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THE SYSTEMS QUALITY SODIUM LOOP - OXYGEN METER CALIBRATION

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STATEMENT OF PROBLEM

To calibrate the oxygen meter on the systems quality sodium loop.

ABSTRACT

An experiment was carried out to calibrate the electrochemical oxygen meter installed in the systems quality sodium loop. The cold trap was valved out of the loop and three injections of oxygen were made by addition through the cover gas. The oxygen was rapidly dissolved by the sodium as shown by a decrease in the oxygen meter output.

The plugging meter was operated in the oscillating mode to estimate saturation temperatures of the dissolved oxygen. Several samples were taken for chemical analysis.

The equation

$$E = 1.174 - 0.0545 \log C$$

where E is in volts and C is wppm oxygen, was developed from the experimental results.

INTRODUCTION

The systems quality sodium loop was constructed in order to maintain a large quantity of well-characterized sodium of constant composition for use on the LMFBR Cladding Program.(1) A few months after operation of the loop was begun, a solid electrolyte electrochemical oxygen meter was installed in the main flow circuit. Since that time, several experiments have been conducted to test the response of the oxygen meter to oxygen additions to the loop sodium.(2) Recently another experiment was conducted in which three injections of oxygen to the loop were made. Several oscillating plugging runs were made to estimate the saturation temperature from which the oxygen level in the sodium could be determined. Also, several samples were taken for chemical analysis for oxygen.

The traditional operation of a plugging meter is to cool the piping preceding the orifice until a flow restriction is noted by the flow meter. The temperature at which this occurs is somewhat below the saturation concentration for oxygen in sodium because a driving force is needed to nucleate and grow the sodium oxide crystals. By operating a plugging meter in the oscillating mode,(3) it is possible to determine the saturation temperature of the dissolved oxygen with reasonable accuracy. McPheeters has determined saturation temperatures within 2°C by this technique.(3)

To operate a plugging meter in the oscillating mode, the procedure is as follows: At the first decrease in the flow meter trace, cooling is stopped so that the hot flowing sodium will increase the temperature at the plugging orifice. When the flow rate starts to increase, cooling is again applied. By repeating this cooling-heating cycle, a sinusoidal flow meter trace results. The peaks and valleys of the trace correspond to temperatures at which oxide is neither precipitating nor dissolving; i.e., the dissolved oxygen in the sodium is at equilibrium with the solid phase in the plugging orifice.

In this report, the correlation between the oxygen meter readings and oxygen level as determined by the oscillating plugging meter and by chemical analysis is presented.

EXPERIMENTAL

The supply loop operates at a nominal temperature of 500°F with the cold trap at 250°F. Before starting the experiment the cold trap was shut down and the sodium in the trap allowed to freeze. The shut-off valve on the trap no longer closes completely so the trap served as a freeze seal.

Oxygen was added to the loop by connecting a bulb to the cover gas system, pressurizing the bulb with oxygen and then slowly bleeding the oxygen into the cover gas. In normal operation 3 psig of helium is maintained over the surge tank. This pressure was relieved prior to the addition and then reapplied in order to flush the residual oxygen in the line into the surge tank. Three separate additions were made, calculated to add 25, 17 and 25 ppm of oxygen to the sodium.

The first addition was made on the morning of March 7. Approximately four hours after the addition, the oxygen meter reading had decreased from 1.172 volts to 1.102 volts. At this time, an oscillating plugging run was made and a sample taken for chemical analysis. The plugging run was made by manually controlling the blowers on the finned section of piping preceding the plugging orifice. The run was made with several cooling-warming cycles in the expectation of obtaining better results for the saturation temperature. By using manual control, it is possible (after the first cycle) to anticipate the onset of plugging, or to allow the plug to build in order to effect a wider fluctuation in the flow meter trace.

Over the weekend, the emf of the oxygen meter increased 7 mv. This represented a small decrease in oxygen content so an oscillating plugging run was made. On the morning of March 11, the second oxygen injection was made. After a few hours, the meter reading decreased to 1.099 volts. At this time, an oscillating plugging run was carried out and a sample taken for chemical analysis.

