OXYGEN MEASUREMENT AND CONTROL IN LIQUID SODIUM SYSTEMS

by

Andrew Napora

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The dissertation is approved by the following members of the Final Examination Committee:

Mark H. Anderson, Professor, Mechanical Engineering
Greg F. Nellis, Professor, Mechanical Engineering
Dane Morgan, Professor, Materials Science and Engineering
Scott T. Sanders, Professor, Mechanical Engineering
Franklin K. Miller, Associate Professor, Mechanical Engineering

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SYMBOLS

S = sodium oxygen concentration [wppm]

T_K = Temperature [K]

t_{res} = residence time of sodium in cold trap isothermal zone [min]

V_{loop} = total volume of sodium in facility [gal]

$\dot{V}_{CT}$ = volumetric flowrate of sodium through cold trap [gal/min]

$K_A =$ distribution coefficient of oxygen in sodium and vanadium at equilibrium [-]

N_{O_V} = mole fraction of oxygen in vanadium [-]

$N_{O_V}^{o}$ = mole fraction of oxygen in vanadium at saturation [-]

$N_{O_{Na}} =$ mole fraction of oxygen in sodium [-]

$N_{O_{Na}}^{o}$ = mole fraction of oxygen in sodium at saturation [-]

$\eta =$ cold trapping efficiency [-]

Q = volumetric flow rate [m^3/hr]

P_F = plugging fraction for PTI [-]

Re = Reynolds number [-]

LIST OF ABBREVIATIONS

GEN IV = Generation IV nuclear reactors
SFR = Sodium Fast Reactor
EBR-I/II = Experimental Breeder Reactor I or II
SRE = Sodium Reactor Experiment
FFTF = Fast Flux Test Facility
AEC = Atomic Energy Commission
RDT = Reactor Development and Technology
DOE = Department of Energy
PTI = Plugging Temperature Indicator
VWE = Vanadium Wire Equilibration
CT = Cold Trap
ppm = part-per-million
wppm = weight part-per-million
ppb = part-per-billion
LECO = LECO corporation, original name **L**aboratory **E**quipment **Co**rporation
UW MIN = University of Wisconsin Minimum Method
UK = United Kingdom
VFD = Variable Frequency Drive
OCCM = Oxygen Concentration Control and Measurement
FM = Flow Meter
MMP = Moving Magnet Pump
SSE = Sum of Squares due to Error
RMSE = Root Mean Square Error
CI = Confidence Interval

INTRODUCTION

As projected electrification demands rise and emissions deadlines draw near, the United States is one of many countries seeking an expanded place for nuclear in its energy portfolio. At the same time, the market must contend with the economic unpalatability of large, decades-long, construction projects like Plant Vogtle. One solution is the deployment of Generation IV (Gen IV) reactors, whose power densities enable a smaller footprint for each plant. These can then either be coupled or used in a more distributed grid structure. One of these designs, the Sodium Fast Reactor (SFR), served as the basis of U.S. research reactors such as Experimental Breeder Reactor (EBR)-I/II, Sodium Reactor Experiment (SRE), and Fast Flux Test Facility (FFTF), though there has not been an SFR in the U.S. since 1994. As the most technologically mature of the proposed Gen IV reactors, the U.S. is moving towards rebuilding the SFR design and operational knowledge to compete as a global leader in the nuclear field.

To this end, TerraPower is designing and building the Natrium Reactor Plant as part of the U.S. Department of Energy Advanced Reactor Demonstration Program. The reactor is to be the United States' first sodium-cooled fast reactor producing commercial power, with operation targeted for 2030. Extensive laboratory-scale sodium experiments are required to prove various reactor components' corrosion resistance and safety. As oxygen content strongly affects the corrosion of alloys in sodium systems, both reactor-scale systems and laboratory-scale research experiments rely on precise control and measurement of sodium oxygen concentration. A robust program of standard practices in oxygen measurement is then crucial to the success of the proposed SFR program. This thesis details, in part, two experimental studies that suggest revisions to now-inactive standards to improve accuracy in the methods that they describe.

Objectives

- Quantify the operator error inherent in Reactor Development and Technology Standard plugging temperature indicator measurements
- Qualify the UW Minimum Method of plugging temperature indicator measurement against the accepted standard method
- Investigate the possible non-equilibrium nature of the vanadium-wire equilibration method
- Investigate sources of variability in the vanadium-wire equilibration method of oxygen measurement, and generate a modified procedure to obtain better reproducibility
- Conduct experiments to fit original correlations to better describe experimental data

LITERATURE REVIEW

CRITICAL BACKGROUND

Reactor Development and Technology Standards

Technology related to the early development of liquid metal reactors in the U.S. was not formally standardized, as is common in new fields. However, in the late 1960s, the Atomic Energy Commission (AEC, predecessor of the Department of Energy) began to implement the knowledge gained from Admiral Rickover's Naval Reactors program [1] in the form of the Reactor Development and Technology (RDT) Standards system. 328 RDT standards were eventually developed, encompassing best practices in component testing, measurement techniques, fabrication methods, sodium handling, and SFR operation in general [2]. These standards were developed in a well-documented manner and formed the basis for the U.S. liquid-metal-cooled reactor program.

As interest in these reactors declined, the RDT program was discontinued by the Department of Energy (DOE), and all associated standards have been labeled "INACTIVE" (in that the program is no longer being maintained, not that the standards were deemed incorrect). It is crucial to the success of any U.S. SFR program to build on the knowledge and experience represented by the RDT standards. Two standard procedures for oxygen measurement were identified for investigation in this work: the plugging temperature indicator (PTI) method, and the vanadium-wire equilibration (VWE) method [3].

Oxygen in Sodium

Discussion of oxygen measurement techniques in sodium necessitates an overview of oxygen’s relevance in sodium systems. Oxygen is a strong driver of corrosion for typical structural materials found in SFRs. For stainless steels in sodium with oxygen concentrations above 10 wppm, ternary oxides such as $NaCrO_2$ can form and dissolve, resulting in a constant corrosion rate [4].

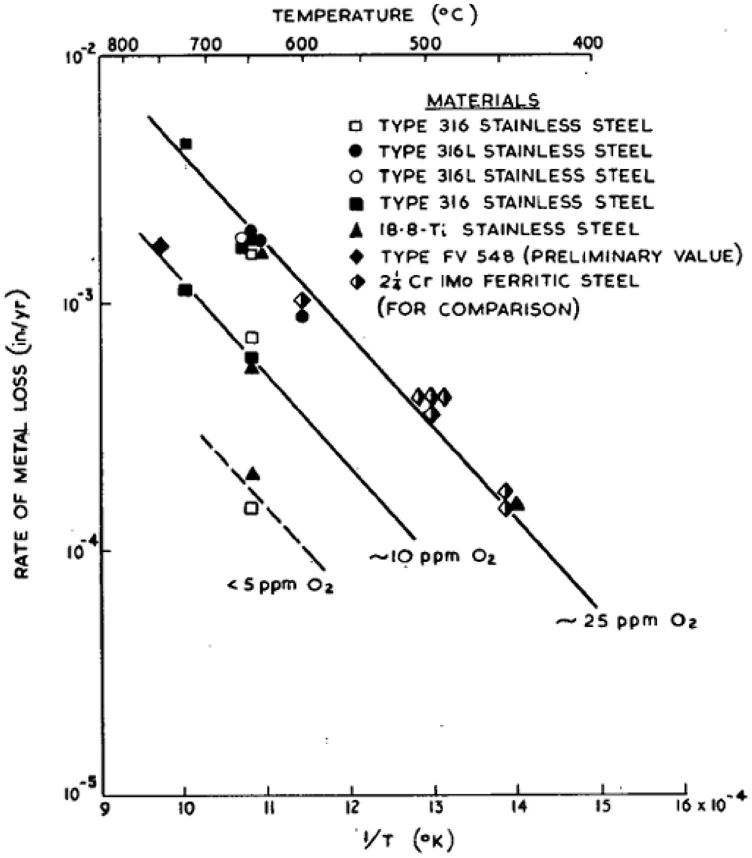

Figure 1: Effect of temperature and O2 level on rate of metal loss of various steels in flowing sodium, reproduced from [5]

Figure 1 shows the results of experiments by Thorley et al., which demonstrate that this oxygen-dependent corrosion rate for SS316 can be lowered to almost negligible levels by reducing oxygen concentration below 5 wppm [5], [6]. With SFRs typically projected to have 60-year operational lives, the minimization of oxygen-related corrosion in key components (and thus minimization of oxygen concentration in the bulk sodium) is critical to maximizing a reactor's lifespan.

Due to the positive temperature-dependent solubility of oxygen in sodium high oxygen concentrations can also lead to the "plugging" of ducts as super-saturated oxides precipitate out onto metal walls. Whereas corrosion of structural materials affects the ultimate lifespan of a reactor, this plugging behavior can affect short-term capacity factors, as plugged lines often necessitate the mechanical removal and replacement of the failed component. The solubility of oxygen in sodium is given by Eichelberger as

$$\log_{10}(S) = 6.239 - \frac{2447}{T_K} \tag{1}$$

where S is the sodium oxygen concentration in wppm, and T_k is the cold trap sodium temperature in Kelvin [7].

The literature contains many expressions for the solubility of oxygen in sodium, obtained through a wide variety of methods and with middling agreement. Eichelberger performed a study encompassing all then-current data sets for this relationship, pruning data sets that were obtained through improper methodologies. Errors in methodology included sampling sodium in glass (high corrosion), presenting data as averaged curves instead of discrete points, and use of a technique (mercury amalgamation) that introduced large amounts of error at low oxygen concentrations. The set of all data and the set producing Eqn. 1 are shown in Figure 2 and Figure 3, respectively. As the pruned data set emphasizes accuracy in the oxygen concentration range relevant to SFR operation (2-20 wppm), Eichelberger's recommended expression was chosen for analysis of all work described here.

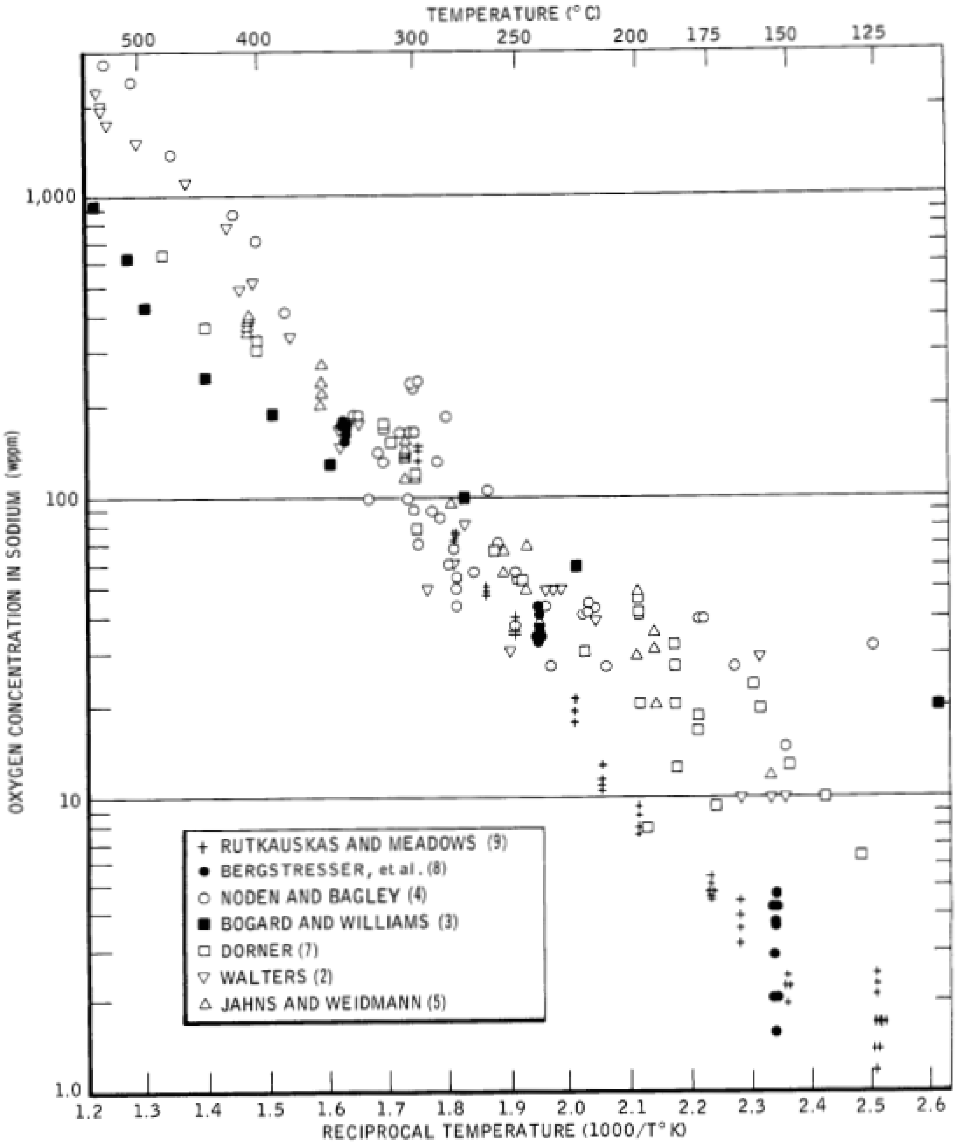

Figure 2: The Solubility of Oxygen in Sodium: All Data, reproduced from [7]

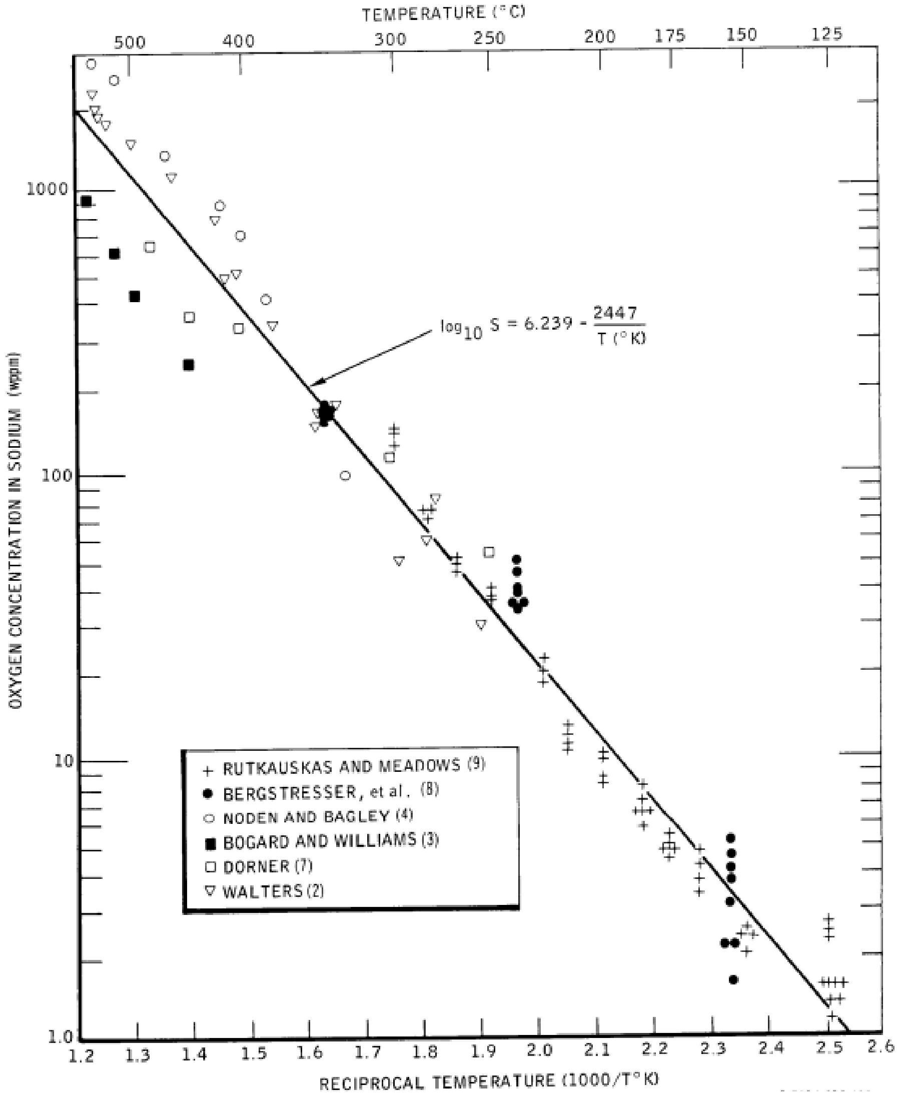

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Figure 3: The Solubility of Oxygen in Sodium: Recommended Curve, reproduced from [7]

Cold Trap

While the normal operation of sodium systems keeps the coolant separate from air and moisture, incidental oxygen contamination through maintenance and refueling cannot be avoided. This holds for large and small systems. Excess oxygen content is removed from the coolant via a cold trap: a device that cools a portion of sodium flow, precipitates out and retains supersaturated oxides on a substrate, and returns clean sodium to the main flow. By selecting a desired oxygen concentration level and using Eqn. 1 to translate this into a saturation temperature, an SFR operator may control the bulk coolant oxygen concentration by maintaining the calculated saturation temperature across the cold trap. In its simplest form, the cold trap is shown in Figure 4.

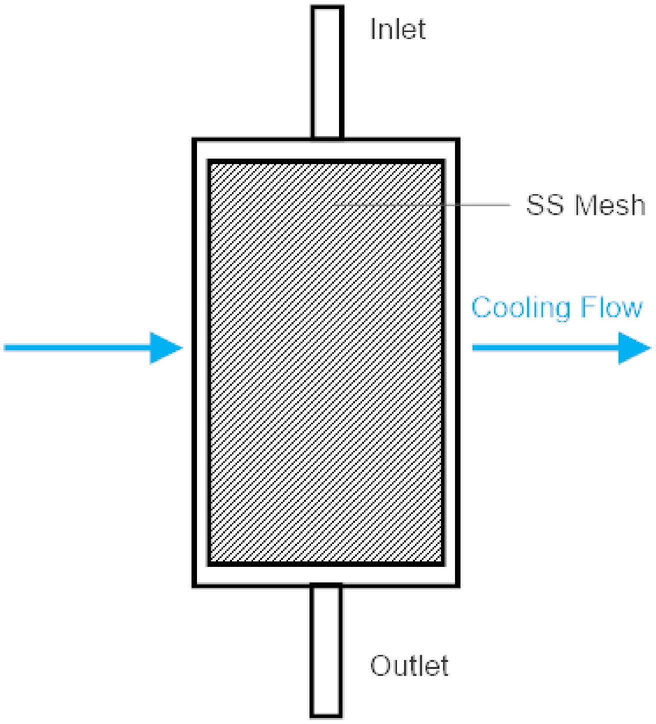


Figure 4: Simplified drawing of a basic cold trap.

Some basic requirements of the cold trap include [8]:

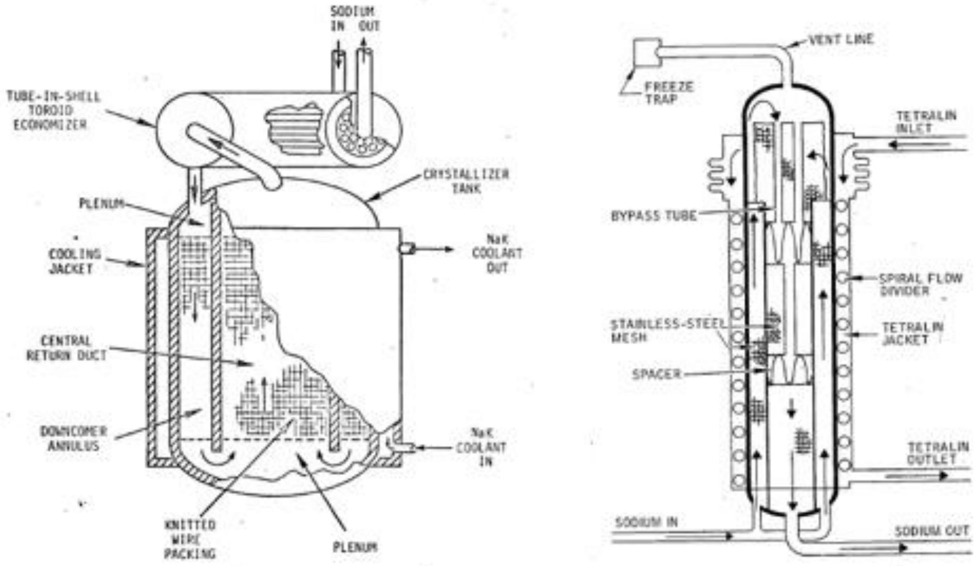
- The ability to purify loop sodium at an acceptable rate during all phases of operation
- The ability to retain sufficient oxide to reduce the number of cold trap replacements required
- Presenting minimal obstruction to flow (i.e., pressure drop across the instrument)

The Sodium-NaK Engineering Handbook [6] provides examples of many cold trap designs that have been proven to satisfy the above requirements, with various fluids used for cooling (atmospheric air, toluene, water, and even sodium itself). These designs are often paired with some form of economizer to reduce cooling loads. Figure 4 shows some collected schematics of cold traps implemented in US sodium fast reactors [9] , while Figure 6 shows the same for Russian reactors.

The efficiency of a cold trap has been shown to rely primarily on residence time, or the amount of time a given volume of sodium will spend at the desired trapping temperature [10]. This quantity is formalized as

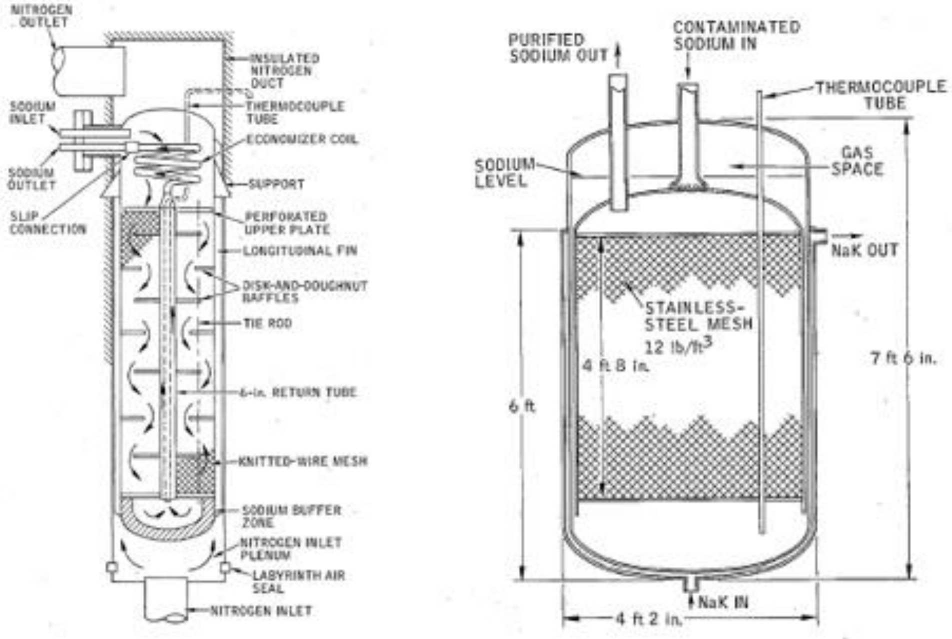
$$t_{res} = \frac{V_{loop}}{\dot{V}_{CT}} \tag{2}$$

where V_{loop} is the total volume of sodium in the facility, and $\dot{V}_{CT}$ is the volumetric flow rate of sodium through the cold trap. The quantity $\dot{V}_{CT}$ is typically orders of magnitude below the bulk flow rate in an SFR.



