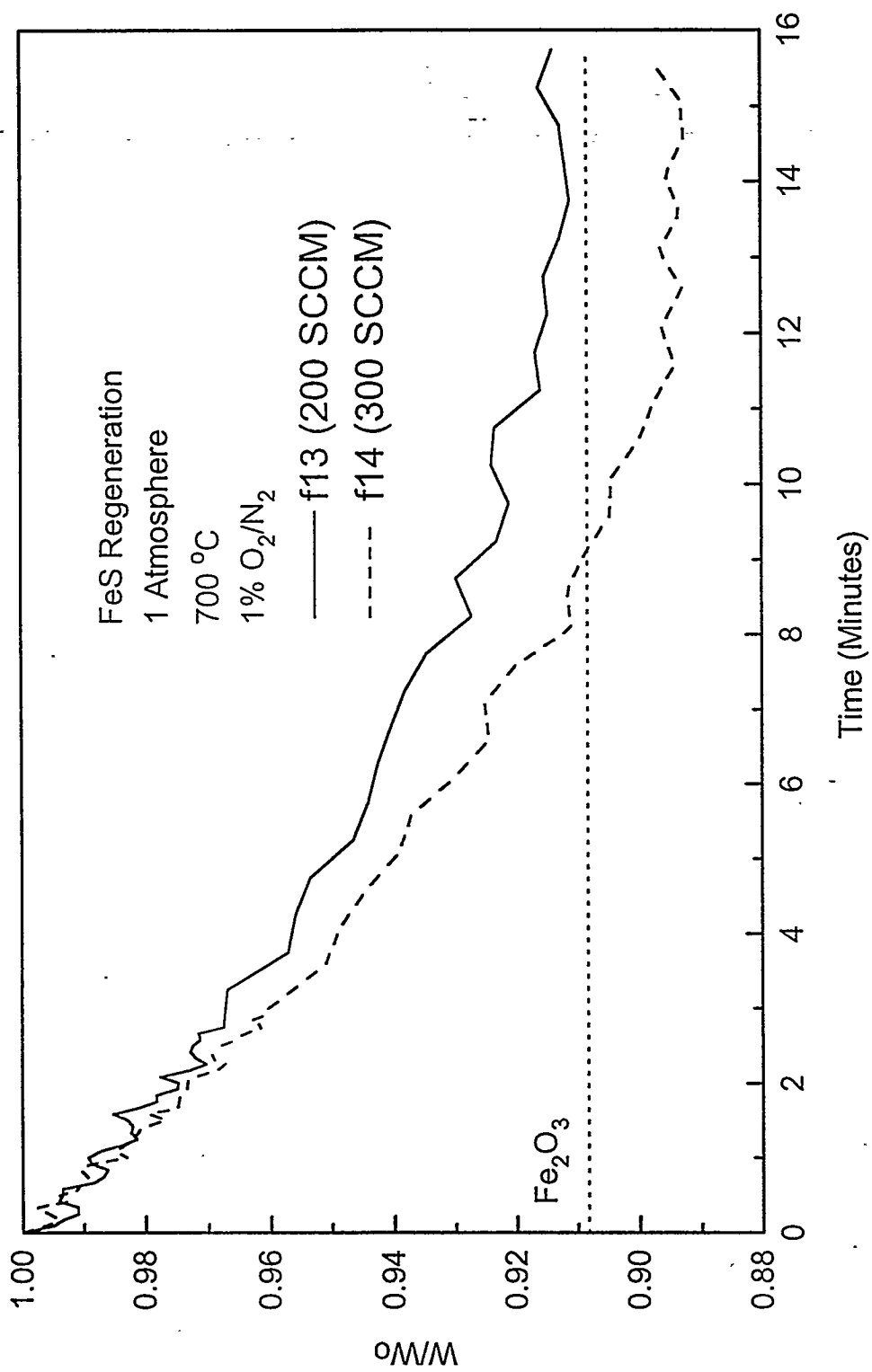


Figure 10. The Effect of Volumetric Flow Rate on FeS Regeneration

of temperature, where mass transfer resistance appeared to dominate. Additional tests at higher gas volumetric flow rates will be done to determine whether the effect of external mass transfer resistance can be eliminated.

Figure 10 shows another problem with the data - the large fluctuations in the signal during the early stages of the reaction. During the first three minutes of the test W/W_0 was recorded every five seconds. Later the sampling period was extended to 30 seconds. The high noise level in the signal is responsible for the erratic results, which are most apparent in the early part of the experiment when the sampling frequency is high. This problem may be more serious at high gas flow rates where fluctuations in aerodynamic drag will be larger. We plan to investigate methods of smoothing the data to permit more consistent determinations of reaction rate.

In summary, the high pressure electrobalance has been put into service and has been given preliminary tests. After some further runs to ensure the consistency and accuracy of the data, we plan to proceed during the next quarter with high pressure studies of the effects of temperature, O_2 concentration, and gas flow rate.

Fixed Bed Reactor

The Alonized stainless steel reactor was pressure tested early in the quarter. Leaks were repaired and it now holds pressure at room temperature. Other components of the reactor system were ordered and most arrived during the quarter. A sulfur dioxide mass flow controller, filters, and a few valves are scheduled for delivery in early July. Construction of the fixed bed reactor system will begin in mid July followed by calibration of the analytical instruments.