A slight increase in emf took place overnight. On the morning of March 12 the third injection was made. After a few hours, the meter reading had decreased to 1.092 volts. Another oscillating plugging run was made, but not without some difficulty. Shortly after the start of cooling (at about 465°F) a massive plug apparently formed as the flow rate decreased sharply. It was necessary to heat the plugging orifice to about 510°F in order to reduce the plug. A few plug-unplug cycles were successfully accomplished. A sample was taken for chemical analysis.

After the third injection, the oxygen meter reading was observed periodically. By March 24, the meter reading had increased to 1.113 volts. On the 24th and 26th, oscillating plugging runs were made. On March 28 the cold trap was melted and circulation re-established. After approximately two hours of cold trapping, an oscillating plugging run was attempted. A plugging temperature of 211°F was noted, followed by freezing at 206°F. Apparently the oxygen level had been lowered more rapidly than had been anticipated. Therefore it was not possible to operate the plugging meter in the oscillating mode.

The samples collected during the experiment were analyzed by the mercury amalgamation technique.[4]

RESULTS AND DISCUSSION

Prior to the first oxygen injection, the oxygen meter read 1.172 volts. Approximately four hours after the injection, the meter reading had decreased to 1.102 volts. Over the weekend, the reading increased to 1.109 volts and, one day later, to 1.111 volts. At this point the second oxygen injection caused a decrease to 1.099 volts. Overnight the reading increased to 1.102 volts following which, the third injection resulted in a decrease to 1.092 volts. Thus, the total decrease in emf was 80 mv.

After the third injection, there was a slow increase in emf which is typical of behavior noted previously. This effect is believed to be due to gettering of the oxygen by the stainless steel in the loop. The response of the meter during the experiment is shown in Figure 1.

An example of an oscillating plugging run is shown in Figure 2. This curve gives 424 and 381°F as the average temperatures for the peaks and valleys of the flow meter trace. This is a larger difference than would be desired and is probably caused by the kinetics of precipitation and dissolution of the oxide particles being slow. However, averaging these temperatures gives 402°F as the saturation temperature which is equivalent to 12 ppm oxygen in sodium.(5) As the oxygen level was increased, the difference between the "unplugging" and "plugging" temperature decreased. Actually, at the highest oxygen level the averages of the two sets of temperature data were 483.5 and 483°F.

A total of four samples was taken during the course of the experiment. The samples are normally collected in 3/8" O.D. tubing which is crimped after the sample is taken. It was attempted to analyze the total sample (the portion between the crimps) for the last three; however, this was accomplished only with the last sample. One of the extraction flasks broke during amalgamation of one of the sub-samples from the second sample. In the third sample, one of the sub-samples was incompletely extracted so the residual sodium negated the results for the sub-sample. In the first sample, only two cuts from the center of the sample tube were analyzed. It appears that in these high oxygen samples, there is segregation on cooling. In those sub-samples which included the sodium adjacent to the crimp, the oxygen level was definitely greater than in center portions. Thus, the analytical results for the first three samples are not considered to be of high accuracy. The fourth analysis appears to be about 2 ppm high; however, this is within the precision of the amalgamation method.

The results are given in Table I. The saturation temperatures are those determined from the oscillating plugging runs and the oxygen corresponding to these temperatures is taken from Eichelberger's correlation.(5) In general, the agreement is good. The three data points around 1.11 volts are a bit scrambled but this may be due to the inability to determine the saturation temperature precisely. The oxygen meter readings do show the expected trends with time so the oxygen concentrations estimated from the plugging runs are probably at fault.

TABLE I

OXYGEN DETERMINATION RESULTS

Date	Sat. Temp.,°F	Sat. O, ppm	Anal. O, ppm	EMF, volts
3-7	430	18	13	1.102
3-10	402	13	-	1.109
3-11	448	24	18	1.099
3-12	483	35	25	1.092
3-24	408	14	-	1.113
3-26	397	12	15	1.114

The results of the experiment are plotted in Figure 3. As can be seen, there are no experimental points between 1 and 10 ppm oxygen. It was planned to determine saturation temperature at approximately 1.13 volts but, as pointed out earlier, this was not possible. Assuming the system was at equilibrium with the cold trap at 250°F, the starting concentration of oxygen was 1.1 ppm. Using this value and the data obtained during the experiment (plugging values) an approximate calibration for the oxygen meter is as shown on the graph. The slope when compared to the theoretical curve[2] is not too different, although the electrode does not develop the theoretical emf. The equation for the line is

$$E = 1.174 - 0.0545 \log C$$

This experiment has demonstrated a method for calibrating an electrochemical oxygen meter. Obviously this technique would not be practical for a large system; however, if the electrode were located in a smaller side stream which could be isolated from the main system, it could be applied. However, the side stream system would require a separate pump and a plugging meter and a means for injecting (and removing) oxygen.