FFTF Primary Cold Trap

SRE Cold Trap



HNPF Cold Trap

EFAPP Primary Cold Trap

Figure 5: Selected schematics of US cold trap designs, reproduced from [6] *and* [9]

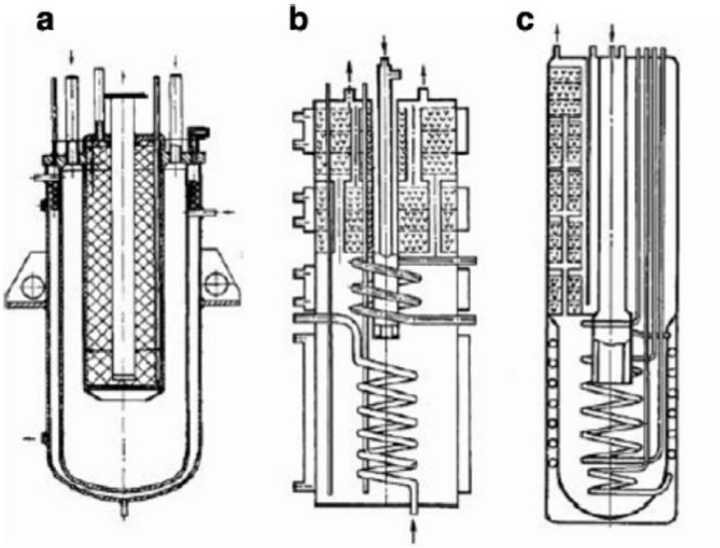


Figure 6: Cold traps of a.) BR-5 reactor b.) BN-350 reactor c.) BN-600 reactor

For an ideal cold trap with 100% trapping efficiency, Equation 1 accurately describes the oxygen concentration in sodium exiting the device. While residence times of 15 minutes will bring this impurity trapping efficiency near unity [10], in practice efficiency has been shown to reach a point of diminishing returns at around 5 minutes of cold trap residence time [6]. In the case of a major impurity addition such as a maintenance event, continual operation of the cold trap at 5 minutes of residence time brings the bulk oxygen concentration to normal conditions within about 6-7 turnovers of system volume [11]. In this way, given a long enough time, the temperature trace of a cold trap provides a good estimate of loop oxygen concentration.

Plugging Temperature Indicator

While an estimate of loop oxygen from cold trap temperature traces is generally acceptable for most operations, there are situations where a positive measurement of loop oxygen is desirable. During expected transients, such as loop startup following a contaminating repair operation, the cold trap is not operating at steady-state conditions and loop oxygen cannot be estimated from the cold trap temperature. The estimation of oxygen from cold trap temperature is not sensitive to the ingress of oxygen due to a leak (such as water from a power generation cycle). In reactor settings, it may be necessary to perform occasional measurements to satisfy the requirements of a reactor health and safety program. Finally, in research situations where the oxygen concentration is a critical parameter (such as in materials testing for fuel cladding/structural alloys) the cold trap temperature cannot be treated as a measurement.

In the U.S. (as well as France, India, Russia, and Japan), one of the traditional methods of measuring oxygen concentration is the plugging temperature indicator (PTI), or “plugging meter” [12], [13], [14], [15]. Generally speaking, the PTI is an instrument that cools sodium flow as it passes through an orifice plate, precipitating out super-saturated oxygen on the inside diameter of the orifices, reducing their cross-sectional area. This reduction in area is measured by a flow meter as a reduction in flow rate across the instrument. The sodium passing over the orifice plate is then heated up, eventually dissolving the precipitated oxides back into the flow and causing the flow rate to recover. Repeated oscillations between these plugging and unplugging regimes allow the calculation of a plugging temperature. This plugging temperature is then translated to a sodium oxygen concentration by Eqn. 1. A typical plugging meter is shown schematically in Figure 7.

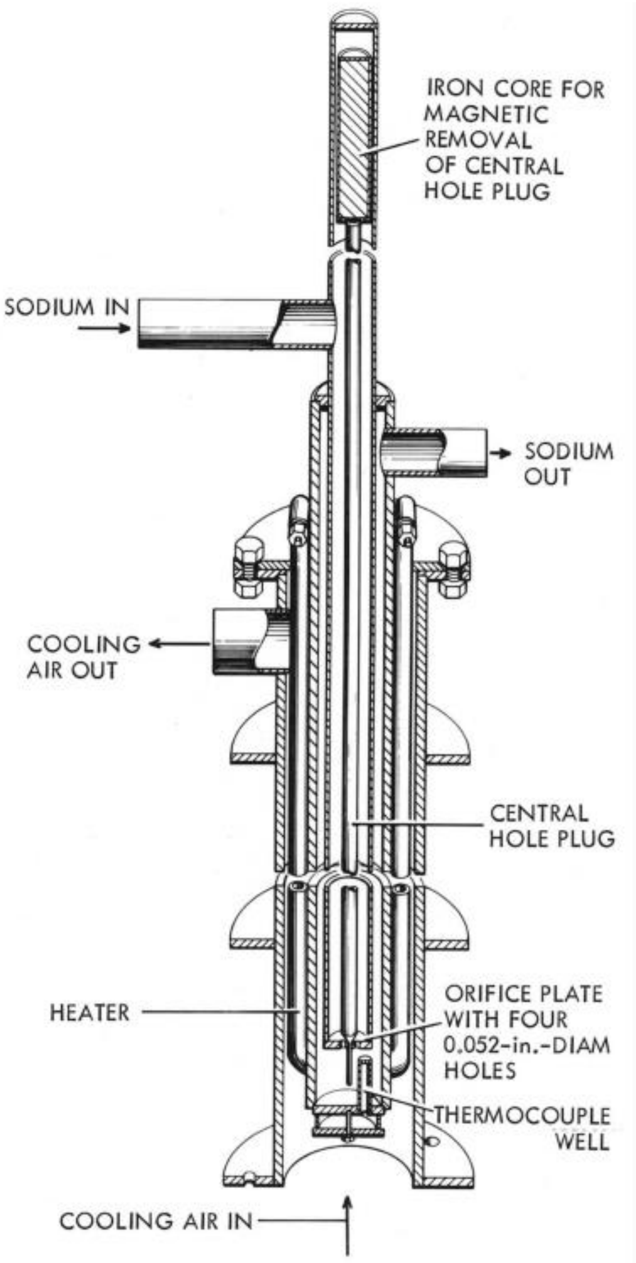


Figure 7: Cross-section view of a plugging indicator, reproduced from [14]

The plugging temperature measured by PTIs is sometimes informally referred to as a “saturation temperature” (implied: saturation temperature of oxygen in sodium). This is not entirely correct, as the PTI cannot differentiate between oxygen and any other temperature-dependent impurity. In sodium systems, these other impurities are most likely to be either hydrogen or carbon, whose solubilities in sodium are given by

$$log_{10}(S_H) = 6.211 - \frac{5021}{T_K} \tag{3}$$

$$log_{10}(S_C) = 6.067 - \frac{2880}{T_K} \tag{4}$$

Where S_H and S_C are the concentration of hydrogen in sodium and the concentration of carbon in sodium, both expressed in wppm [16], [17]. For typical reactor cold trap temperatures (<200^{o}C), carbon solubility has values in the sub-ppb range, and hydrogen solubility has values in the sub-ppm range. These solubilities are considered small enough to neglect their effect on PTI measurements. Therefore, **for sodium systems subject to continuous cold trapping**, the contributions of hydrogen and carbon to plugging behavior are neglected and the plugging temperature is treated as a saturation temperature for oxygen in sodium.

The procedure for PTI operation and actual determination of the plugging temperature varies widely across the literature, though a best practice method was codified in the RDT Standard F 3-40T: Methods for the Analysis of Sodium and Cover Gas [3]. This procedure will be referred to as the RDT PTI method moving forward.

The RDT PTI procedure requires that measurements be made with an instrument conforming to RDT standard E 4-19T: Plugging Temperature Indicator Assembly for Sodium Service. The primary characteristic of this PTI is the size and orientation of holes in the orifice disk, which are shown in Figure 8:

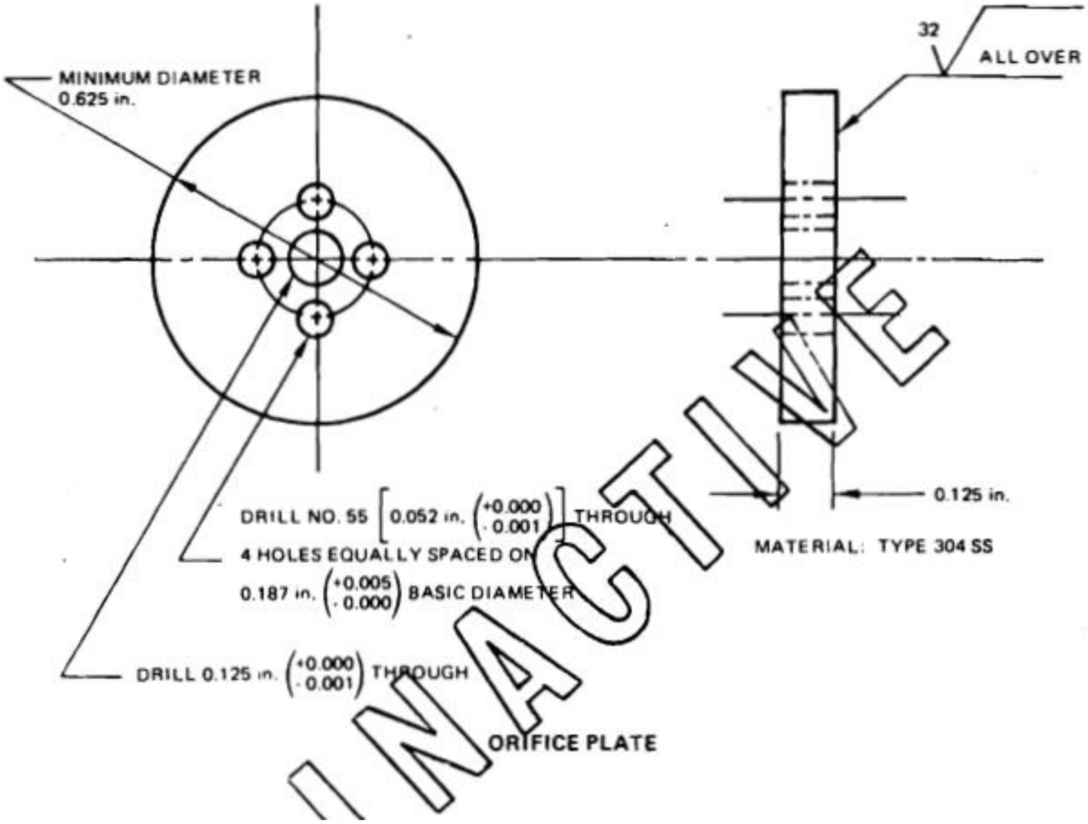


Figure 8: Orifice Plate Detail, reproduced from [18]

The RDT PTI method prescribes cooling rates not to be exceeded in specific temperature ranges- these values are tabulated below, along with a Quick Cooldown temperature above which any cooling rate may be chosen, and a constant heating rate for “unplugging” cycles.

Table 1: RDT PTI cooling parameters

Quick Cooldown [^{o}C]	204.4
Cooling rate above 163 ^{o}C [^{o}C/s]	0.1852
Cooling rate above 149 ^{o}C [^{o}C/s]	0.0926
Cooling rate below 149 ^{o}C [^{o}C/s]	0.0463
Heat Rate [^{o}C/s]	0.0278

The RDT PTI procedure requires that sodium be cooled until plugging is sufficient to reduce the flow rate by 50%, at which point the sodium is heated. The orifice temperature at the points in time when the flow sharply decreases and sharply increases are termed the “plugging” and “unplugging” temperatures, respectively. These points are determined visually by the operator for at least 5 flow oscillations. A typical temperature/flow trace annotated according to the RDT procedure is shown in Figure 9. The saturation temperature associated with these cycles is given by Eqn. 5.

$$Saturation\ temperature = \frac{\bar{P} + \bar{U}}{2} \tag{5}$$

where $\bar{P}$ is the average plugging temperature, and $\bar{U}$ is the average unplugging temperature. This procedure has produced satisfactory measurements of sodium oxygen concentration in the range >5wppm, though the method encounters operational difficulties at lower concentrations [14], [19]. The RDT PTI procedure can be found in full in Appendix A and a flowchart detailing the procedure’s steps is shown in Figure 10.

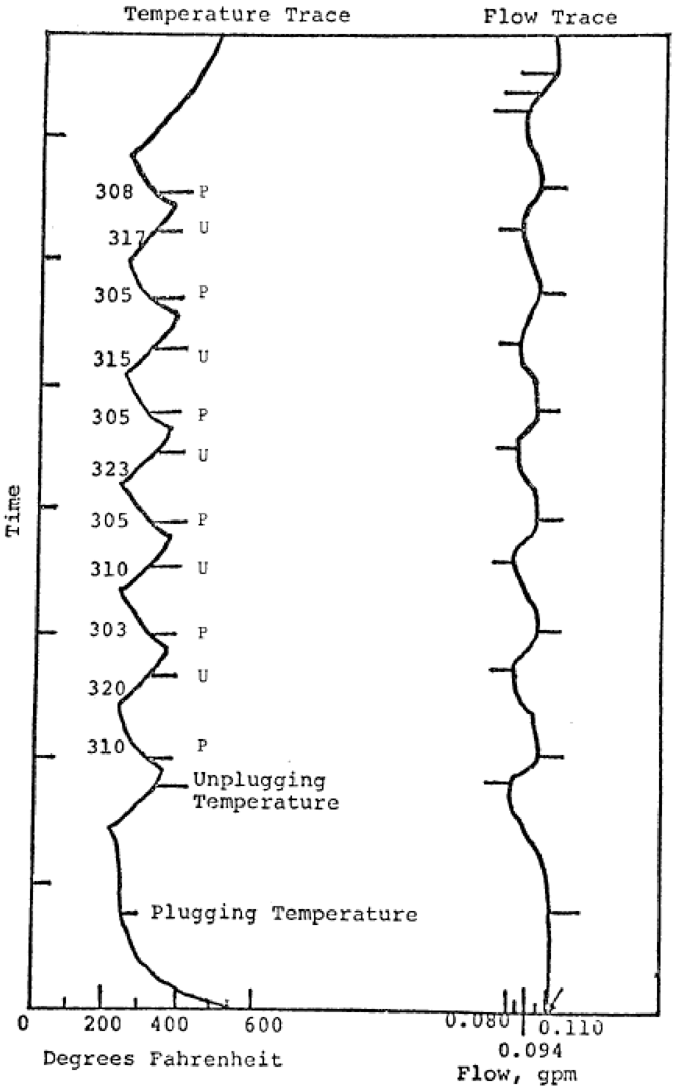


Figure 9: Example of plugging run, reproduced from [3]

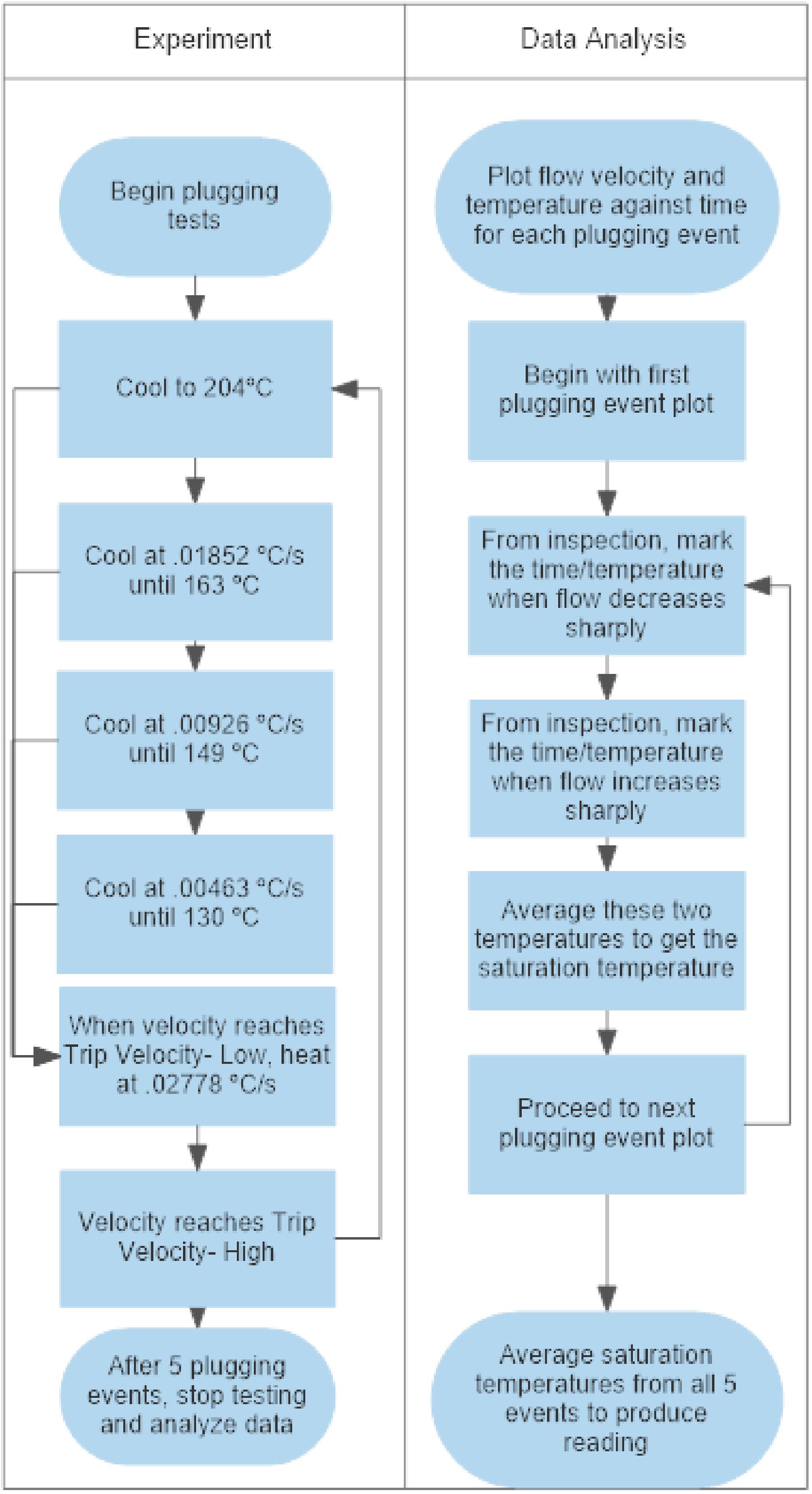


Figure 10: Flowchart showing the experimental procedure and data analysis for the RDT PTI method.

Vanadium Wire Equilibration

Given that a PTI measurement cannot differentiate between impurities, a measurement method that selects for oxygen is desirable as additional verification. . In the U.S. this was generally accomplished via vacuum distillation [20] until the relatively simple and cheap method of vanadium-wire equilibration (VWE) was developed by Dale Smith at Argonne National Laboratory [21].

VWE involves the exposure of a vanadium wire to liquid sodium until the free oxygen in the sodium is in equilibrium with the oxygen in solid solution in vanadium. The exposed wires are removed from the sodium flow, cleaned, polished, and then analyzed via an inert-gas fusion technique to produce a weight percentage oxygen measurement. Smith formulated the following modified Nernst equation to relate the mole fractions of oxygen in sodium and vanadium at equilibrium to the energy of formation for the respective oxides [22].

$$K_A = \frac{N_{O_V}}{N_{O_{Na}}} = \frac{N_{O_V}^{o}}{N_{O_{Na}}^{o}} exp\left[\frac{\Delta F_{Na_2O}^{o} - \Delta F_{V_5O}^{o}}{RT}\right] \tag{6}$$

where K_A is the calculated distribution coefficient, $N_{OV,}$ and N_{Ona} denote the mole fraction of oxygen in solution in vanadium and sodium, $\Delta F_{Na_2O}^{o} - \Delta F_{V_5O}^{o}$ is the free-energy change for the transfer of oxygen from sodium to vanadium, and the superscript ^{o} denotes the quantity at saturation of oxygen in sodium and vanadium.

In the absence of information on the free energy of formation of the vanadium oxide in question (reported to be V_5O by x-ray analysis), Smith evaluated the exponential term by experimentally determining the saturation limit of oxygen in alpha-vanadium at three sodium temperatures (selected results shown in Figure 11), identifying the limit as the “plateau” observed past a certain sodium oxygen level. The results of these experiments were used to produce an expression for the saturation limit of oxygen in vanadium (Eqn. 7 [22], [23]). From this, they formulated a final expression relating the number fractions of oxygen in vanadium and oxygen in sodium at equilibrium conditions (Eqn. 8, also expressed as Eqn. 9 in a later study). This analysis assumes that no vanadium-oxygen phase other than the bcc α is formed until the α-phase bulk is saturated with oxygen.

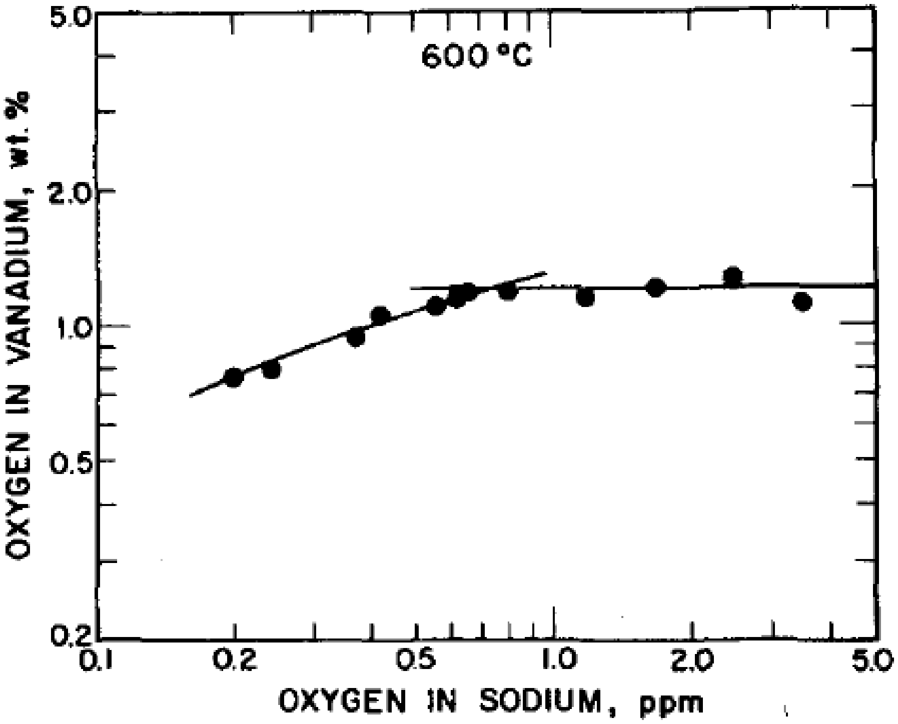


Figure 11: Measured oxygen concentration in vanadium after exposure to sodium with various oxygen concentrations, reproduced from [24]

$$N_{O_V}^{o} = exp\left[-1.89 - \frac{1210}{T_K}\right] \tag{7}$$

$$\ln(K_A) = \ln\left(\frac{N_{O_V}}{N_{O_{Na}}}\right) = \left\{17{,}560 + 30{,}070\left[\left(1 - N_{O_V}\right)^2 - \left(1 - N_{O_V}^{o}\right)^2\right]\right\}\frac{1}{T_K} - 9.567 \tag{8}$$

$$\ln(K_A) = ln\left(\frac{N_{O_V}}{N_{O_{Na}}}\right) = -28.22 + 39.42\left[1 - N_{O_V}\right]^2 \tag{9}$$

The VWE method was accepted and widely used in the U.S. following its inclusion in RDT standard F 3-40T [25].

The RDT standard VWE procedure requires that a 0.25-mm diameter vanadium wire be equilibrated in sodium at 750 ± 5 °C for a period of 4 to 30 hours [3]. The wires must be exposed to a sodium flowrate given by Table 2.

Table 2: Flow-Rate Parameter for Vanadium Wire Equilibration, reproduced from [3]

	Equilibration time for 0.25-mm Wire, hr				
Sodium oxygen, wppm	4	5	10	20	30
	Min Flow Rate Parameter, gal/min per cm of wire				
10	1.5 X 10-4	1.2 x 10-4	6.0 x 10-5	3.0 x 10-5	2.0 x 10-5
1	7.4 x 10-4	5.9 x 10-4	3.0 x 10-4	1.5 x 10-4	1.0 x 10-4
0.1	2.2 x 10-3	1.8 x 10-3	9.2 x 10-4	4.4 x 10-4	2.9 x 10-4
0.01	3.3 X. 10-3	2.6 x 10-3	1.3 x 10-3	6.6 x 10-4	4.4 x 10-4

Following equilibration, the wires must be removed from sodium and cooled to ambient temperature before being cleaned in a volume of ethanol. The wires must be electropolished with a current between 0.2-0.5 Amp for ~15 seconds per side, in a solution of 80% methanol-20% sulfuric acid using a tantalum cathode. The oxygen content in the wire is then determined by an inert-gas fusion method (LECO analysis). Eqn. 9 is then used to determine the oxygen concentration in the sodium at the time of equilibration. The RDT standard VWE procedure may be found in full in Appendix A.

ADDITIONAL BACKGROUND

Cold Trap

The trapping efficiency, previously described as it relates to residence time, is formally defined as

$$\eta = \frac{C_{in} - C_{out}}{C_{in} - C_{sat}} \tag{10}$$

where C_{in} is the inlet oxygen concentration, C_{out} is the outlet oxygen concentration, and C_{sat} is the concentration at the cold trap set temperature [26]. Free oxygen in sodium precipitates out to form Na_2O, which crystallizes on the wire mesh packing inside the cold trap[27].

The total volume of sodium oxide retained by the cold trap during operation is then

$$V_{Na_2O} = \int_0^t (C_{in} - C_{sat}) Q\eta \, dt \tag{11}$$

where Q is the volumetric flow rate across the cold trap [28]. This can also be expressed as an instantaneous purification rate *r* [29]:

$$r = \eta \dot{m}_{Na} (C_{in} - C_{sat}) \tag{12}$$

In the current work at UW Madison, the operation of the cold trap ensures a constant oxygen concentration, enabling comparison of PTI and VWE measurements against a known quantity. Given that it accomplishes this the performance of the cold trap is not closely scrutinized. In particular, we give little consideration to the cold trap's ultimate capacity and the distribution of impurities in the wire mesh. These can lead to a failure mode in an actual reactor where the pressure drop across the cold trap becomes too high and the component requires replacement. When this is encountered in a research facility, however, the operator can "regenerate" the cold trap by flowing hot sodium through the instrument, dissolving trapped oxide, and circulating it around the loop. The hot and impure sodium is then emptied into a dump tank, where supersaturated oxygen crystallizes on stainless-steel walls as the sodium cools. When the loop is filled again, as long as the oxide removed in the previous process is not dissolved into the fill (i.e., the fill temperature is low enough), the dumped oxygen will remain in the dump tank, and the cold trap returns to normal operation. This has proven to be an effective method of circumventing this "failure mode" in a research facility. For this reason, we largely ignore considerations of ultimate capacity when designing cold traps.

If maximal trapping capacity is desired, the flow path should change from straight-through operation to a radial mode (Figure 12). This provides a much greater cross-sectional area for trapping, reducing the possibility that oxide will crystallize disproportionately in one spot and constrict the flow. There is indeed evidence to suggest that during normal cold trap operation, the oxide is trapped primarily in the first 50-80 mm of the wire mesh [30]. For this reason, a two-tiered mesh is suggested, using mesh with a larger pore size in the outer radius of the wrap, and a smaller pore size in the inner radius [26].

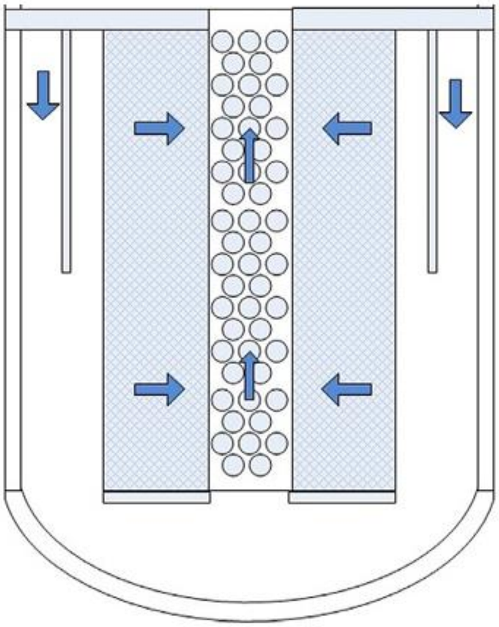


Figure 12: Radial-flow cold trap geometry, reproduced from [26]

Plugging Temperature Indicator

The rate at which sodium oxide is deposited on the orifices of the PTI is given by

$$\frac{dm}{dt} = kS(C_{in} - C_{sat}) \tag{13}$$

where m is the mass deposited, t is the time in hours, S is the orifice surface area, and k is a mass transfer coefficient that varies with flowrate [31]. We can then define a plugging fraction P_F which describes the fraction of the orifice being plugged:

$$P_F = \frac{m}{A_0 l \rho} \tag{14}$$

where A_0 is the cross-sectional area of the bare orifice, l is the orifice thickness, and ρ is the density of Na_2O. Differentiating Eqn. 14 and substituting into Eqn. 13 produces

$$\frac{dP_F}{dt} = \frac{2k}{r_0 \rho}\left(\frac{r}{r_0}\right)(C - C_{sat}) \tag{15}$$

Where r_0 is the bare-orifice radius, and r is the radius of the orifice open to flow (not occupied by oxide). McPheeters and Biery [31] were able to measure the mass transfer coefficient k as a function of the Reynolds number in the flow orifices, with results shown in Figure 13.

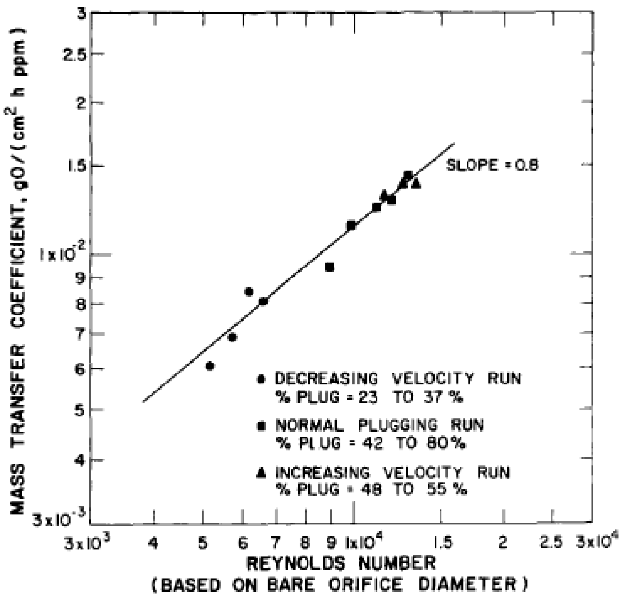


Figure 13: Effect of velocity on Na2O mass transfer coefficients as measured in a partially plugged orifice, reproduced from [31]

Together with an estimate of the required reduction in orifice area to measure a flow rate reduction, these results should allow for the calculation of an ideal rate of cooling in the PTI, or at least a degree of sub-cooling at which a flow rate change *should* be measured. These equations, then, can serve as a basis for the design of a PTI that does not conform to the RDT standard construction.

RDT method drawbacks and UW Minimum Method

The RDT method of data analysis relies on the operator to visually determine at which point the plugging and unplugging events occur, marked by a sudden sharp increase/decrease in sodium velocity. This leads to a certain amount of variability in the data collected and the determination of the temperature used to estimate the oxygen content, estimated in previous literature as greater than 3^{o}C [6].

Experiment duration is another operational drawback in making RDT PTI measurements. The procedure specifies that below 204^{o}C, cooling must occur very gradually. For oxygen measurements with a saturation temperature between 180-200^{o}C (i.e., oxygen concentration 6.9-11.7 wppm) this usually results in a runtime of 30-45 minutes for one plugging event and 2.5-4 hours for the full measurement. At oxygen concentrations with a saturation temperature below 160^{o}C (i.e., oxygen concentration < 3.9 ppm) this increases dramatically, and individual events at 140^{o}C (i.e., oxygen concentration= 2.1 wppm) can each take 2-3 hours to complete. Most of this excess runtime is attributed to gradual cooling below 204^{o}C yet below the expected oxygen concentration.

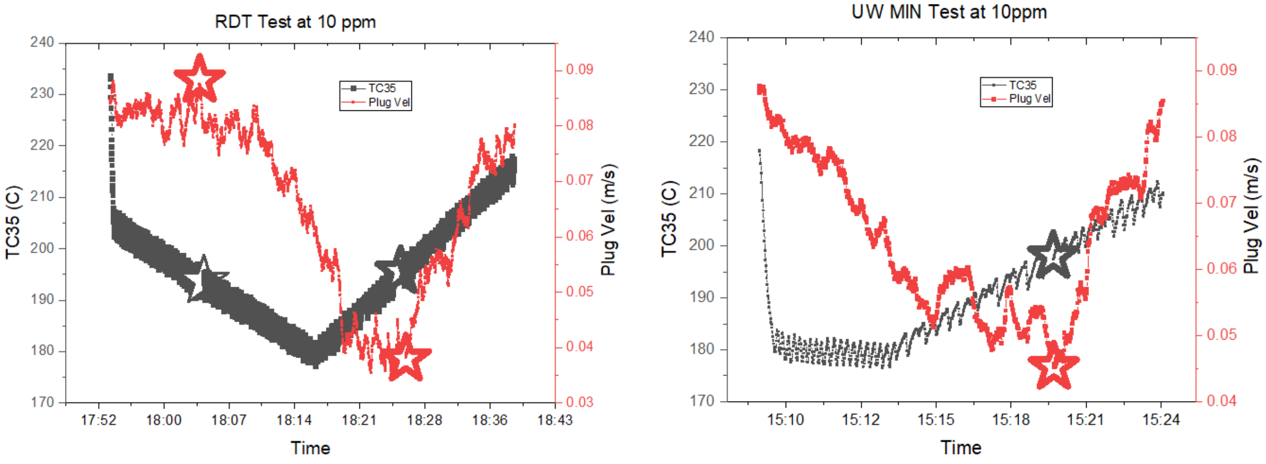
This timescale for oxygen measurement can be incompatible with concurrent experiments and may not adequately capture changing loop conditions.

The UW Madison Minimum (UW MIN) method was developed to address these issues and provide accurate, repeatable, and objective oxygen concentration measurements.

The primary novelty of the UW MIN method was the replacement of a gradual cooling period with quasi-instantaneous cooling to a chosen degree of sub-cool (usually 20^{o}C below expected saturation temperature). This degree of sub-cooling enabled the quicker formation of better quality (i.e., more noticeable in the flow rate) sodium oxide plugs. This also avoided the expected no-measurement cooling period encountered in low-temperature RDT experiments, with plugging observed near-immediately. Smaller sodium loops can often produce indeterminate measurements of "plugging" temperature due to the small amount of oxygen available in the system—loss of this information through rapid sub-cooling should have little effect on saturation temperature measurement.

In the UW MIN procedure, once this degree of sub-cooling is reached, the sodium flow across the orifice plate is held at this temperature until oxide plugs cause a velocity decrease of 50%. The sodium is then allowed to warm at a rate of 3^{o}C per minute until the flow reaches 80% of its bare-orifice value, when rapid cooling begins again. The minimum velocity across the PTI during the heating period is treated as the point where free oxygen in the sodium flow was in equilibrium with the oxide plugs [32]. The temperature at this point is the saturation temperature and averaging the results of 10 plugging events produced the final measurement. A comparison of data from PTI tests at 10 wppm using both methods is shown in Figure 14, a flowchart detailing the UW MIN procedure is shown in Figure 15, and the full UW MIN procedure can be found in Appendix A.

Contrasted with the RDT method's visual data analysis, the UW MIN method does not require operators to estimate a "sharp increase" or "sharp decrease" in flow rate. This avoids variability in data analysis between operators as a potential source of error. For this reason, the UW MIN method lends itself well to automation. Data can be filtered through a minimum function to find the exact time of minimum velocity and associated orifice temperature. Analyzing data in this way has the added benefit of returning the same measurements regardless of operator. Test times range from 20-30 minutes at higher oxygen concentrations to 45-60 minutes at 2 ppm (i.e., saturation temperature of 140^{o}C), allowing the instrument to respond to changes in loop condition more rapidly than for the RDT method.



RDT Test at 10 ppm

UW MIN Test at 10ppm

Figure 14: Data from UW MIN and RDT PTI tests at 10 ppm are shown. In the RDT case, stars denote plugging/unplugging points and their associated temperatures; in the UW MIN case, stars denote the local minimum velocity and its associated temperature

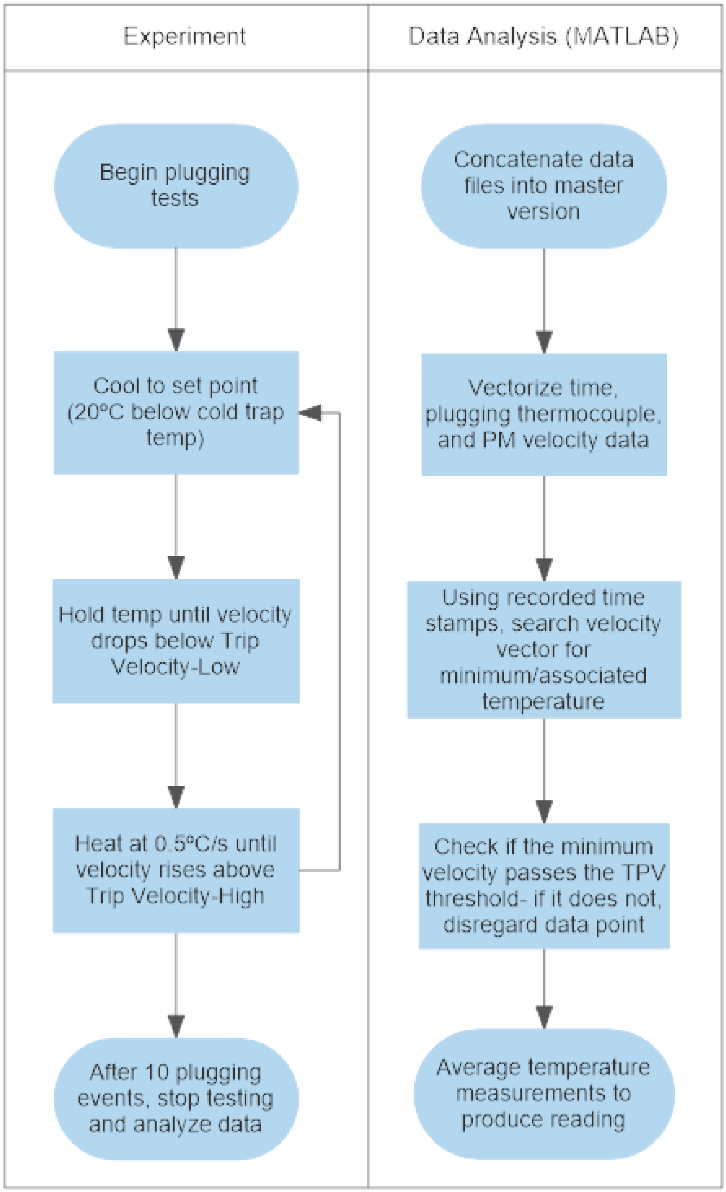


Figure 15: Flowchart showing experimental procedure and data analysis for the UW Minimum Method

Vadadium Wire Equilibration

Another research group at Berkeley Laboratory (UK) published papers and comments from 1973-1977 discussing the correctness and utility of the VWE method. Their initial critique highlighted the disagreement between Smith's measured solubility values and contemporary measurements of the same quantity (results shown in Table 3).

Table 3: The solubility of oxygen in α-vanadium (wt.%), reproduced from [33]

T (ºC)	T(K)	Henry et al. [13]	Alexander and Carlson [14]	Fromm and Kircheim [6]	Smith [10]
600	873.2	2.27	2.15		1.21
650	923.2	2.3	2.18	2.09	1.31
700	973.2	2.32	2.25	2.15	1.4
750	1023	2.42	2.31	2.18	1.48

The Berkeley group performed a separate thermodynamic analysis relating the partial pressure of oxygen above solutions of oxygen in α-vanadium to that above solutions of oxygen in sodium. Their calculated distribution coefficient at equilibrium (K_A) led to the conclusion that the maximum concentration of oxygen in sodium measurable by VWE was 1.905 wppm [33], far lower than the 15.502 wppm of Smith's analysis [34].

By performing x-ray crystallography measurements on exposed wires, the Berkeley group was able to confirm the presence of beta, gamma, and delta vanadium-oxygen phases [35] (Figure 16 shows a vanadium-oxygen binary phase diagram). This proved that for the sodium oxygen concentrations investigated (2-23 wppm), the activity of oxygen in sodium was sufficiently high to transform alpha-phase vanadium oxide into higher-wt.% phases *before* the bulk of the wire reached saturation. They concluded that alpha-vanadium is not an equilibrium phase for the range of sodium oxygen concentrations investigated, and that the "vanadium wire equilibration" method may only be applicable as an empirical technique [36].

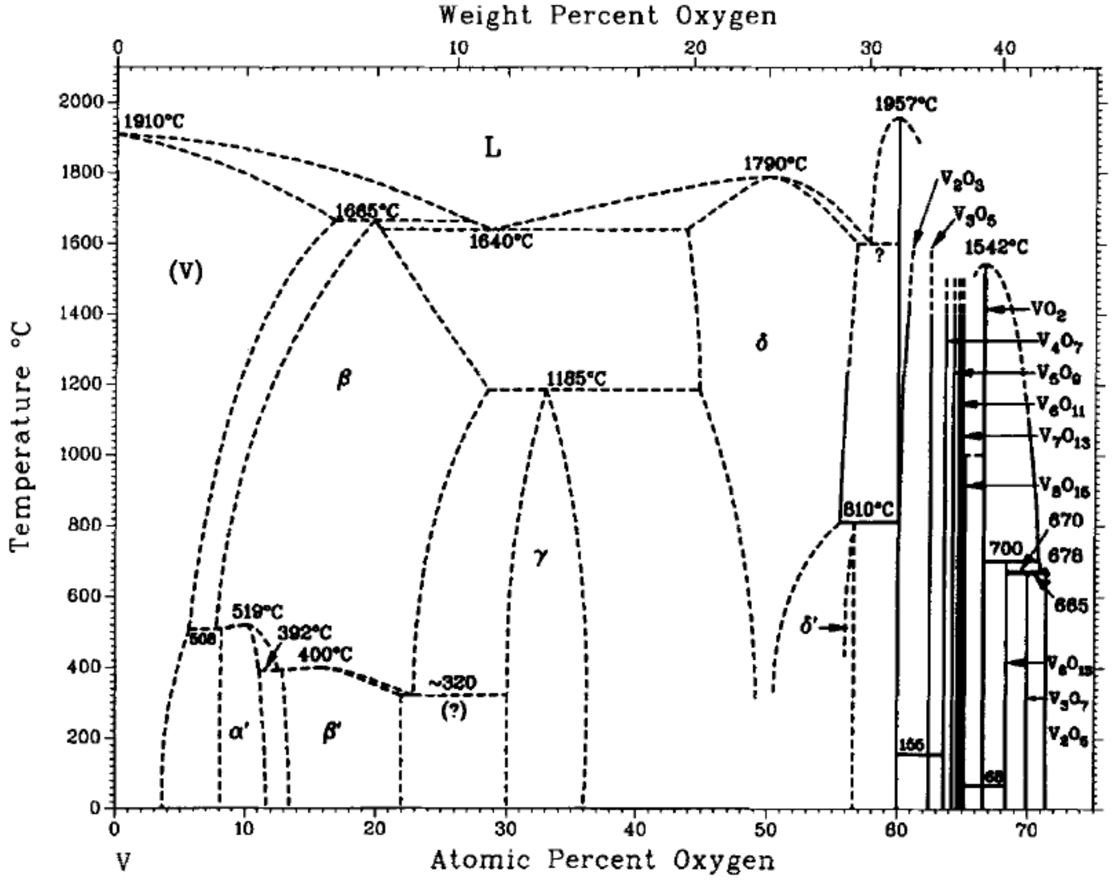


Figure 16: Assessed V-O Phase Diagram (Condensed System, 0.1 MPa), reproduced from [37]

They outline two primary hurdles in repeating this type of measurement: first, that one of the observed phases (δ-phase) was prone to spalling from the wire's surface in the presence of turbulence, and that the repeated flaking off and formation of this δ layer may hurt reproducibility; and second, as VWE is not a true equilibrium process, that an oxygen concentration gradient must exist within the bulk wire. Thus, they conclude that repeatable measurements might only come from precisely controlling both exposure time and the amount of post-exposure surface material electropolished off during the standard procedure.