Some data points should be obtained between 5 and 10 ppm oxygen, probably by starting with smaller oxygen additions so that data could be obtained "going up the line." McPheeters has successfully operated the oscillating plugging meter at relatively low oxygen levels.[3] Additional points would improve the present calibration curve.

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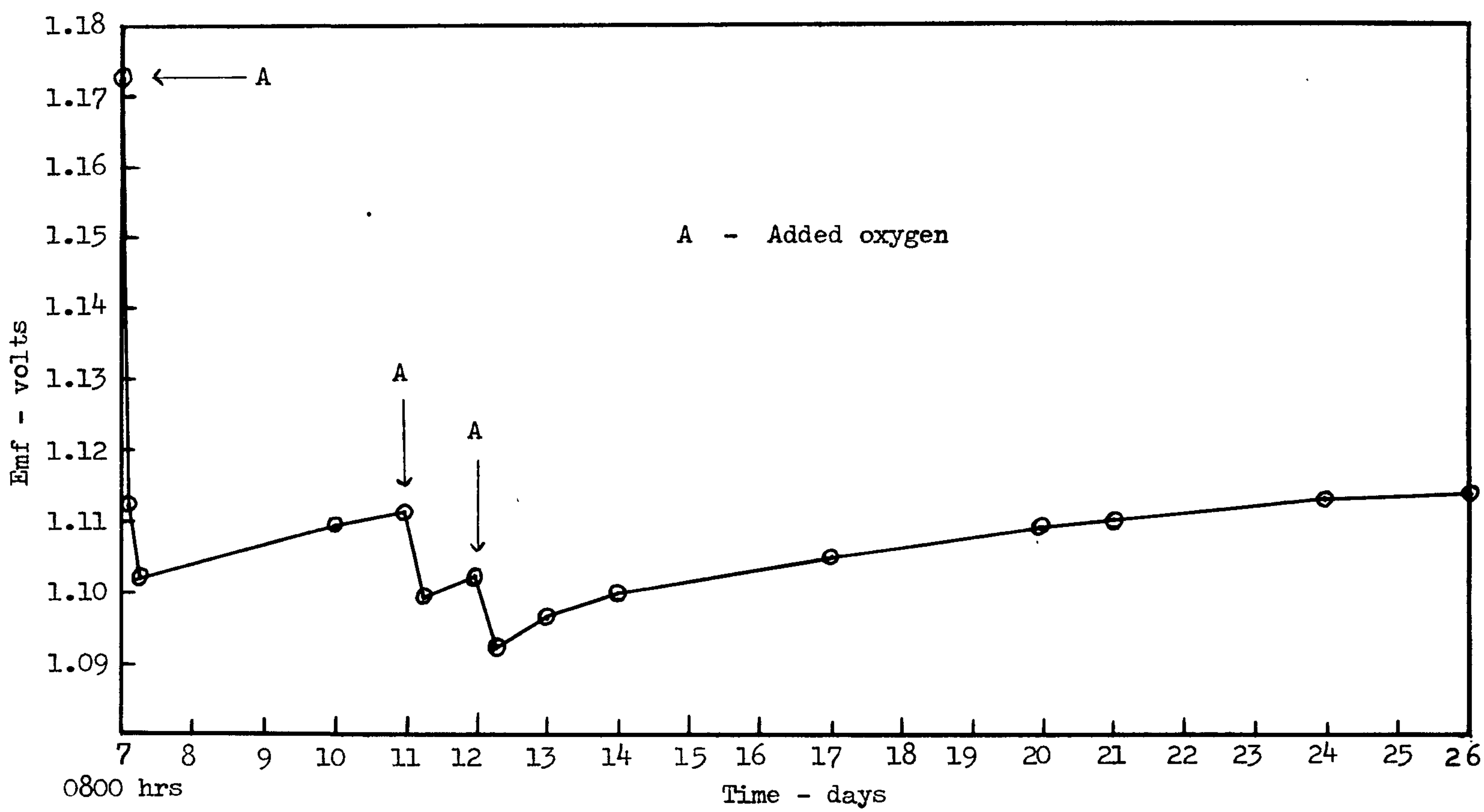

Figure 1. Oxygen meter results.