Smith claimed that the presence of a surface oxide indicated that the bulk of the wire had been saturated with oxygen. This approach assumed that the phase identified as V_5O was not formed until the terminal solubility of oxygen in α-vanadium was reached. If other phases of vanadium-oxygen were formed before this solubility limit was reached, the presence of these phases may have limited the diffusion of oxygen dissolved in sodium into the bulk of the wire. The discrepancy between the saturation values of oxygen in α-vanadium measured by Smith and those measured by others supports this idea. The observed “plateau” in Smith’s measurements of vanadium oxygen concentration with increasing sodium oxygen concentration could be explained by the growth of a surface oxide placing an ultimate limit on oxygen uptake in the α-vanadium core of the wire [38]. Though the presence of a second surface phase indicates that this is not a true equilibration, if the conditions driving the formation and retention of this surface oxide can be controlled precisely, the technique may still be capable of producing repeatable data.

CONCLUSIONS OF LITERATURE REVIEW

- Cold trapping is well understood as a method of oxygen control. We can use this technique to set test conditions, but the temperature trace does not function as an actual measurement of oxygen concentration.

- The Plugging Temperature Indicator technique is a standardized method of oxygen measurement, but the standard as written allows for error in operator interpretation. There is a need for modification of the standard to increase the objectivity of measurements and allow for fully automated operation.

- The Vanadium Wire Equilibration technique is also standardized, but there is a significant amount of discussion in the literature questioning the validity and repeatability of the method. The concerns raised by Hooper and Trevillion should be investigated, and the standard procedure should be revised if necessary.

EXPERIMENTAL FACILITY

Overview

The experimental apparatus consisted of a closed loop, schematically shown in Figure 17 and depicted in Figure 18. All loop piping was composed of 316L stainless steel. The primary loop operated at a maximum temperature of 650^{o}C and a maximum gauge pressure of ~150 kPa. The sodium inventory of approximately 7 liters was driven through the loop by a Moving Magnet Pump (MMP) [39], whose speed was controlled by a variable frequency drive (VFD) (Hitachi WJ200, 5.5 kW). Downstream of the pump, the sodium was divided into two streams: one supplying the oxygen concentration control and measurement (OCCM) lines, and a high liquid volume bypass simulating reactor flow. The OCCM consisted of three branches. The first led to the vanadium wire test section, returning to the main flow through the upper reservoir connected to the bypass line. The second and third branches fed into the cold trap and plugging meter before meeting downstream valve V-6 and merging with the bypass. Sodium then flowed through the main heater (Chromalox 4kW) and returned to the pump. Electromagnetic flow meters (FM) were positioned in each branch after the pump (bypass, cold trap, plugging meter, and vanadium wire) as shown in Figure 17: Schematic of a.) the experimental apparatus and b.) the gas panel.. Details about the standard design, operation, and calibration of electromagnetic FMs for use in liquid sodium are found in [6].

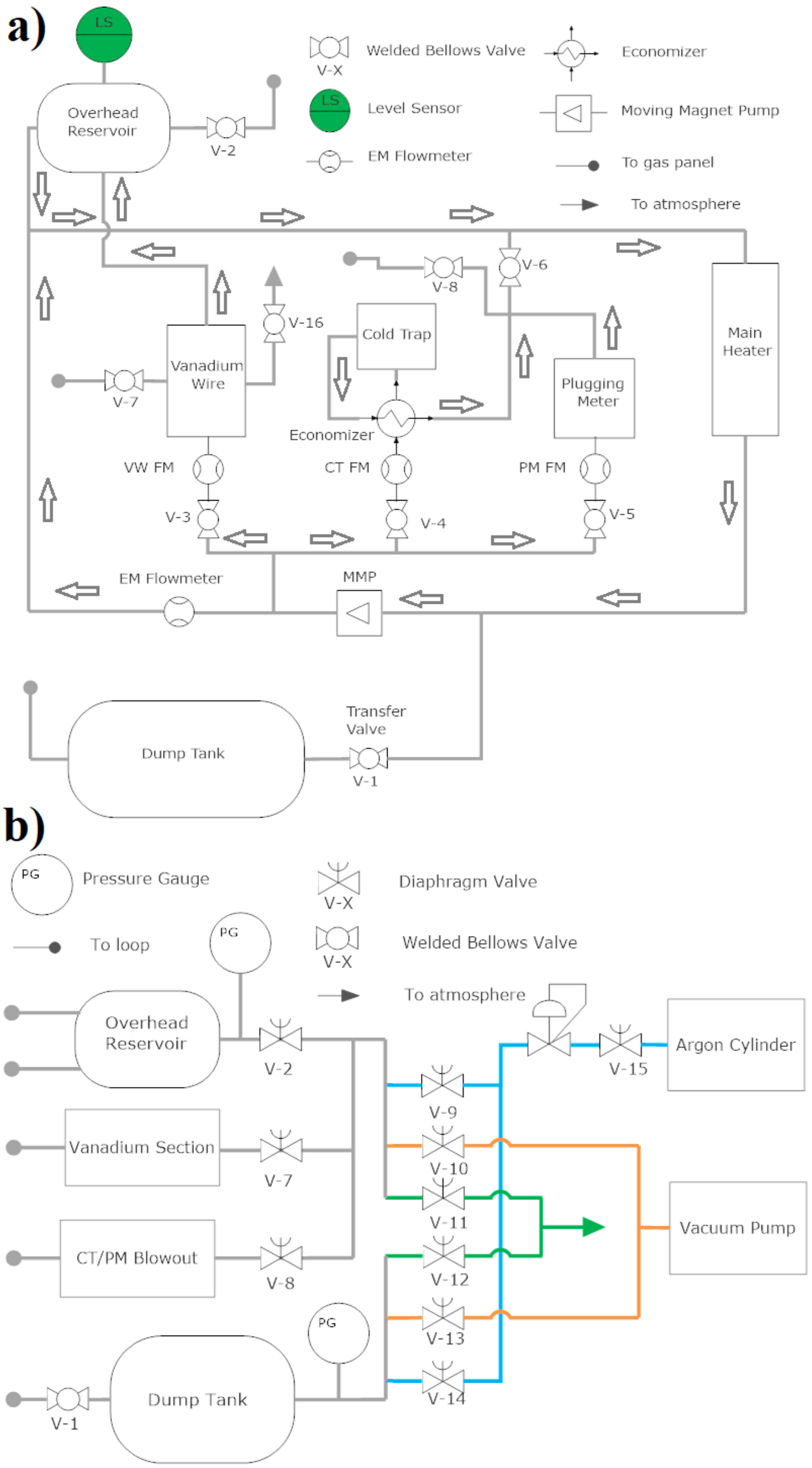


Figure 17: Schematic of a.) the experimental apparatus and b.) the gas panel.

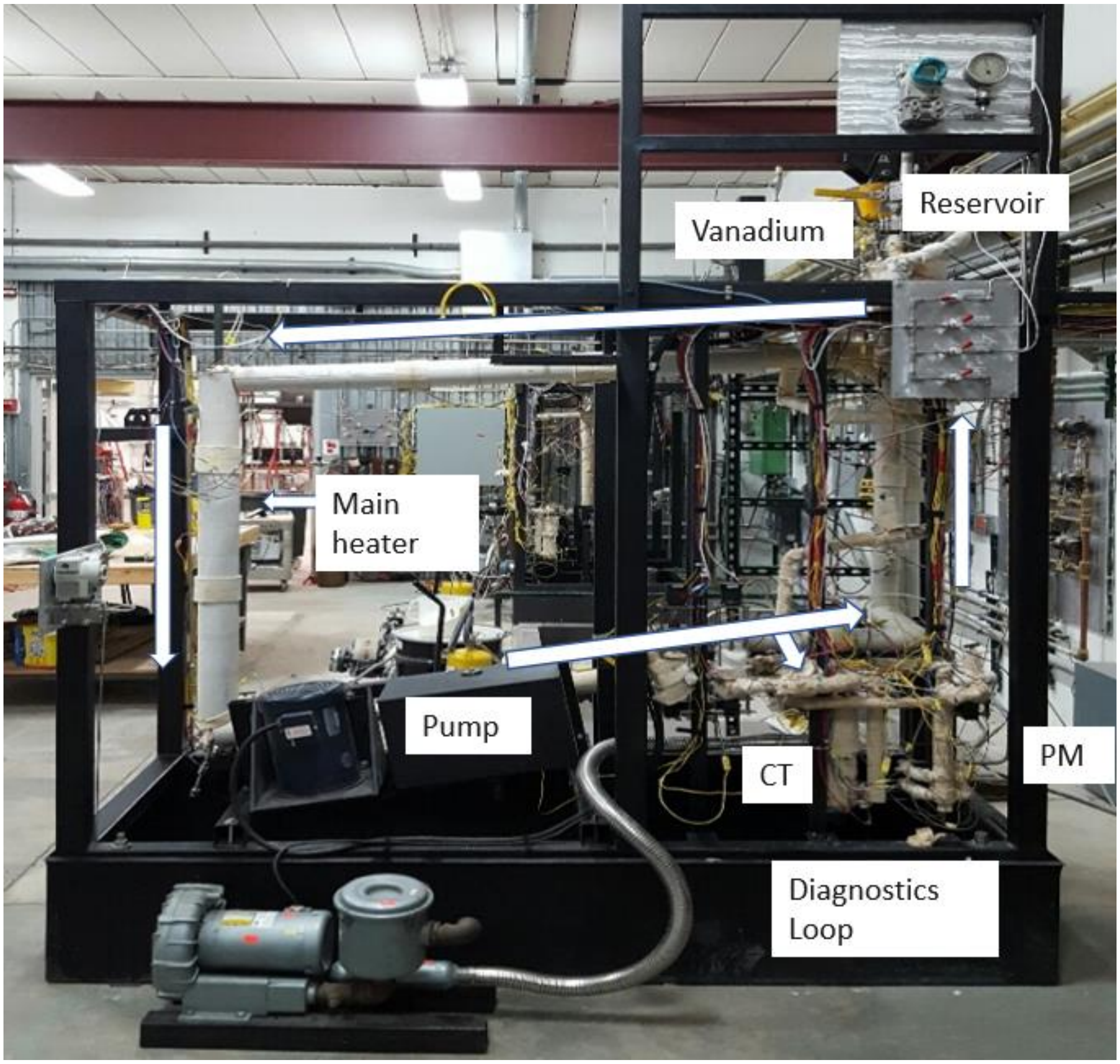


Figure 18: Annotated picture of the sodium facility, with arrows denoting flow path around the primary ducting.

The sodium temperature was controlled along the loop through local AC and DC trace heat wrapped along the entire loop tubing, as well as the previously mentioned main heater. The power delivered to those heaters was controlled through solid-state relays, in turn, controlled by a LabVIEW PID routine [40] using outer wall and local fluid temperature measurements as input. The facility contained both an upper and lower reservoir. The lower reservoir was a 316L stainless steel tank, labeled “Dump tank” in Figure 1, connected to the loop at its lowest point. The upper reservoir was located at the highest location of the loop, acting as an expansion tank. As shown in Figure 1, the incline in the main loop ducts helped to completely drain sodium to the dump tank following experiments. An electric level sensor in the upper reservoir ensured proper sodium volume in the loop during the experiments. The level sensor was of the point-contact type, consisting of a stainless-steel rod held at +5V via connection with a DC power supply.

Except for the inlet and outlet of the vanadium wire section whose thermocouples were obtained from Temprel Inc., all temperature measurements throughout the loop were performed by K-type thermocouples from Omega Inc. Welded bellows valves from Swagelok Co. (Swagelok, SS-8UW) were used where sodium control and sealing were required. Diaphragm valves were used in the gas panel (see Figure 1-b) as this part of the system was not sodium wetted. The positive side of two differential pressure transducers (Siemens 7MF4432, ±160 kPa range, error <0.1% of range), see Figure 1-b, were connected to the upper reservoir and dump tank with their negative side open to the atmosphere. Measurements from these transducers were used to monitor manometric pressure within the system.

Except for the MMP, the loop piping and components were insulated first with a layer of mineral wool (6.35 mm), then covered with two layers of Pyrogel^{TM} (5 mm each) to reduce heat losses along the circuit. The line connecting the OCCM to the gas panel was not insulated. This allowed for the formation of a freeze plug to form in it during loop operation, which kept any sodium vapor from reaching the gas panel valves during loop operation.

Operation/Components

Experimental Procedure

For each set of experiments, liquid sodium was loaded into the loop from the lower reservoir and drained after the end of the daily experimental campaign. Sodium was never left in the loop piping, which was filled with argon if experiments were not being performed. Below the filling and draining procedures are detailed:

Filling: The dump tank containing frozen sodium was heated up to 200^{o}C in advance of the experiment. A vacuum pump was used to evacuate gas simultaneously from the loop and lower reservoir to an absolute pressure of less than 33.33 Pa (250 mTorr) by manipulating the valves in the gas panel, see Figure 1-b). Absolute pressure was measured with a vacuum gauge (Kurt J. Lesker model KJL275800LL, ±10% in mTorr range) connected to the vacuum pump inlet. The evacuated loop was then brought to 200^{o}C in 50^{o}C increments, as measured by external tube wall thermocouples, by sending power to the main heater and DC/AC trace heating. The pump duct was brought to fill temperature, i.e., 200^{o}C, by dry running the magnet disks and heating the duct through induction. The pump power was then ramped to zero shortly before filling. With the main loop under vacuum conditions, the lower reservoir was pressurized with argon gas up to 20.7 kPa (manometric) by manipulating the valves in the gas panel. The transfer valve was then opened, allowing sodium to flow from the lower reservoir into the main loop. The transfer valve was closed once the sodium level reached the point-level sensor, and the upper reservoir was pressurized to 69 kPa (manometric). Once the filling process was finished, pump power was increased until a volumetric flow of 0.3155 l/s (5 gpm) was measured by the main loop FM.

Draining: For draining procedures, the loop temperature was cooled to 200^{o}C, the pump power MMP was decreased until zero flow was measured by the main loop FM, the lower reservoir was vented to atmospheric pressure, and the upper reservoir was pressurized up to 34.5 kPa (manometric). The transfer valve was then fully opened, and sodium was drained into the lower reservoir by gravity and pressure difference. The sodium freeze plug separating the argon line from the OCCM sections was heated, allowing the flow of pressurized argon into the OCCM section to remove the remaining sodium in the plugging meter and cold trap. Once the sodium in the loop was fully drained, the transfer valve was closed, the DC/AC heaters were turned off, and both the loop and dump tank were cooled by natural convection to room temperature.

The sodium oxygen concentration was controlled and/or measured through three different techniques/devices: (i) a cold trap, (ii) a plugging meter, and (iii) vanadium wire. Construction and operation details of each component are provided below:

Cold Trap

The cold trap, schematically shown in Figure 19, regulated the sodium oxygen concentration through the impurity's temperature-dependent solubility. The cold trap itself was composed mainly of two regions, a cooling zone, where the sodium was cooled to the desired oxygen solubility temperature, and an isothermal trapping zone, where the sodium was kept at this temperature to allow for supersaturated oxygen to precipitate and be retained by a stainless-steel wool packing. With enough time, the cold trap temperature dictated the oxygen concentration of the sodium flowing along the loop according to the relationship shown in Eq. 1.

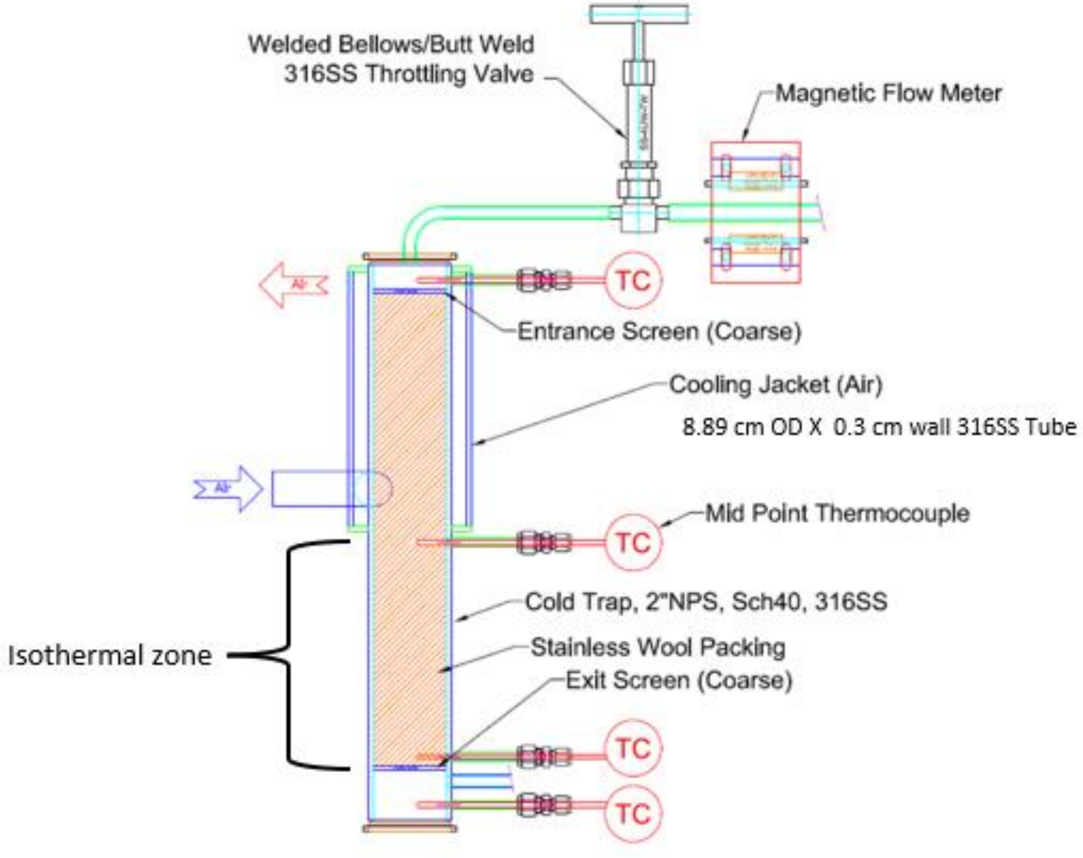


Figure 19: Cold trap schematic

The cold trap was fabricated from 50.8 mm (2”) Schedule 40, 316SS pipe and contained 316SS wool (0.12 mm fiber size, 172 g packed at a density of 144 kg/m^3) dispersed inside the pipe to increase surface area and promote entrapment of sodium oxide. In the cold trap, the sodium needed first to be cooled from the loop flow temperature to the desired oxygen concentration solubility, and then, later, brought back to the loop temperature before returning to the main flow path to avoid thermal striping in the piping junction. To reduce cooling and heating requirements a concentric tube economizer was placed upstream of the cold trap (Figure 1), where the cold sodium leaving the cold trap is heated while cooling the inlet sodium flow. Under typical operating conditions used in the present study, the residence time in the economizer was less than 4 seconds and within limits recommended by the RDT standard for cold traps [41].

Sodium entered the top part of the cold trap and flowed down vertically through the 50.8 mm (2”) pipe, exiting through the side wall about 25.4 mm (1”) from the bottom. Air at room temperature was flowed through a blower in a jacket around the cooling zone of the cold trap to control the sodium temperature. This jacket was composed of stainless steel and placed around the upper half of the cold trap (sodium entrance side) to form the annular path of a counter-current tube-in-tube heat exchanger. The airflow rate was controlled by a VFD (Hitachi WJ200, 3.7 kW) actuating the blower motor. The frequency output of the VFD (cooling air flow rate) was controlled by a PID within the LabVIEW program referencing the mid-point internal thermocouple in the cold trap.

A heater tape was placed on the lower half of the cold trap to minimize axial temperature gradients in the isothermal trapping zone. The power input to the heater tape was also controlled via a PID within the LabVIEW program referencing the internal thermocouple just above the cold trap exit line. This configuration allowed for reasonable control of the cold trap temperatures with a null temperature gradient from the mid to the bottom parts (outlet) of the cold trap. The cooling of the sodium inside the cold trap occurred only at the top region, i.e., the cooling zone. Through this procedure it was possible to guarantee that the oxygen concentration in the loop matched the one calculated from Eq. (1) based on the cold trap outlet and mid temperatures, see Figure 3.

To maintain the minimum sodium residence time of 5 minutes within the cold trap (specified by RDT Standard E 4-5T [41], the flow was set and controlled to be around 0.01 m^3/hr (0.04 gpm) by throttling a Swagelok SS-4UW (¼”) 316 stainless steel bellows valve. This valve was manually operated and only needed adjustment if the sodium pump speed was drastically changed. The robust nature of this setup was due to the variable cooling delivered by the regenerative air blower and the reduction in inlet sodium temperatures provided by the upstream economizer.

Before oxygen measurement experiments, sodium was circulated through the cold trap at a specified temperature for a minimum of 6 hours, and in general 18-24 hours. As normal operating conditions produce a system turnover time between 45 minutes and 1 hour, this period provided the required 6-7 turnovers of loop volume to reach the desired oxygen concentration.

Vanadium Wire Equilibration

VWE measurements were performed according to the RDT standard for wire preparation and equilibration [3]. The only difference was that the ISO:17025-accredited laboratory hired for sample analysis used a modern version of the LECO analyzer referenced in the standard. Further, the standard's guidance on electropolishing of the wires is vague: it specifies that "an electropolishing current, 0.2 to 0.5 amp, should flow for about 30 seconds total, 15 seconds for each end." All polishing for analysis in the present work was performed at 0.3 amps for the recommended time. Smith and Lee noted in the original works that this process was needed only to remove surface contaminants associated with the handling of the wire [42].

During a typical test, a 30-mg vanadium wire sample loaded into a holder (Figure 20) was inserted in the sodium flow path via a double ball-valve inert gas lock system once the cold trap operation established a constant oxygen concentration. Once inserted in the 3/8" (9.525 mm) 316 stainless steel equilibration section, the sample was allowed to equilibrate with loop sodium at 750°C. Equilibration temperature was measured at the inlet and outlet of the test section with sodium-wetted K-type sheathed thermocouples obtained from Temprel Inc. The cold trap was operated normally for the entire equilibration process.

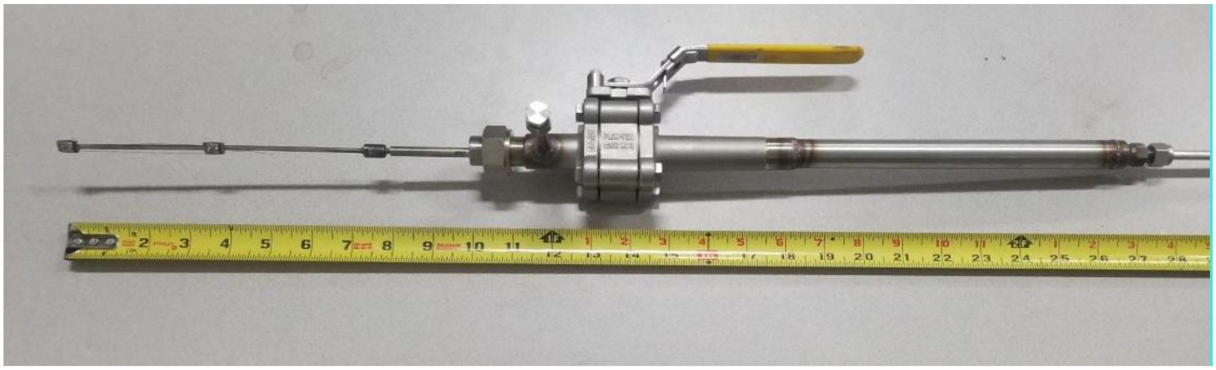


Figure 20: Vanadium wire sample holder attached to a rod for insertion/retrieval. One-half of the double ball-valve gas lock is shown.

Following exposure, the vanadium wire sample was removed and allowed to cool in the inert gas lock, then cleaned of residual sodium in 1 liter of ethanol to avoid excessive heating. Electropolishing was performed according to the parameters mentioned previously in a solution of methanol and sulfuric acid using a tantalum cathode. The wires were then rinsed with distilled water and stored in sample jars for analysis by an ISO:17025-accredited laboratory, which reacted the wires in a graphite crucible under inert gas using a LECO ONH836 analyzer. This inert-gas fusion process provided a weight percentage of oxygen in the exposed vanadium wires. These measurements were translated into a measurement of free oxygen in the sodium at the time of equilibration by Eqn. 7.

Plugging Temperature Indicator

The plugging meter, schematically illustrated in Figure 21, was designed and built to follow the RDT E 4-19T standard and specifications [18]. An economizer (formed by the central annulus and outer annulus) was incorporated into the plugging meter body (as specified by the RDT standard) to facilitate temperature changes and reduce the propensity for oxide particles to form prior to reaching the orifice plate. The plugging meter height was determined based on an ANSYS Fluent analysis to maximize economizer efficiency. Cooling jacket dimensions were also based on ANSYS Fluent calculations to maximize efficiency and provide the cooling necessary for low oxide concentration testing.

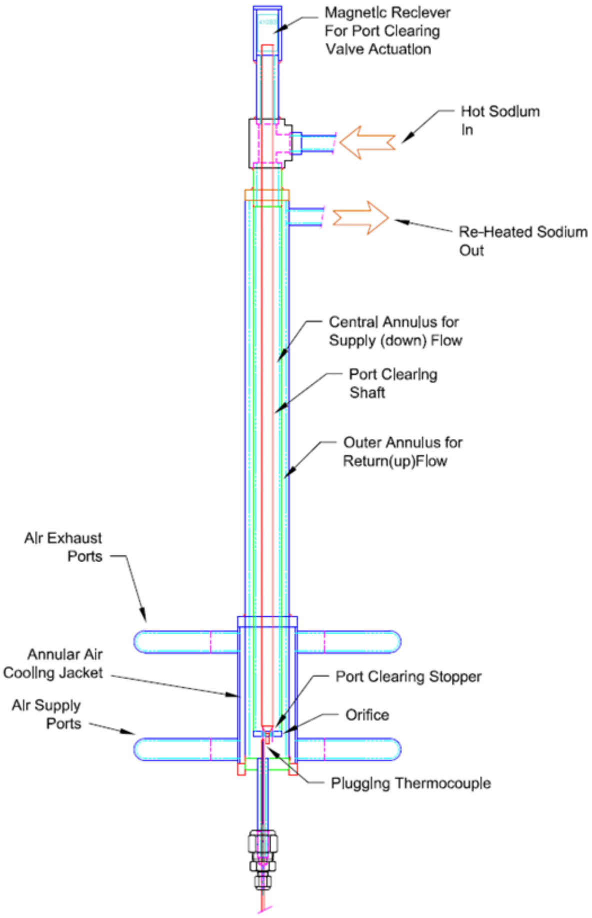


Figure 21: Plugging meter schematic

Sodium entered the plugging meter, running down the central annulus of the economizer towards the orifice plate. Once through the orifice plate the sodium turned 180° and flowed up the outer annulus of the economizer, cooling inlet sodium flow and exiting the plugging meter. A clearing pin located in the middle of the center tube was used to allow hot sodium to flow through the plugging meter in the event of an intractable plug. The orifice plate outer diameter and clearing pin dimensions were taken directly from the RDT standard on plugging temperature indicators. Compressed air was supplied to the air-cooling jacket and was used to cool the sodium passing through the orifice plate to below the oxide saturation temperature. This air supply was metered by a Jordan control valve (12.7

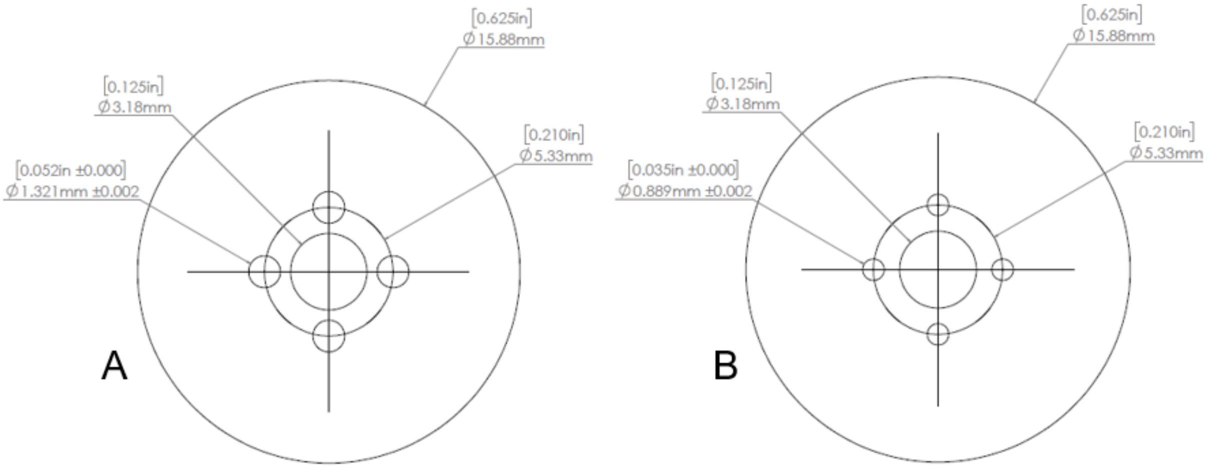


Figure 22: Schematic of the a.) RDT and b.) modified orifice plates

mm, 1/2”, pipe size, CV=0.5, air supply regulated to 551.581 kPa, 80 psi) to provide precise temperature control at the orifice plate, which was measured by a calibrated, sodium wetted 1.5875 mm diameter (1/16”) stainless steel sheathed K-type thermocouple.

The first study used two different plugging meters, with identical geometry and construction as shown and described above. The first was built according to the RDT standard with four 1.3208 mm (0.052”) holes, and the second one was identical save for the orifice diameter of the four holes of 0.889 mm (0.035”). These two orifice plates are shown in Figure 22. The as-built tolerances (± 2 µm) were obtained through a wire EDM process.

Throughout this paper, the first plugging meter is referred to as the 0.052” PTI and the second as the 0.035”. Smaller orifice sizes were hypothesized to increase the stability and speed of plug formation by requiring less oxide to perform a quality measurement. In theory, the smaller orifices should decrease measurement time and increase accuracy without operational drawbacks, regardless of loop size or oxygen inventory. However, the benefits of larger orifice sizes should be most significant in laboratory-scale systems. Further, in small loops such as the current facility, the oxide required to form a quality plug in larger orifices at low concentrations may represent an appreciable fraction of the loop's oxygen inventory. Smaller orifice sizes would decrease the amount of oxide needed to make a measurement, reducing the degree to which the bulk oxygen concentration changes throughout a measurement.

Typical measurement parameters for RDT PTI and UW MIN testing in this facility are located in Table 4 and Table 5.

Table 4: RDT PTI test parameters

Quick Cooldown [^{o}C]	204.4
Cooling rate above 163 ^{o}C [^{o}C/s] (^{o}F/min)	0.01852 (2.0)
Cooling rate above 149 ^{o}C [^{o}C/s] (^{o}F/min)	0.00926 (1.0)
Cooling rate below 149 ^{o}C [^{o}C/s] (^{o}F/min)	0.00463 (0.5)
Trip Velocity- Low [m/s]	0.06
Trip Velocity- High [m/s]	0.08
Heat Rate [^{o}C/s]	0.0278

Table 5: UW MIN test parameters

Quick Cool [^{o}C]	180.0
Trip Velocity- Low [m/s]	.05
Trip Velocity- High [m/s]	.08
Heat Rate [^{o}C/min] (^{o}C/s)	3.0 (0.05)

Data Acquisition/Quality Assurance

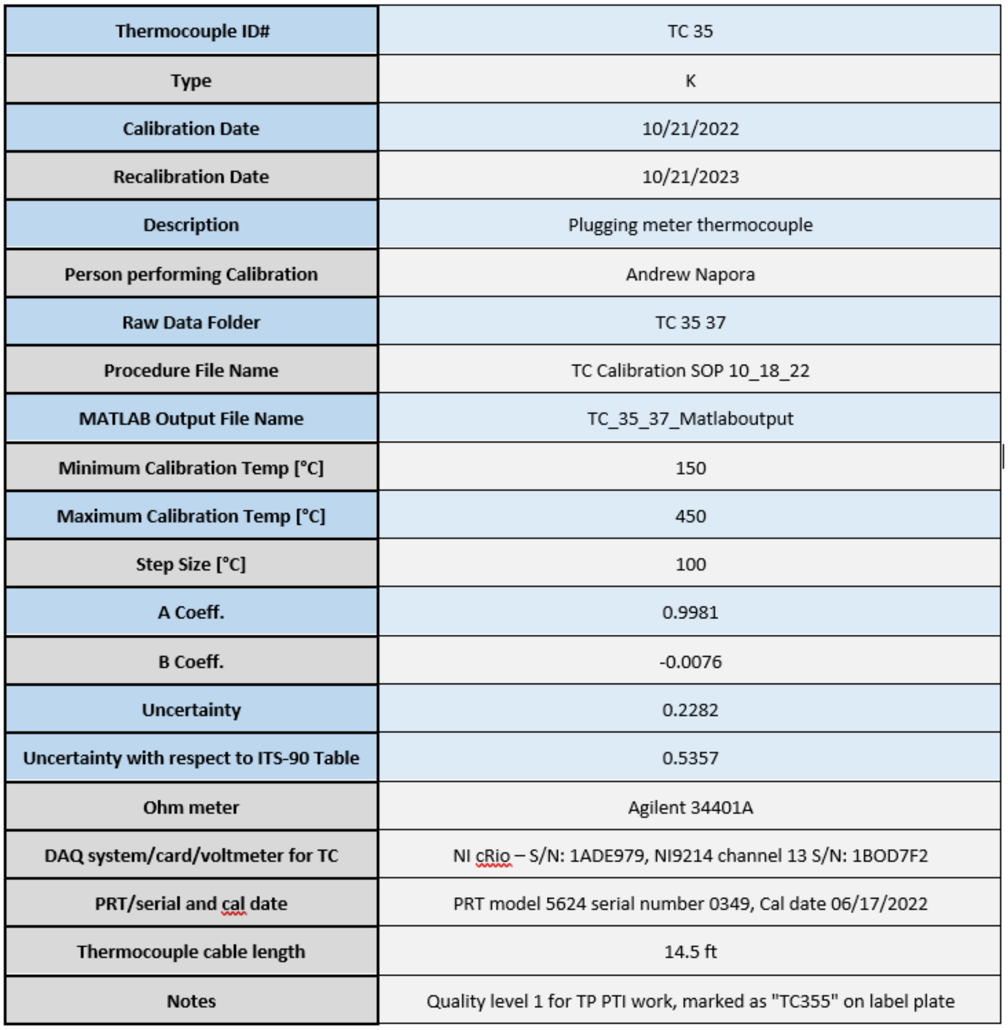
A LabVIEW [40] program, associated with a National Instruments data acquisition system (Rio-9000 series) was developed to monitor and control the experimental facility and record all data.

The experimental facility included several critical wetted K-type thermocouples designated Quality Level 1 (PTI orifice (1), cold trap (4), vanadium wire inlet/outlet (2)), and Quality Level 2 (electromagnetic flowmeters (3)). These instruments and their signal chains were calibrated against a NIST-traceable platinum resistance thermometer (PRT) (Hart 5624 SN:0349, 0.05 °C uncertainty verified by Fluke Corporation), which resistance was measured by a Digital Multimeter (HP 34401A). These calibrations took place in a custom-built furnace comprising a well-insulated silicon carbide block cast with thermowells (Figure 23).

Figure 23: Model and fabrication photos of the custom-built calibration furnace.

In the case of the vanadium wire thermocouples, measurements were scaled using this calibration to minimize error in the 700-800°C temperature range. This was performed in compliance with a quality control program developed jointly between the University of Wisconsin-Madison and TerraPower with the primary goal of commercially dedicating the experimental data for regulatory purposes [43]. A sample calibration sheet generated by this calibration process can be found below.

Table 6: Calibration sheet for Plugging Thermocouple, calibrated in SiC furnace



Thermocouple ID#	TC 35
Type	K
Calibration Date	10/21/2022
Recalibration Date	10/21/2023
Description	Plugging meter thermocouple
Person performing Calibration	Andrew Napora
Raw Data Folder	TC 35 37
Procedure File Name	TC Calibration SOP 10_18_22
MATLAB Output File Name	TC_35_37_Matlaboutput
Minimum Calibration Temp [°C]	150
Maximum Calibration Temp [°C]	450
Step Size [°C]	100
A Coeff.	0.9981
B Coeff.	-0.0076
Uncertainty	0.2282
Uncertainty with respect to ITS-90 Table	0.5357
Ohm meter	Agilent 34401A
DAQ system/card/voltmeter for TC	NI cRio – S/N: 1ADE979, NI9214 channel 13 S/N: 1BOD7F2
PRT/serial and cal date	PRT model 5624 serial number 0349, Cal date 06/17/2022
Thermocouple cable length	14.5 ft
Notes	Quality level 1 for TP PTI work, marked as "TC355" on label plate

PTI STUDY

Motivation

Obtaining an accurate value for oxygen concentration from RDT PTI measurements can take upwards of 12 hours at lower oxygen levels (2-4 wppm). As the oxygen concentration in cold-trapped laboratory scale loops can vary on a time scale of as little as 6 hours, a quicker measurement method is desired.

In the past, PTIs have typically been used to produce a less stringent go/no-go measurement, though reactor health monitoring would benefit greatly from a more precise reading. As SFR coolant under normal conditions is normally held at an oxygen concentration closer to ~2 wppm, a new/updated measurement method, and equipment are needed to ensure the applicability of experimental work and measurement in the reactor.

The subjectivity of RDT PTI measurements is another area for improvement. Designed for strip chart data collecting, RDT analysis requires that operators make visual determinations of flow increase/decrease to produce a measurement. While measurements performed by the same operator in general present a reasonable agreement, two operators will produce different measurements from the same data. For research and reactor purposes, an objective and reliable measurement would be beneficial.

In this study, the inactive RDT standard was modified and used in the development and validation of a new oxygen concentration measurement device and procedure. The new device/procedure avoids error from operator interpretation inherent to the inactive standard, allowing fully automatic and objective determination of the plugging temperature (and thus oxygen concentration). Depending on the oxygen concentration considered, the new device and procedure are also capable of producing measurements in about half the time required for RDT PTI readings.

Experiments

Experiments were performed for both PTI designs at oxygen concentrations set by the cold trap of 10, 8, 4, and 2 wppm. Each experiment consisted of an RDT measurement (5 plugging events) and a UW minimum measurement (10 plugging events) concurrent with one vanadium wire equilibration. For 2- and 4-wppm tests using the .052” PTI, separate vanadium wire equilibrations were performed for UW Minimum and RDT testing.

Uncertainty

For UW Minimum testing, variability in PTI measurements was represented by the standard deviation of the 10 separate minimum velocity temperatures. This was added in quadrature with the plugging thermocouple uncertainty following from calibration to produce the total measurement uncertainty.

The RDT PTI standard does not directly address how to quantify measurement uncertainty. Based on prior experience it was assumed that the largest source of error came from the operator’s visual analysis of the data. Five operators made separate analyses of the experimental data and produced five sets of plugging temperatures and unplugging temperatures. The average disagreement between temperatures was considered the variability, and the plug variability, unplug variability, and plugging thermocouple uncertainty were added in quadrature for the overall uncertainty.

Uncertainty in cold trap operating temperature was determined by the standard deviation of all cold trap temperature measurements over the experiment. In all cases, this uncertainty was negligible (less than 0.5°C) and is not represented in any figures.

For vanadium wire data, the original literature suggests the error to be 15% of measurement.

RDT PTI Uncertainty/variability

Some of the results shown in this section compare measurements of oxygen concentration against the independent axes representing the cold trap set point as the "true" value. This is not strictly accurate as the trapping trace was more a control parameter than a concrete measure of oxygen concentration. However, this representation is common in the literature [6][42] including in the reactor programs that developed the RDT standards. In all cases, the cold trap temperature variability was less than 1°C.

The largest contribution to uncertainty in RDT standard PTI measurements was the subjectivity in operator analysis. To quantify this, five operators processed the RDT plugging events from all experiments (all measurements shown in Figure 24). The average "plug" measurement was determined for each oxygen concentration and PTI size, and the appropriate mean was subtracted from the set of all "plug" measurements. The same was done for the set of all "unplug" measurements. These modified sets of "plug" and "unplug" measurements were collected for each PTI size. Based on a level of confidence of 95% and 95 degrees of freedom, an expansion factor of 1.661 was chosen and the total measurement uncertainty for RDT method tests was calculated (shown in Table 7).

Table 7: Uncertainty in RDT measurements for both 0.052" and 0.035" PTI sizes.

PTI size	0.052”	0.035”
The standard deviation for “plug” measurements (°C)	7.4	3.6
The standard deviation for “unplug” measurements (°C)	5.9	7.4
“Plug” uncertainty (±°C)	12.3	6
“Unplug” uncertainty (±°C)	9.8	12.3
Thermocouple uncertainty (±°C)	1	1
Total uncertainty in RDT measurement (°C)	±15.8	±13.7

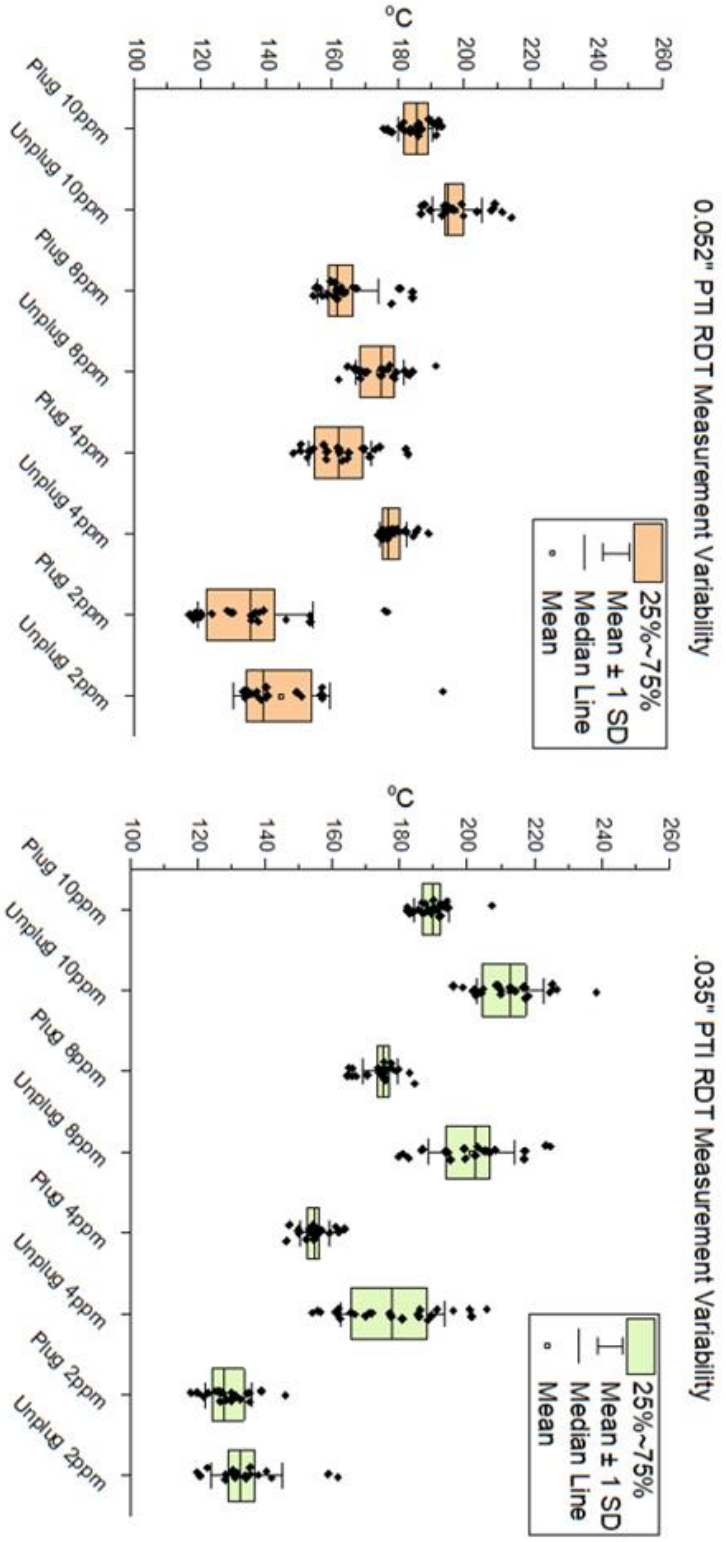


Figure 24: All RDT "plug" and "unplug" measurements made by 5 operators from the same data set, shown for two PTI orifice sizes.