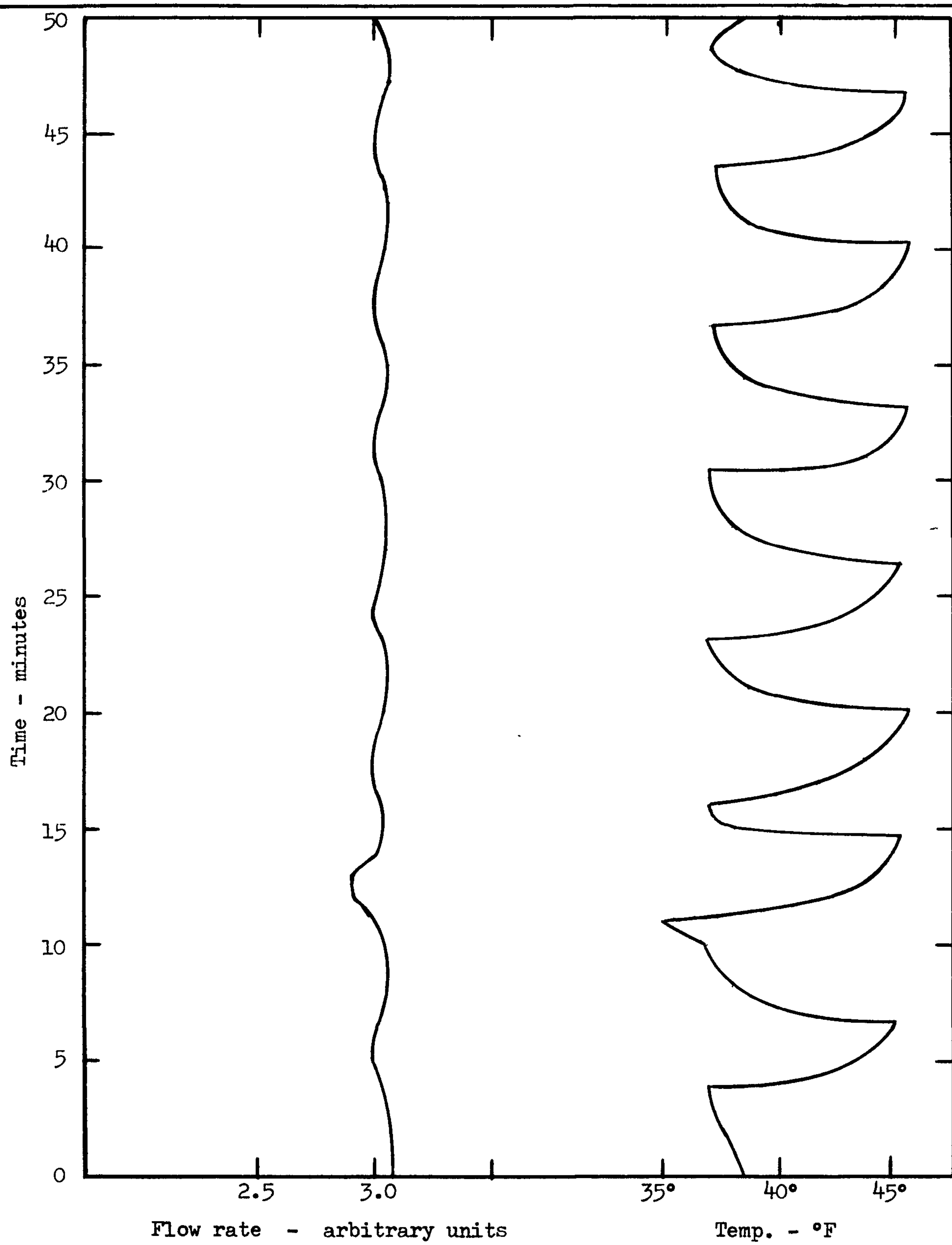

Figure 2. Typical oscillating plugging meter run.