The Sodium-NaK Engineering Handbook considered the variability of RDT measurements between operators to be relatively minor: the stated 6^{o}C of variation constitutes less than 1 ppm difference in oxygen concentration across most of the regions of interest [44]. The results from duplicate RDT analyses shown here were more substantial, showing a total uncertainty of ± 15.8^{o}C in the 0.052” PTI measurements and ±13.7^{o}C in the 0.035” PTI measurements.

It should be noted that the group of 5 operators all had at least some experience with this analysis method, with some having extensive experience. In a reactor setting, training programs will aim to reduce variability between experienced operators. However, given the level of experience of this study’s operators, we do not believe that further training would drive this figure down significantly.

The above uncertainty results may cast unnecessary doubt on the RDT method as a whole; this was not the authors’ intent. The RDT method was developed for different data collection/analysis techniques when removing human error by automation was not possible/practical. For a set of measurements from the same experienced operator, the method performs well, producing accurate and repeatable data. Figure 25 shows the level of agreement between data analyzed by a single operator.

The spread of data points equated to roughly ±5^{o}C at every temperature except 140^{o}C, where variability increased. Contrasting these single-operator data with the multiple-operator variability analysis illustrates the quality of RDT tests performed/analyzed by a single experienced operator. However, drawing conclusions about the RDT measurement uncertainty from single-operator data would lose critical information about the method’s subjectivity, highlighting the need for an objective measurement. For this reason, all comparisons between UW MIN and RDT results will use the uncertainty bounds produced by the multiple-operator variability analysis.

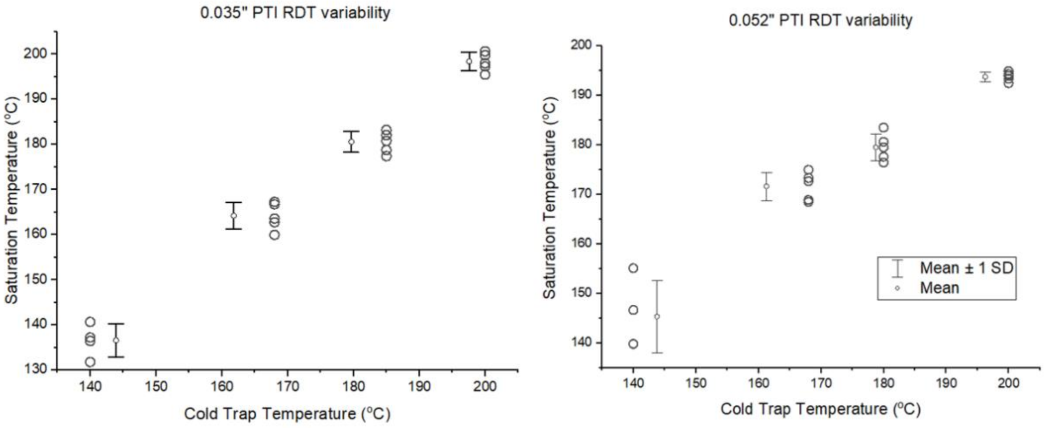


Figure 25: Variability in RDT data for all tests. Data was analyzed by a single operator

UW MIN Uncertainty/variability

Determining uncertainty in a UW MIN measurement was a much simpler task than the above RDT analysis. Figure 26 shows the spread of data for UW MIN PTI readings. Numerical values for mean and standard deviation of UW MIN PTI readings are shown alongside the same values for RDT PTI tests in Table 8 and Table 9.

While there was larger variability in UW MIN data than for the single-operator RDT data at each cold trap temperature, the UW MIN method allowed representative statistics (i.e., standard deviation) to be used with confidence for uncertainty analysis. In all cases, the standard deviation of the UW MIN data shown in Figure 26 is smaller than the uncertainty bounds suggested by the RDT subjectivity analysis. A comparison of the RDT and UW MIN variability shows that the UW MIN method greatly benefits from being developed with automated data collection/analysis in mind.

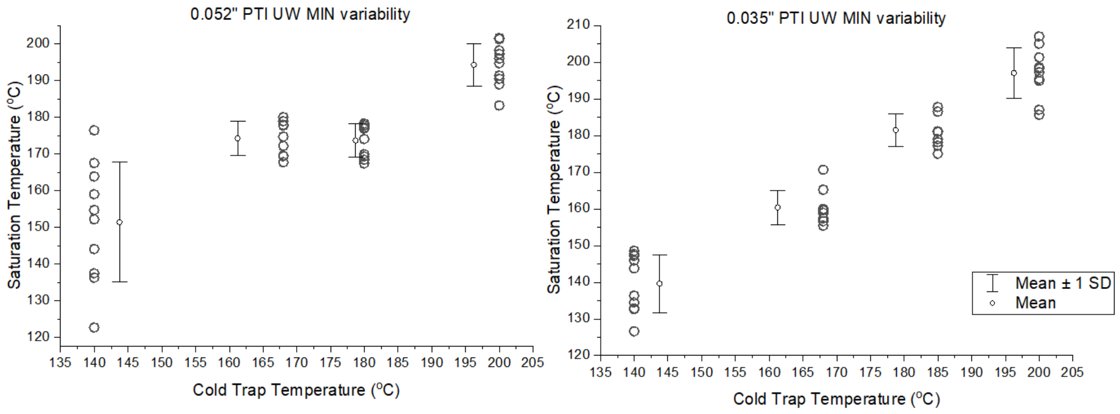


Figure 26: Variability in UW MIN data for all tests

Table 8: .052" PTI measurements in oC, with wppm values in parentheses. UW MIN error includes thermocouple uncertainty of ± 1°C.

Cold trap temperature	RDT mean	RDT error	UW MIN mean	UW MIN std	UW MIN error
140 (2.1)	145.3 (2.5)	±15.8	151.4 (3.0)	15.5	±15.6
168 (4.9)	171.6 (5.5)	±15.8	174.2 (5.9)	4.4	±4.5
180 (6.9)	179.5 (6.8)	±15.8	173.7 (5.8)	4.2	±4.4
200 (11.7)	193.8 (10.0)	±15.8	194.3 (10.1)	5.5	±5.6

Table 9: 0.035" PTI measurements in °C with wppm values in parentheses. UW MIN error includes thermocouple uncertainty of 1°C.

Cold trap temperature	RDT mean	RDT error	UW MIN mean	UW MIN std	UW MIN error
140 (2.1)	136.5 (1.8)	±13.7	139.6 (2.0)	7.5	±7.6
168 (4.9)	164.2 (4.4)	±13.7	160.4 (3.9)	4.5	±4.6
185 (7.9)	180.4 (7.0)	±13.7	181.4 (7.2)	4.3	±4.4
200 (11.7)	198.2 (11.2)	±13.7	197.0 (10.8)	6.5	±6.6

PTI Summary

The direct correlation of UW MIN measurements with RDT measurements yielded good agreement between the methods, as shown in Figure 27. The 0.052” PTI UW MIN data were within ±20% of RDT readings through the range, except for the 2-ppm test. Unstable/fragile plug formation was observed during these tests for both methods and was believed to be a consequence of the larger orifice and low oxygen inventory. This may represent the limit of measurement sensitivity for 0.052” orifice PTI measurements in general.

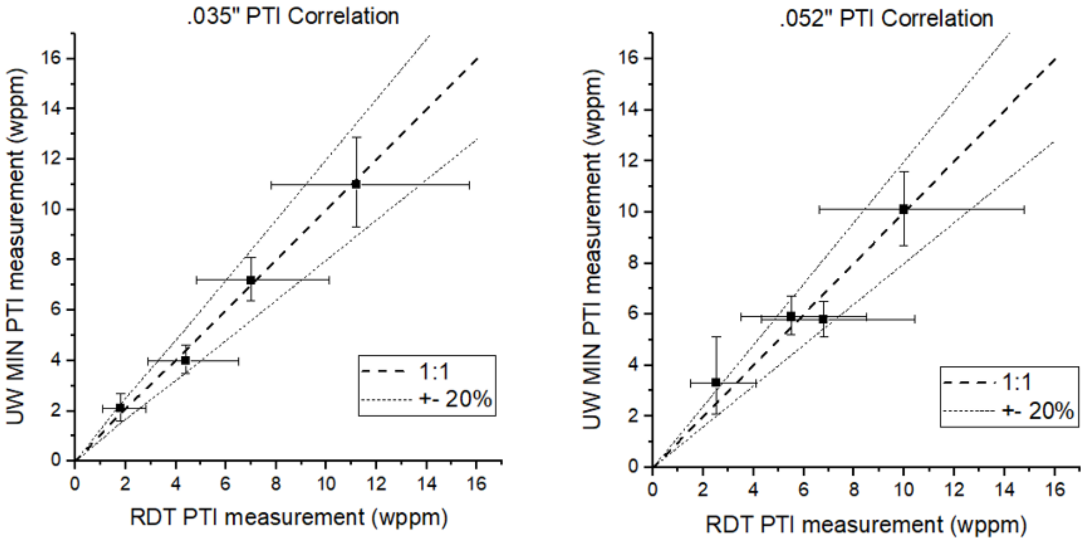


Figure 27: Correlation between UW MIN PTI measurements and RDT PTI measurements in the range 2-12 wppm.

The 0.035” PTI testing showed excellent agreement throughout the whole range of measurements, even for 2-ppm testing. Fragile plug formation at low oxygen concentrations was observed, but to a much smaller extent than in 0.052” PTI testing. These results suggested that the smaller orifice PTI can accurately measure 2 wppm oxygen in sodium.

The ratio "C" between the UW MIN and RDT measurements (Figure 28) was calculated by dividing the UW MIN saturation temperature by the associated RDT measurement at each PTI size/saturation temperature (Eqn. 16). All means were within ±5% of a 1:1 ratio, and all 0.035" PTI means were within 2.5%. In terms of saturation temperature (°C), this translates to maximum differences of ± 10°C in the 0.052" PTI and ± 5°C in the 0.035" PTI.

$$C = \frac{UW\ MIN\ saturation\ temperature\ [^{\circ}\mathrm{C}]}{RDT\ saturation\ temperature\ [^{\circ}\mathrm{C}]} \qquad (16)$$

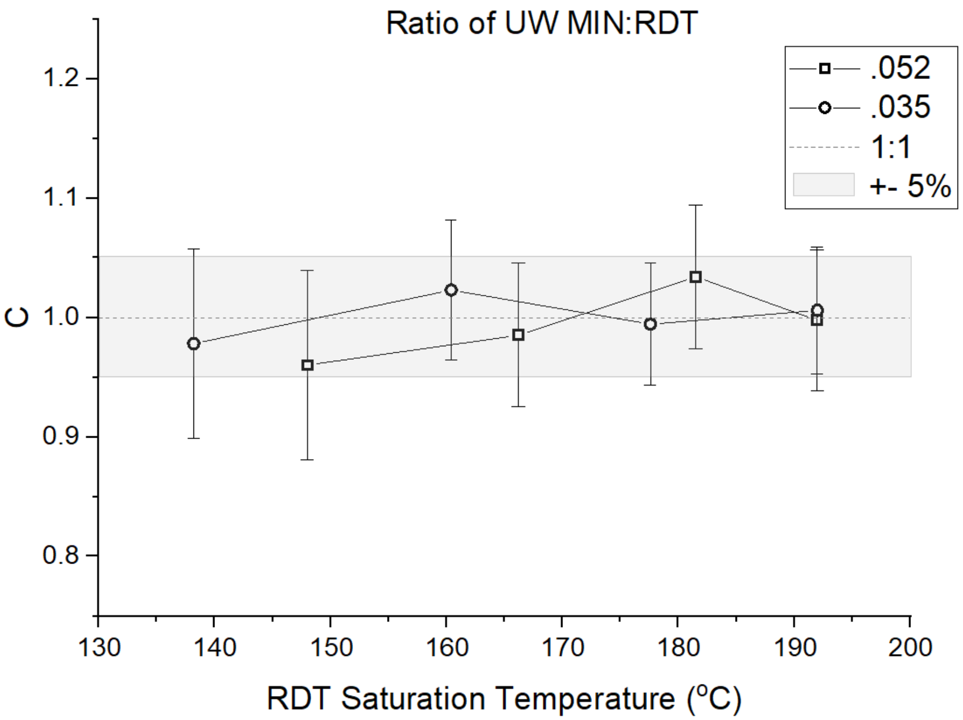


Figure 28: Calibration coefficients for UW MIN method, calculated using RDT measurements as a reference.

The data in Figure 27 have been translated into wppm readings by Eq. (1) for readability/practical use and direct comparison against the vanadium wire measurements and are also shown in Table 8 and Table 9. Please note that the error bars for all RDT measurements are consistent with the uncertainty analysis presented earlier.

Vanadium Wire

The results from the vanadium wire analysis, shown in Figure 29, were not as well-correlated with RDT plugging measurements as the UW MIN data, reading lower than the RDT plugging measurements in nearly all cases. Further, the data were distributed differently between PTI orifice sizes, indicating some change in experiment parameters between PTI sizes not captured by the standard operating procedures governing testing. This prompted a further search for extant data sets with which to compare the current study's findings. Vanadium wire data is scarce in the literature, and one of the only flow-loop data sets known to the authors is shown in Figure 30, taken from a report on EBR-II coolant purity [45]. Here, the vanadium wire measurements appear to vary widely with no clear relationship to the fluctuations in cold trap temperature. Investigation of the repeatability and quality of the original correlations for VWE are the subject of the following study.

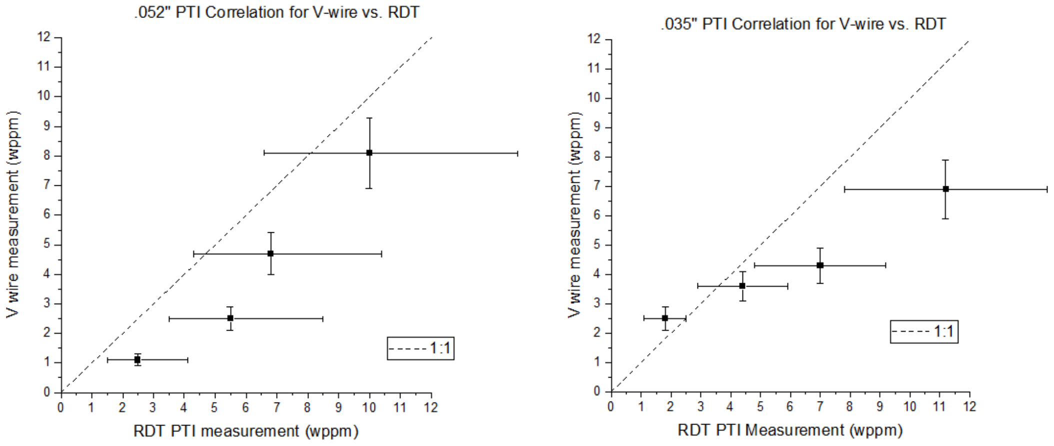


Figure 29: Correlation between vanadium wire measurements and RDT measurements in the range 2-12 wppm

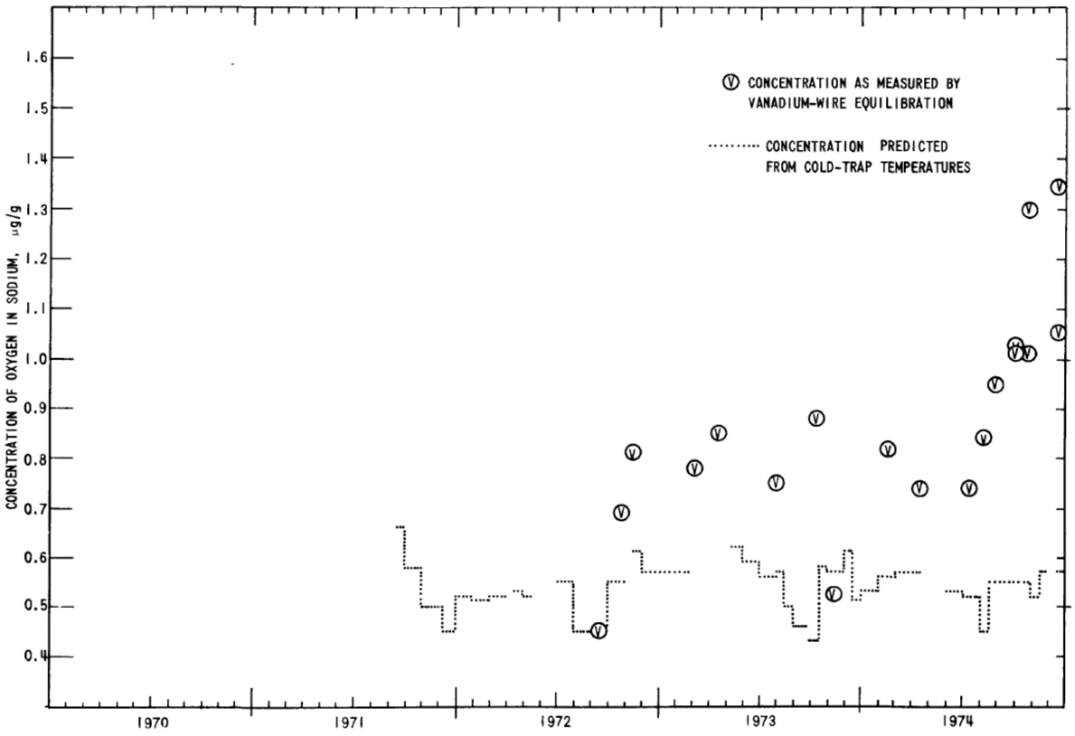


Figure 30: Reproduction of figure from a report on the purity of EBR-II sodium. Note that the oxygen concentration reported in microgram/g is equivalent to wppm.

Highlighted Conclusions

- The UW MIN PTI method was developed and shown to perform similarly to or better than the RDT standard method across all oxygen concentrations tested in the present study, which are typical and expected in sodium fast reactors. This new method also presented a narrower range of uncertainty along with the reassurance of objective data analysis with an automated method. The UW MIN method presented itself as repeatable, quick, accurate, and operator-independent.
- The error associated with the operator's visual measurement on the RDT standard method was quantified, and a thorough uncertainty analysis was performed to give the method's accuracy.
- Automation of the RDT standard data analysis would eliminate operator error and give greater precision in oxygen measurements, though
- Using a PTI with 0.889 mm (0.035") diameter holes provided better data more quickly than the same procedure using 1.3208 mm (0.052") diameter orifices. This was demonstrated in a small sodium facility but should carry over to large reactor-scale systems without any issue and was shown to be able to measure accurately down to 2 wppm.
- Vanadium wire tests were conducted in parallel with the PTI measurements as a third indication of oxygen concentration in the sodium and to confirm the PTI measurements. Overall, middling agreement [differences of up to ~60% observed] was found between the PTI and vanadium wire data, which involves a completely different process to measure oxygen concentration.

- The vanadium wire results showed much more variability than expected, prompting a more thorough analysis of the procedure and equilibration process.

VANADIUM WIRE STUDY

Motivation

Our previous study [46] qualified a new method for PTI operation against both an older PTI procedure and cold trap measurements, with simultaneous measurement of oxygen by VWE performed as an additional check on experimental conditions. All VWE experiments were performed according to Smith's standardized method [47], though the resulting data displayed an unexpected level of variability. At the upper range of oxygen concentrations, VWE measurements were lower than PTI readings by as much as 30%.

We also observed a thin, fragile surface layer on exposed wires consistent with descriptions of the more oxygen-dense phases (β, γ, δ). Data from VWE measurements taken in flowing, oxygen-controlled loops and analyzed via inert-gas fusion are almost nonexistent, and the only results available to contextualize our data were found in a report detailing EBR-II coolant purity. These data, taken from 1971-1974, also display a large variation against a relatively constant cold trap operating temperature. The vanadium wire technique is relatively simple and cheap compared to nearly all other methods of oxygen determination in sodium, and it is an oxygen-selective method. If VWE can be proven to be accurate and repeatable, it stands to be a very useful tool for researchers and reactor operators as the SFR field advances.

In this study, the standard VWE procedure was modified to improve measurement reproducibility, and good reproducibility was demonstrated. Experiments were performed to investigate the existence of an oxygen gradient in the wire bulk, as well as the effect of exposure time and surface condition on reproducibility. A revised procedure was formulated based on these findings. An experimental campaign was performed following the revised procedure, and the original correlations were modified to reflect the results of that campaign. The revised correlations describe the experimental data more accurately than the original correlations and display prediction errors commensurate with the uncertainty of other accepted oxygen measurement techniques.

Methods/Procedures

Sample Holder

All equilibrations were performed using the basket-style holder shown in Figure 31. Wire samples were affixed first to the rigid retaining ring by bending their ends around the ring. The free ends of the samples were then placed into retaining holes in the floating ring and again bent to fix them in place. The outer covering was made from 200-size SS316 mesh spot-welded to a round nut, which was then threaded onto the holder once the wire samples were fixed into the retaining holes.

Electropolishing Procedure

All electropolishing steps were performed with a solution of 1 part high-molar sulfuric acid to 4 parts lab-grade methanol. A strip of tantalum served as the cathode, with the wire sample (grasped in forceps connected to a DC power supply) serving as the anode. All electropolishing procedures were performed with a current of 0.3A, and unless specified otherwise, were performed for 15s on each half of the wire.

UW MIN PTI Procedure

All PTI measurements were performed according to the standard procedure for UW Minimum Method testing.

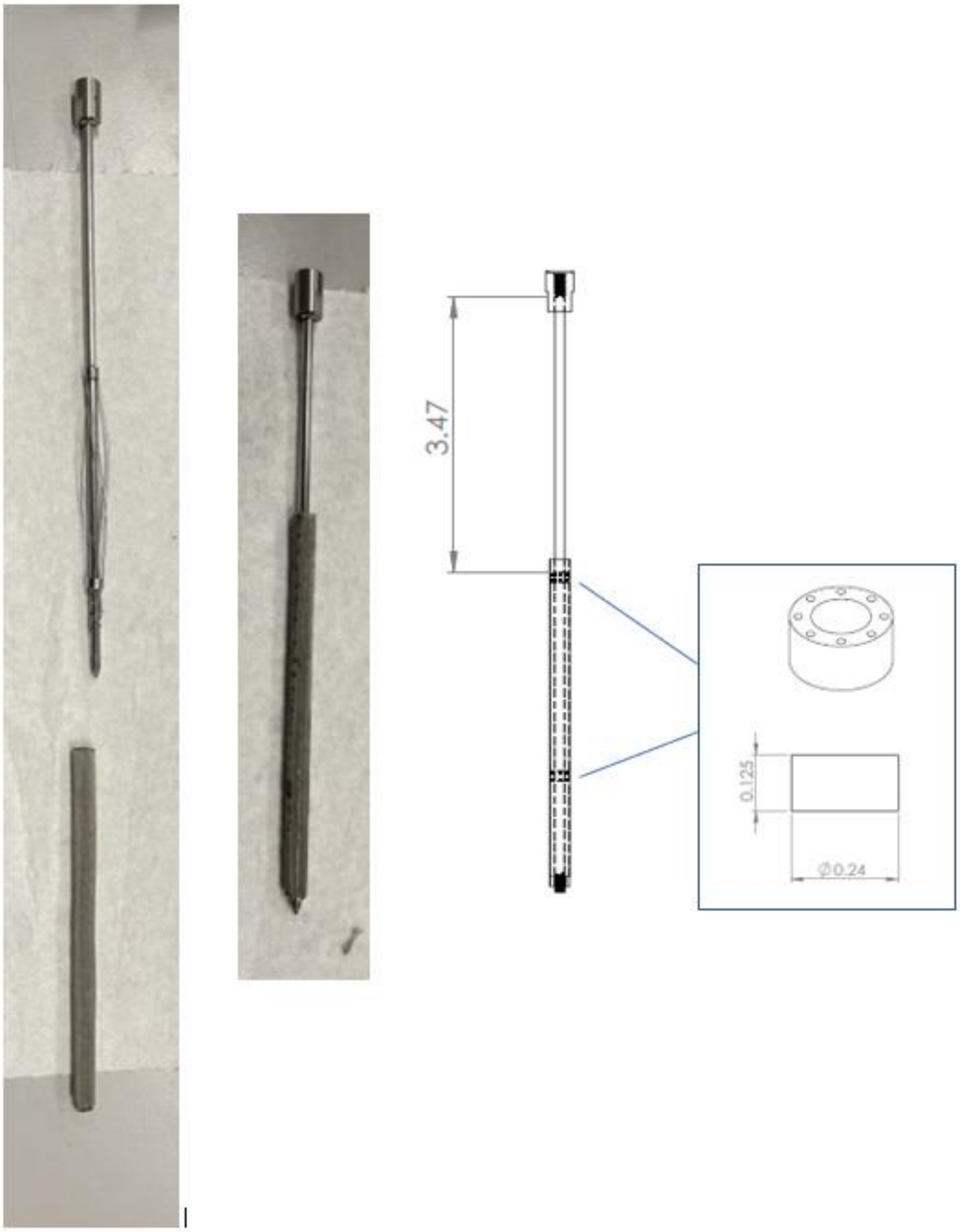


Figure 31: Basket holder for VWE measurements

Reproducibility Testing

Four wire samples were simultaneously exposed to sodium cold-trapped to 200°C for 24 hours. The samples were cleaned, polished, and analyzed identically.

Gradient Testing

Four wire samples were simultaneously exposed to sodium cold-trapped to 200°C for 24 hours. The samples were cleaned. Mass measurements were recorded for each sample with a balance (Sartorius 64-1S, 60g range, $\sigma = 0.1$ mg). Diameter measurements (average of three locations) were taken for each sample with an optical microscope (Keyence VHX-5000, 200x magnification, $\sigma = 10$ µm). One set of wires was set aside for analysis without polishing. The three remaining sets were electropolished for 20, 40, and 60 seconds and analyzed. The oxygen concentration in the outermost shell O_{shell} is given by:

$$O_{shell} = \frac{O_{outer} * V_{outer} * \rho_{outer} - O_{inner} * V_{inner} * \rho_{inner}}{V_{shell} * \rho_{shell}} \tag{17}$$

With V_X and ρ_X calculated from mass and diameter measurements, with uncertainty due to measurement added in quadrature.

Prepolish Testing

Four wire samples were electropolished before being simultaneously exposed to sodium cold-trapped to 200°C for 24 hours. The samples were cleaned, polished, and analyzed identically.

Exposure Time Testing

Two wire samples were exposed to sodium cold-trapped to 200^{o}C for 4, 8, and 12 hours, and one wire sample was exposed to sodium cold-trapped to 200^{o}C for 24, and 48 hours. The wires were cleaned, polished, and analyzed identically.

Correlation testing

2 wire samples were electropolished before being simultaneously exposed for 4 hours to sodium cold-trapped to the temperatures shown in Table 10. UW MIN PTI testing was conducted for the duration of the equilibration Table 11 contains parameters that were held constant within the range shown for all testing. These parameters are consistent with the revised RDT VWE measurement procedure which may be found in Appendix X.

Table 10: Cold trap temperatures/oxygen concentrations investigated for correlation testing

Cold Trap Temp (^{o}C)	194	190	181	175	169	161	152	139
Oxygen concentration (wppm)	10	9	7	6	5	4	3	2

Table 11: Parameters held constant for correlation testing

Reynolds Number	2500 ± 500
Equilibration Temp (^{o}C)	750 ± 3
Equilibration time (min)	240 ± 5
Wire length (cm)	10 ± 1
Electropolish current	0.3 A
Electropolish time (s per side)	15
Wire surface condition	Electropolished before exposure

Correlation Data Analysis/Uncertainty

We fit both Eqn. 8 and the formulation suggested by Smith in 1972 (Eqn. 9) to our experimental data. We accomplished this by replacing selected constant terms in both equations with scaling coefficients *a* and *b* (producing Eqns. 18 and 19) and using curve-fitting tools in MATLAB to determine fit parameters.

$$\ln(K_A) = \ln\left(\frac{N_{O_V}}{N_{O_{Na}}}\right) = \Big\{a + b\Big[\big(1 - N_{O_V}\big)^2 - \big(1 - (N^o_{O_V})^2\Big]\Big\}\frac{1}{1023.15\,K} - 9.567 \quad (18)$$

with $N^o_{O_V} = 0.04893$, as specified in [23]

$$\ln(K_A) = ln\left(\frac{N_{O_V}}{N_{O_{Na}}}\right) = a + b\big[1 - N_{O_V}\big]^2 \quad (19)$$

Uncertainty in PTI and vanadium measurements was accounted for by weighting each data point by the inverse of the effective variance (Eqn. 20) [48]:

$$w_i = \frac{1}{\left(\sigma^2_{y_i} + \frac{dy}{dx_i}^2 \sigma^2_{x_i}\right)} \quad (20)$$

where the local slope $\frac{dy}{dx_i}$ is estimated from the local slope of the original equation.

The function minimized in the weighted least-squares analysis is then

$$SSE = \sum_{i=1}^{n} w_i \left(PPM_{Smith,corrected_i} - PPM_{PTI_i}\right)^2 \quad (21)$$

Uncertainty in PTI measurements was obtained from the results of the previous study [46]. Uncertainty in vanadium wire measurements was taken as the reproducibility calculated from the results of variability testing ($\sigma = 0.03$ wt.%).

R^2 values for each original correlation and each corrected correlation were calculated as normal and were treated as the figure of merit representing the quality of each correlation for predicting sodium oxygen concentration. Adjusted R^2 values are reported for the corrected correlations to avoid artifacts from overfitting.

To visualize the results of the correlations and fits in the most useful form $\left\{PPM_{O_{Na}} = f(wt.\%\ O_v)\right\}$, results obtained from correlations in terms of mole fractions were translated to mass fractions as normal.

Findings/Discussion

Figure 32 shows results for reproducibility tests using wires that were not polished before exposure ("VARIABILITY"), and wires that were polished before exposure ("PREPOLISH"). Equilibration results at 200C cold trap temperature from the previous study are also included. The mean oxygen concentration of this population was 1.267%, and the standard deviation (σ=0.03%) was taken as the reproducibility of the measurement. Though the variability between sets of wires equilibrated simultaneously was smaller than this figure ($\sigma_{\text{variability}} = 0.01\%$, $\sigma_{\text{prepolish}} = 0.02\%$), analyzing the entire data set encompassing measurements taken on different days provides a more conservative estimate of reproducibility. When translated by Eqn. 8 into expected ppm oxygen in sodium, the resultant measurement is 7.9 ppm +/- 0.6. These bounds were considered sufficiently small to justify pursuing VWE as a measurement technique.

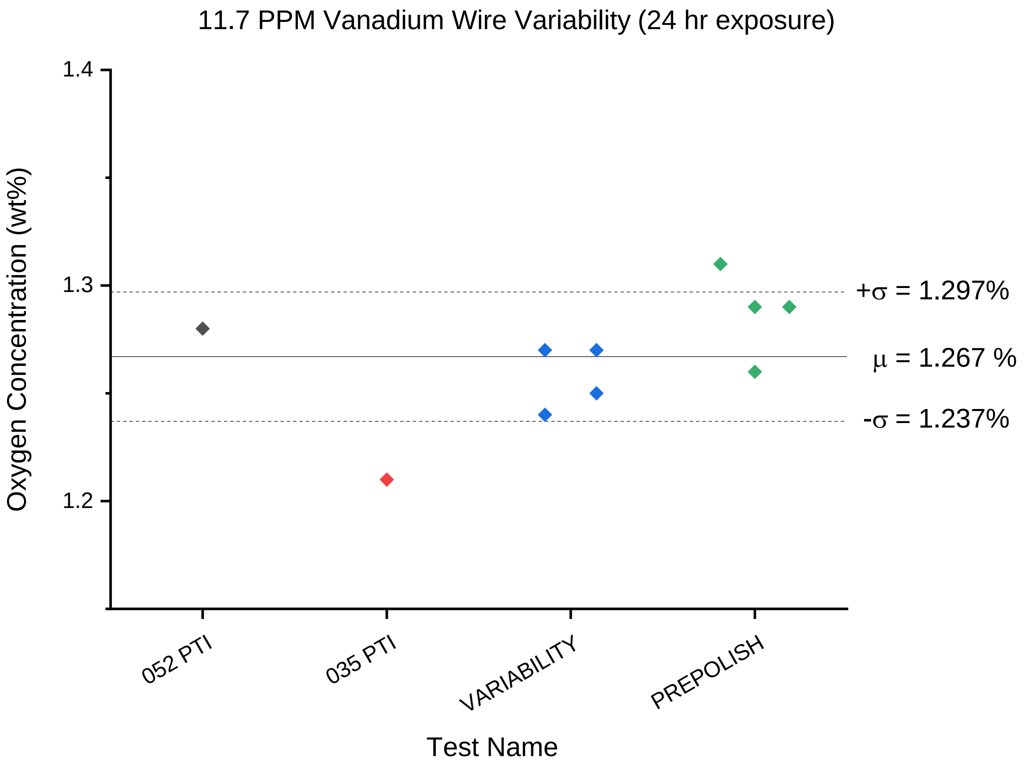


Figure 32: Results of VWE variability and prepolish testing

From the data in Figure 32, electropolishing the wires beforehand did not have a measurable effect on the final oxygen concentration. However, a comparison of optical microscope images of the wires before/after prepolish, and after exposure shows a much more cohesive and homogenized surface layer (Figure 33). In addition to the qualitative effect on the formed surface layer, the prepolishing step removed any existing passivation layer and was incorporated into the final revised procedure.

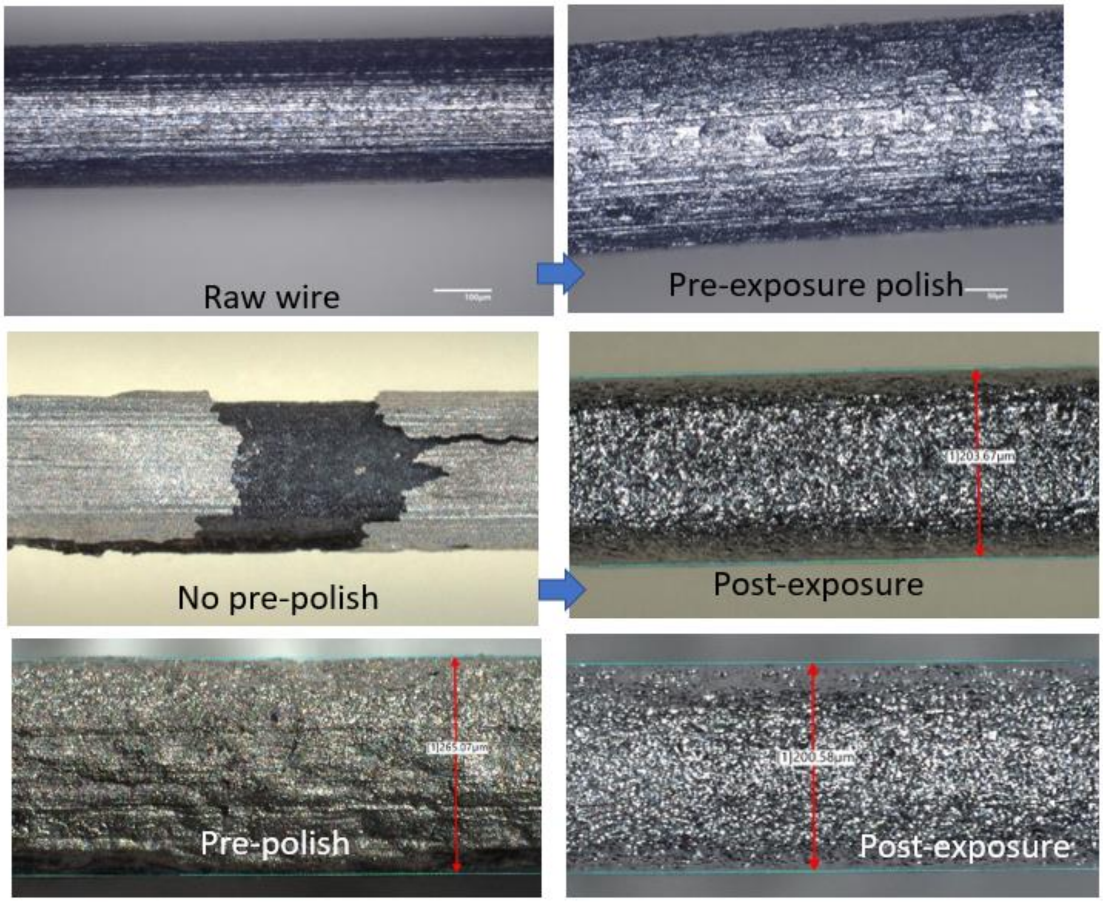


Figure 33: Optical microscope images of vanadium wires at various stages in prepolish testing

Figure 34 shows results from 4-, 8-, 12-, and 48-hour equilibrations along with the previous measurements at 24-hour equilibration time. Measurement mean and uncertainty calculated from the results of 24-hour experiments are shown as lines of μ ± σ. Though there appears to be a slight positive relationship between measured oxygen wt.% and exposure time between 4-12 hours, the uncertainty associated with measurement variability makes it difficult to conclude that exposure time meaningfully affects the measured value.

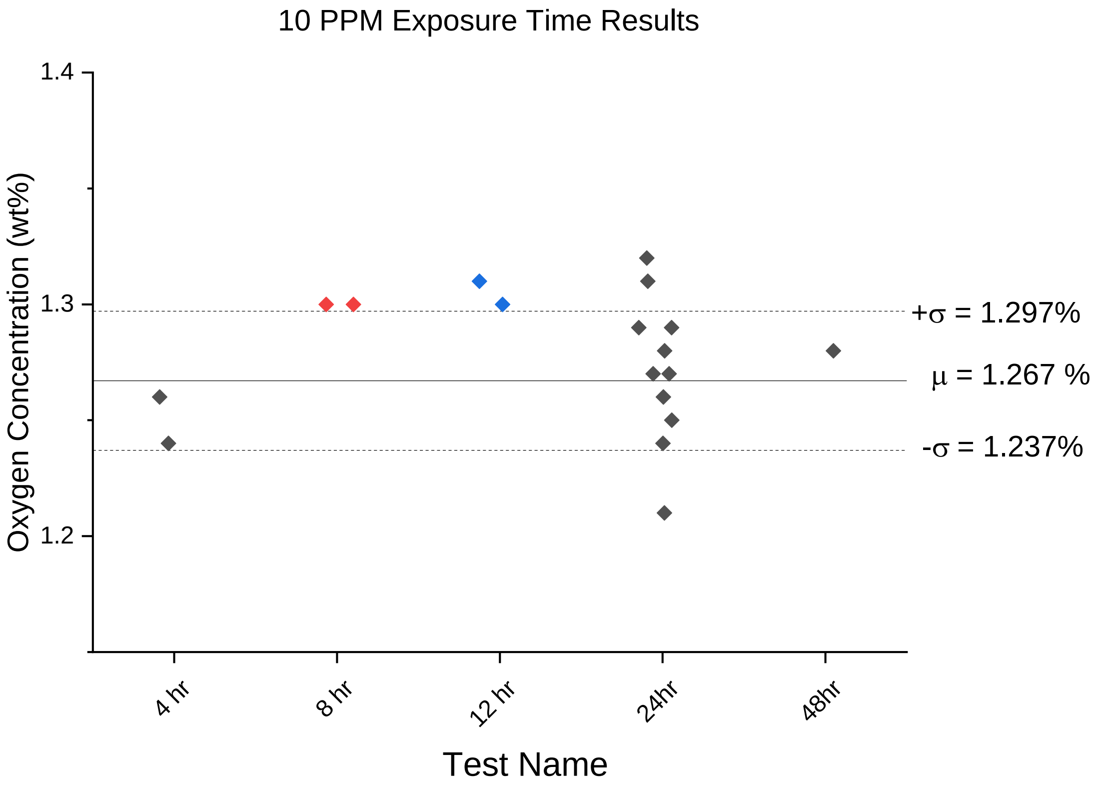


Figure 34: Oxygen concentrations in vanadium wires exposed to sodium for various times at the same sodium oxygen level.

Gradient testing showed that the observed surface layer holds a higher concentration of oxygen than the bulk of the wire (Figure 35), and past this surface layer, there is no measurable gradient within the wire through a ~25% reduction in diameter. At a reduction in diameter of 16+/-10 [micron] the region of higher oxygen concentration was completely removed, and the remaining “shells” contained oxygen concentrations consistent with the results of the earlier variability experiments (shown as lines of $\mu \pm \sigma$). By Eqn. 10 the oxygen concentration of this outer layer is estimated to be 3.76+/-0.33 wt.% oxygen. This translates to around 11.5% atomic percent oxygen, which suggests that these test parameters cause the β-phase to form at 750C which then transforms into the peritectoid α’-phase as it cools below 519C [37]. These data confirm the existence of a phase separate from α-vanadium, supporting the claim that the VWE measurement is not a “true” equilibrium. However, the absence of a gradient, along with highly repeatable measurements of the ultimate oxygen concentration of a sample after VWE indicates the existence of a functional equilibrium. The growth of the high-oxygen surface phase may inhibit the continued transformation of α-vanadium by free oxygen in the sodium, while presenting a large enough barrier to diffusion that the ultimate oxygen concentrations are roughly equal.

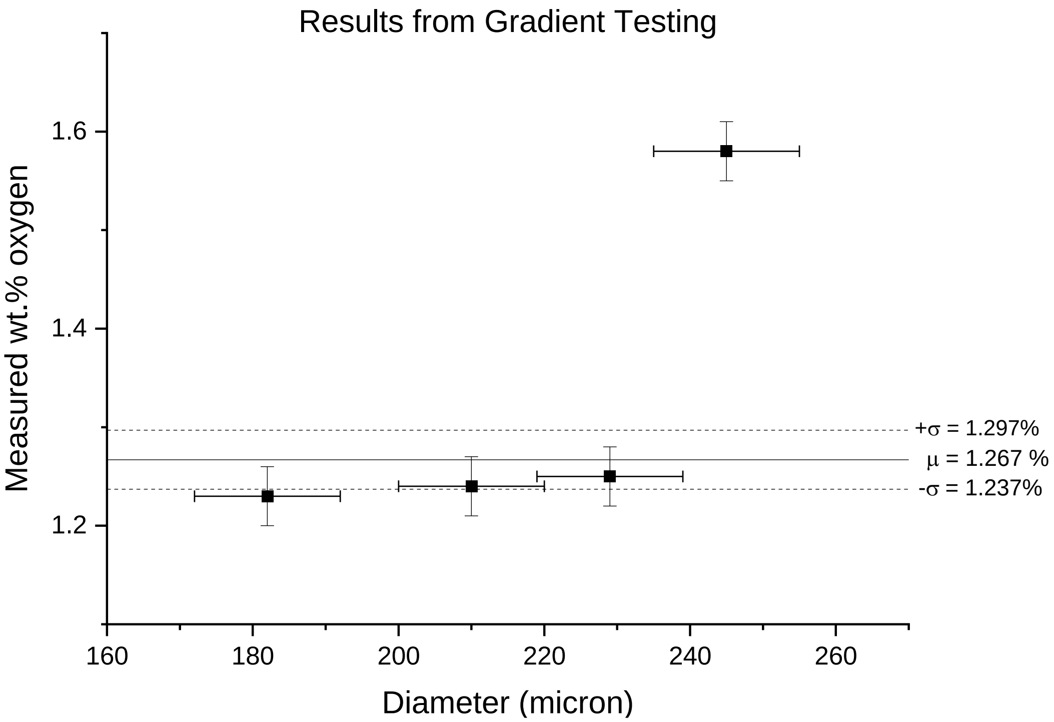


Figure 35: Oxygen concentrations at various depths of electropolish into diameter of vanadium-wire specimens.