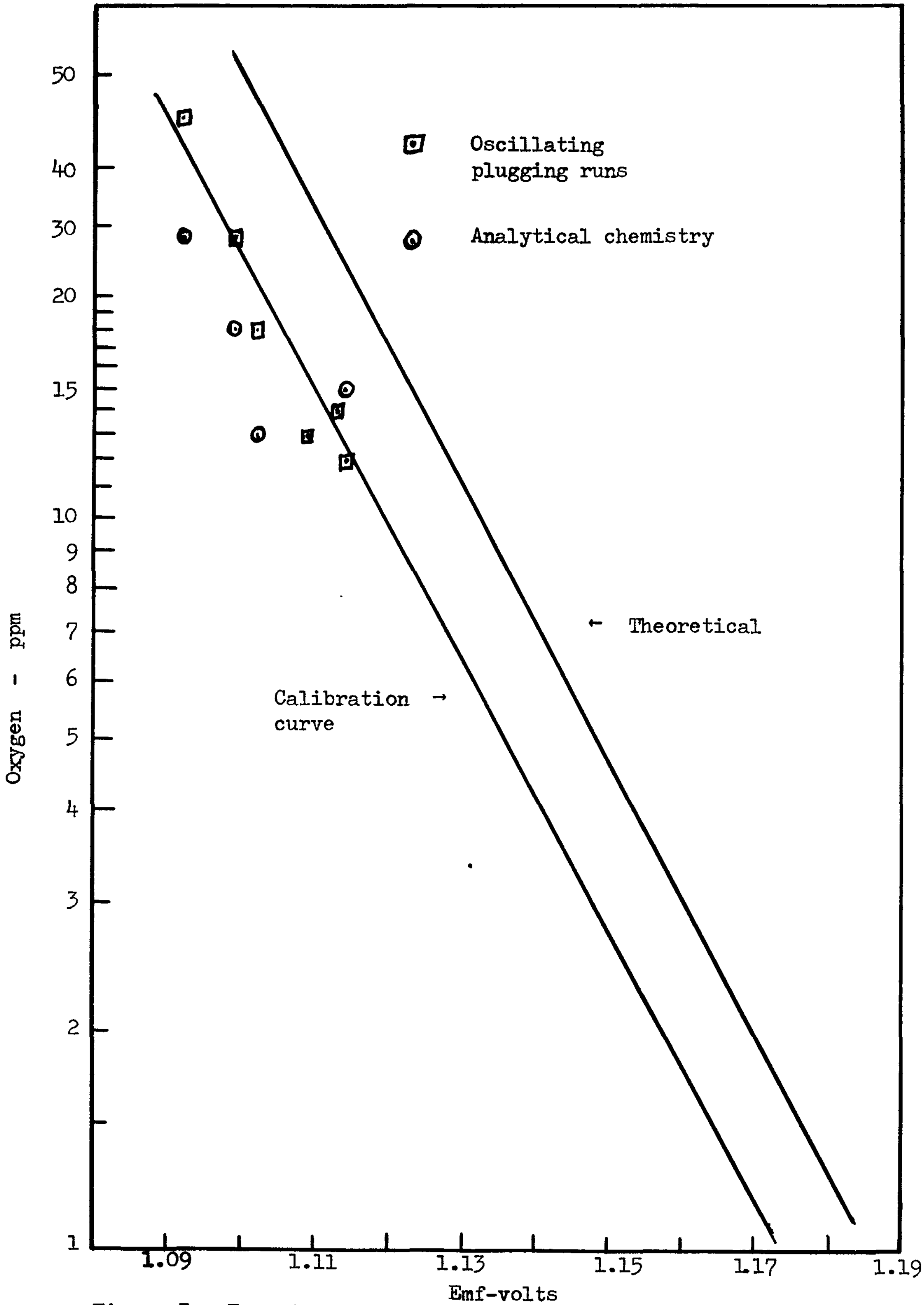

Figure 3. Experimental results and oxygen meter calibration curve.