Correlation Results

Figure 36 shows the results of correlation experiments, with oxygen measurements from UW MIN PTI tests plotted against vanadium wire oxygen concentrations. Predicted results from the original Smith 1971 and Smith 1972 correlations are also plotted. Again, we observe an under-prediction of experimental results by the original correlations, with differences being most pronounced in measurements taken at a 200°C cold trap temperature.

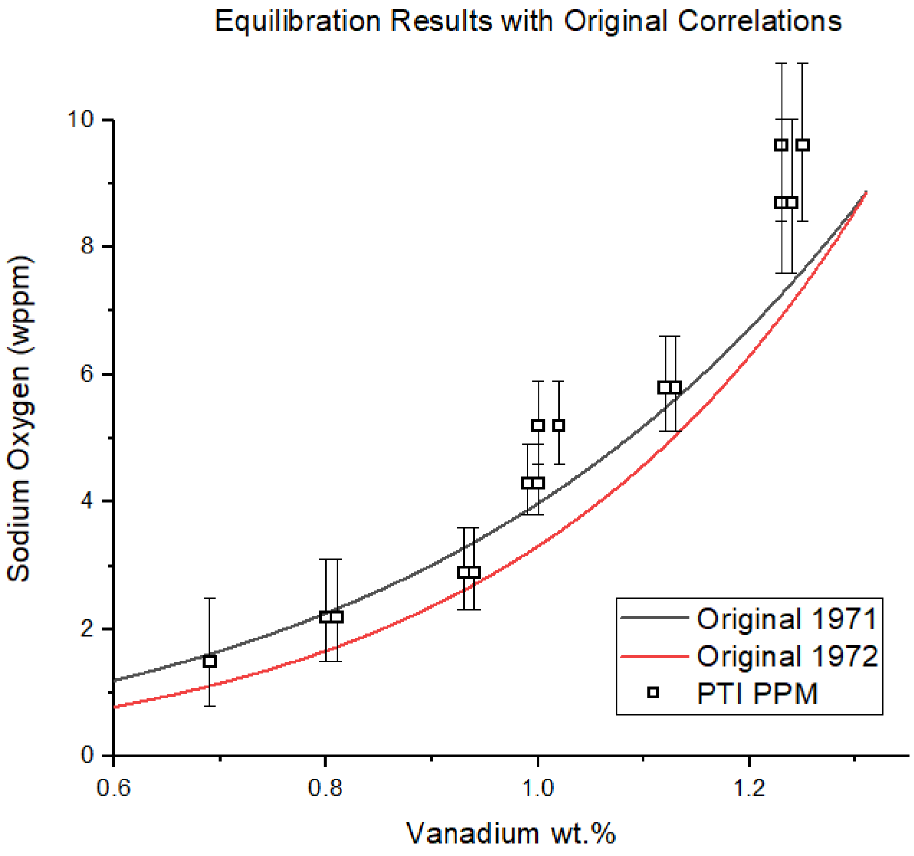


Figure 36: Results from correlation experiments. Experimental results are shown along with curves of the original two correlations proposed by Smith

Results from fitting the two correlations to PTI data are shown in Figure 37. and Figure 38., with fit parameters in Table 12. The dashed lines are non-simultaneous observational prediction bounds at a confidence level of 95%. Table 12 also includes statistics for the original correlations for easy comparison.

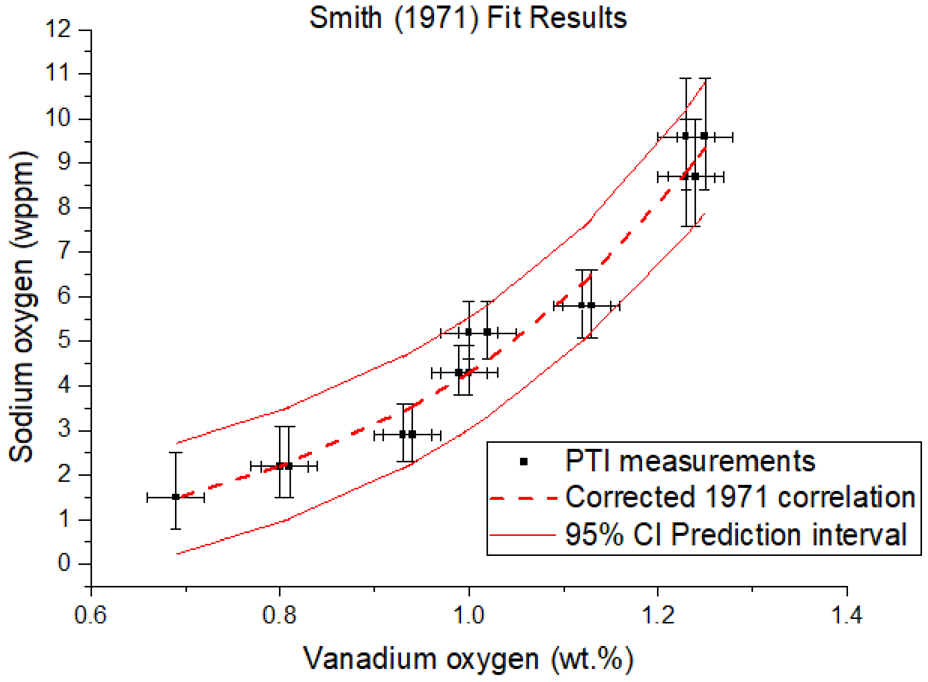


Figure 37: Curve fit results for the original Smith correlation, with prediction intervals are shown.

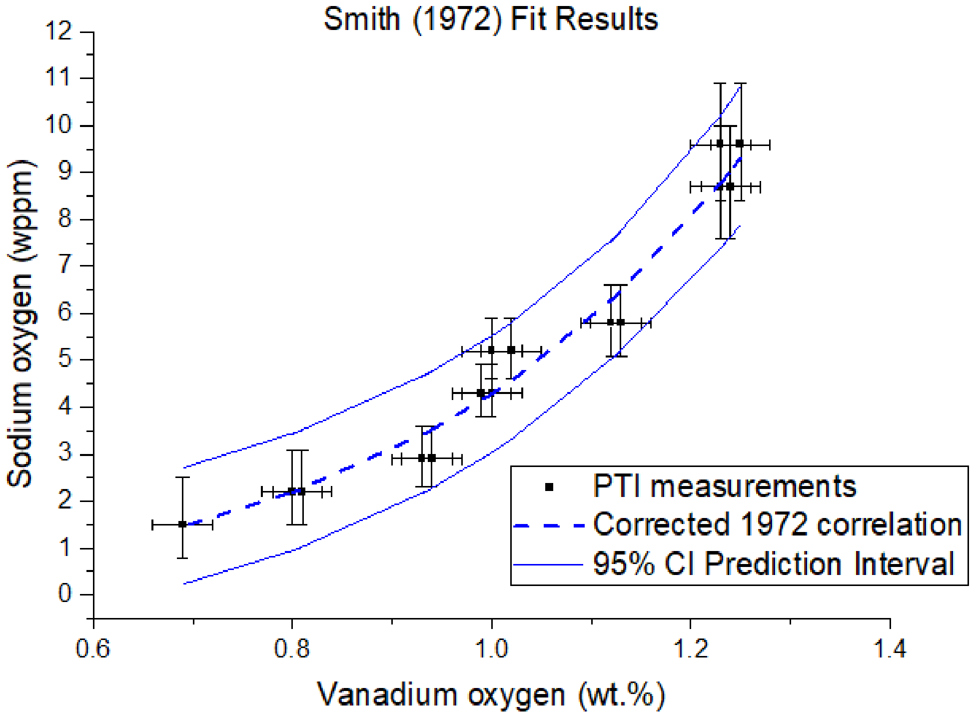


Figure 38: Curve fit results for 1972 Smith correlation, with prediction intervals shown.

Table 12: Fit parameters for corrected correlations. Selected parameters are also shown for original correlations.

Fit	***a* value**	***b* value**	**SSE**	**R^2**	**RMSE**	**Average 95% CI Prediction Interval (wppm)**
Corrected (1971)	17,180	38,930	5.46	0.94	0.62	±1.3
Corrected (1972)	-27.41	38.29	4.43	0.94	0.56	±1.3
Smith (1971)	17,560	30,070	12.25	0.87	0.88	N/A
Smith (1972)	-28.22	39.42	26.4	0.73	1.28	N/A

By comparison of the fit statistics, we see that the corrected correlations are essentially equivalent, but both improve greatly on the original correlations. The average 95%-CI prediction interval for each new correlation is ±1.3 wppm, which is acceptable when compared to other methods of oxygen measurement in sodium (PTI, electrochemical methods, vacuum distillation, mercury amalgamation [19], [49], [50]).

It should be noted that in the lower range of sodium oxygen concentrations (2-4 wppm), the stated prediction interval may be an overestimation of uncertainty associated with VWE measurements. The authors believe that the width of this interval arises from the uncertainty in PTI measurement, which has been shown to approach a maximum at 2 wppm oxygen in sodium. Conversely, the factors affecting VWE measurement repeatability should have a reduced impact at lower sodium oxygen concentrations. Comparison of VWE measurements with another technique with less uncertainty may greatly reduce the prediction interval at low oxygen concentrations.

The corrected equations are shown below:

$$\ln(K_A) = \ln\left(\frac{N_{O_V}}{N_{O_{Na}}}\right) = \left\{17{,}180 + 38{,}930\left[\left(1 - N_{O_V}\right)^2 - \left(1 - (N_{O_V}^o\right)^2\right]\right\}\frac{1}{1023.15\ K} - 9.567 \tag{22}$$

$$\ln(K_A) = ln\left(\frac{N_{O_V}}{N_{O_{Na}}}\right) = -27.41 + 38.29\left[1 - N_{O_V}\right]^2 \tag{23}$$

Table 13 contains absolute residuals of the original and corrected correlations and shows the marked improvement of the corrected correlations over the original formulations in describing the experimental data.

Conclusions

The Berkeley lab concluded its research with a rather dim view of the vanadium wire equilibration method, posing concerns about the repeatability of a non-equilibrium technique and the degree to which different processes must be controlled to achieve reproducibility. The results of this study show that good repeatability is attained through stringent, though not prohibitive control of various process parameters. Further, the measurement is not meaningfully affected by exposure time, nor does there appear to be a radial oxygen gradient in exposed wires. This points to at least a pseudo-equilibrium which can serve as the basis for an empirical correlation. However, the semi-empirical correlation derived by Smith assumes that equilibrium conditions are achieved, and therefore the correlations were corrected to account for this fact. Proving the vanadium wire method repeatable and accurate gives the SFR community another tool with which to investigate oxygen in sodium—and a relatively cheap and simple tool compared with other methods. Below are some highlighted conclusions from this work:

Table 13: Absolute residuals for original and corrected correlations.

Sample ID	V wt.%	PTI ppm	Smith 1971	abs. err	Smith 1971 (corrected)	abs. err	Smith 1972	abs. err	Smith 1972 (corrected)	abs. err
10ppm A	1.23	8.7	7.2	-1.5	8.8	0.1	6.9	1.8	8.8	0.1
10ppm B	1.24	8.7	7.4	-1.3	9.1	0.4	7.1	1.6	9	0.3
9 ppm A	1.25	9.6	7.6	-2	9.3	-0.3	7.4	2.2	9.3	-0.3
9 ppm B	1.23	9.6	7.2	-2.4	8.8	-0.8	6.9	2.7	8.8	-0.8
7 ppm A	1.12	5.8	5.5	-0.3	6.3	0.5	4.9	0.9	6.3	0.5
7 ppm B	1.13	5.8	5.6	-0.2	6.5	0.7	5.1	0.7	6.5	0.7
6 ppm A	1.02	5.2	4.2	-1	4.6	-0.6	3.6	1.6	4.6	-0.6
6 ppm B	1	5.2	4	-1.2	4.3	-0.9	3.3	1.9	4.3	-0.9
5 ppm A	0.99	4.3	3.9	-0.4	4.1	-0.1	3.2	1.1	4.1	-0.2
5 ppm B	1	4.3	4	-0.3	4.3	0	3.3	1	4.3	0
4 ppm A	0.93	2.9	3.3	0.4	3.4	0.5	2.6	0.3	3.4	0.5
4 ppm B	0.94	2.9	3.4	0.5	3.5	0.6	2.7	0.2	3.5	0.6
3 ppm A	0.8	2.2	2.3	0.1	2.2	0	1.7	0.5	2.2	0
3 ppm B	0.81	2.2	2.3	0.1	2.3	0.1	1.7	0.5	2.3	0.1
2 ppm A	0.69	1.5	1.6	0.1	1.5	0	1.1	0.4	1.5	0
2 ppm B	0.69	1.5	1.6	0.1	1.5	0	1.1	0.4	1.5	0
			Avg	-0.6		0		1.1		0
			std	0.8		0.5		0.7		0.5

<u>Highlighted Conclusions</u>

- The VWE method was shown to be a non-equilibrium procedure, as a high-percentage oxygen phase was detected at the surface of exposed wires
- The VWE method was shown to produce a constant oxygen profile within the bulk of an exposed wire
- The VWE method is not sensitive to changes in equilibration time in the range 4-48 hours

- The VWE method was shown to produce highly repeatable measurements when performed according to a revised RDT procedure
- Corrections to existing correlations were produced by fitting to experimental data

FURTHER WORK

Plugging Temperature Indicator work

The trade-off between measurement time and accuracy should be investigated. The UW Minimum Method specifies much quicker cooling and heating rates than the RDT Method, resulting in a nominally larger spread of measurements but smaller uncertainty. Studies examining the effect of modifying the UW MIN heating rate between 2-5^{o}C/min should give a better understanding of how much uncertainty is introduced by increasing the temperature gradient. Theory suggests that an increase in the gradient should necessarily result in an increase in uncertainty, but I suggest that the temperature at the orifice affects the plug formation/dissolution dynamics fairly instantaneously. In other words, it’s possible that UW MIN measurements taken using higher heating rates will return the exact same results as measurements taken using the standard heating rate of 3^{o}C/min. If this is true, then UW MIN measurement time may be reduced while retaining the method’s accuracy.

If higher heating rates result in a decrease in measurement accuracy, then various forms of adaptive heating rate can be considered. At a very simple level this could mean that as the sodium heats to the expected saturation temperature, the heating rate is decreased to provide more accuracy in determining the “minimum” velocity and associated temperature.

Optical plugging meters are another avenue for decreasing measurement time. Preliminary experiments and analysis have been performed by Jojo Jacob at UW-Madison [51], replacing the plugging thermocouple in a PTI with an optical fiber polished at a 45^{o} angle. Shining light down the length of the fiber while the fiber is immersed in pure sodium results in the light being dumped to the fiber's coating and returning no light. When the angled tip of the fiber is coated in sodium oxide, an operator can measure a reflected signal. We hope to read changes in the thickness of this oxide layer much more quickly than an electromagnetic flowmeter can observe changes in flow rate, and preliminary results show that this is possible. The current challenges to implementing this method are the fragility of the fiber sensor- both to physical perturbation and to chemical erosion. Insertion of the optical fiber requires exposure of residual loop sodium to atmospheric air, and in normal operation the exposed section would simply be exposed to hot, flowing sodium and cold trapped. However, the fiber used in current prototypes cannot survive exposure to sodium over 200^{o}C for extended periods, and so cold trapping must occur over the course of days while the trap slowly depletes the oxide stores around the instrument. If the fiber could withstand temperatures of 250 or 300^{o}C this days-long trapping process could be reduced to the normal length of 6-24 hours.

Vanadium Wire Equilibration work

Future work for VWE characterization must include a more explicit identification of the vanadium-oxygen phases present at the surface of exposed wires. Exposing wires to sodium at a known oxygen concentration in increments of 15 minutes from 0-4 hours would provide duplicate sets for analysis by LECO measurement and some material-identifying process, possibly XPS or similar. The LECO measurement would provide a total oxygen concentration, and the XPS method could provide elemental analysis as a function of wire radius. In this way, we could construct a profile of the vanadium-oxygen phases present as the wire approaches its pseudo-equilibrium identified by our study.

Another avenue for future VWE work involves the modulation of exposure temperature. In this work, VWE measurements were taken at a constant exposure temperature of 750^{o}C, though the method's original authors claimed its applicability to temperatures as low as 600^{o}C. As the equilibration temperature lowers, theoretical maximum oxygen sensitivity also decreases, but for reactor conditions at < 2 wppm, this may be acceptable. The primary advantage of the VWE measurement is its simplicity and cost; reducing temperature/heating requirements to be closer to a typical SFR's maximum temperature of 550^{o}C only adds to these benefits. Investigation of the applicability of VWE at lower temperatures would entail a similar correlation campaign to the experiments described in the above study, except exposure temperatures would be lowered to 600-700^{o}C. The primary result of the study would be new correlation parameters for describing the behavior at lower temperatures.

-

SUMMARY OF CONCLUSIONS

- RDT standard procedures for oxygen measurement were revised to improve accuracy, repeatability, and automation
- The uncertainty associated with RDT PTI measurements was formally quantified
- The UW MIN PTI procedure was qualified against the RDT PTI procedure, and was found to perform as well or better in the examined oxygen range
- Reduction in PTI orifice size was found to increase measurement fidelity and reduce variability across the oxygen range 2-12 wppm
- Concerns about the repeatability and validity of the VWE technique were investigated and addressed; while the measurement is not a true equilibrium process, high repeatability and the absence of a gradient point to the process being quasi-equilibrium and useful for empirical measurements
- Correction factors for original VWE correlations were calculated from a weighted-least squares regression of experimental PTI data. The corrected correlations describe the experimental data more accurately than the original correlations
- The U.S. SFR program will be able to make use of these techniques in both research and reactor settings to better understand the health and operation of their facilities

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Appendix A: RDT Procedures and Revisions

RDT MEASUREMENT PROCEDURE

The detailed steps for the RDT standard test procedure producing the data shown in Fig. 5 are as follows [52], with original temperature values in Fahrenheit converted to Celsius for ease of use:

1. Start the run with the plugging temperature indicator (PTI) at 260 to 315°C, or well above the cold trap and the probable plugging temperature. If the system is operating at less than 260°C, start the run with the PTI at system temperature.
2. Adjust the sodium flow to a convenient rate which is not less than 0.1 gpm (0.02271 m^3/hr). Whenever possible, valves close to and in series with the orifice flow should be at least 75% open.
3. Reduce the temperature of the PTI to 204°C as rapidly as desired and then at a rate of <1°C/min from 204 to 163°C, <0.5°C/min from 163 to 149°C, and <0.25°C/min below 149°C. Incremental temperature decreases as large as 10°C may be used, provided that the average cooling rates specified are maintained.
4. If a sodium flow decrease of at least 25% and preferably of 50% is observed while the temperature of the PTI is being reduced, proceed to step 5.
5. Stop the cooling and begin a heat-up at a rate of ~1.6^{o}C/min and record the temperature at which flow increases sharply. This is the unplugging temperature.
6. Resume cooling at the rate specified for the applicable temperature range. Record the temperature at which flow decreases sharply. This is the plugging temperature.
7. Adjust the sodium flow trip values to flows above and below the partially plugged flow of step 4 and within 0.04 gpm (0.00908 m^3/hr) of that value and observe the time required for one cycle of flow oscillation.
8. Adjust the trip values to produce a flow cycle time between 30 and 90 minutes. The oscillation cycle time and amplitude may change spontaneously,

but they need not be readjusted unless the time exceeds 5 hours, or the flow rate falls outside the range of 20% to 90% of bare orifice flow.

9. Record at least 5 flow oscillations.
10. For 5 or more oscillations determine plugging and unplugging temperatures. Calculate the average plugging temperature, $\bar{P}$, and the average unplugging temperature, $\bar{U}$. Then, $Saturation\ Temperature = \frac{\bar{P}+\bar{U}}{2}$.

UW MIN MEASUREMENT PROCEDURE (ADAPTED FROM RDT)

1. Ensure that the central plugging meter clearing pin is in the closed position.
2. Start the run with the plugging temperature indicator (PTI) at 260 to 315°C, or well above the cold trap and the probable plugging temperature. If the system is operating at less than 260°C, start the run with the PTI at system temperature.
3. Record the "bare-orifice" flow value. If the flow rate is lower than 0.1 gpm (.02271 m^3/hr), increase pump speed until the bare-orifice flow rate exceeds this number.

Optional steps if expected saturation temperature is not known:

- Reduce the temperature of the PTI by 3^{o}C/min until a sodium flow decrease of 50% is observed.
- Stop cooling and begin a heat-up at a rate of 3^{o}C/min.
- Identify the minimum velocity reached during this flow oscillation; the PTI temperature at the time of this minimum will serve as the expected saturation temperature for subsequent tests.
- Allow flow to recover to 100% of bare-orifice value. Proceed to step 4.

4. Reduce the temperature of the PTI to 20^{o}C below the cold trap set-point (or expected saturation temperature) as rapidly as desired.

5. Once the desired degree of sub-cool is reached, hold sodium temperature at the orifice constant. Flow velocity will begin to decrease as oxide precipitates and blocks the orifices.
6. If a sodium flow decrease of 50% is observed while the PTI temperature is held constant, proceed to step 7.
7. Stop the cooling and begin a heat-up at a rate of 3^{o}C/minute.
8. If sodium flow recovers to 80% of the bare-orifice value while the PTI temperature is increasing, proceed to step 9.
9. Repeat steps 4-8 to produce at least ten total oscillations in flow. Proceed to step 10.
10. Identify the minimum velocity reached in each of the flow oscillations. If the difference between this minimum and 50% of the bare-orifice velocity is less than .005 m/s, do not include this minimum in the data set.
11. Identify the temperature of the orifice plate at the time of each minimum. This is the “minimum temperature”.
12. Average the set of minimum temperatures to obtain the mean UW MIN “saturation temperature”. The standard deviation of the set of minimum temperatures is considered the error in this method. Total uncertainty will depend on individual facilities/instruments/data acquisition.

UW MIN MATLAB CODE

```
%% UW MIN routine

MINstarttime = "13:11:13";                              % index = 7615, string
variable input manually from lab notebook
MINendtime= "12:56:00";                                 % index = 35537,
string variable input manually from lab notebook

startindex = find(ismember(time(:,:),MINstarttime));    %Search time array for
start time string
```

```
endindex = find(ismember(time(:,:),MINendtime));        %Search time array for
end time string
MINstart = startindex(2);                               %Set start time
MINend = endindex(1);                                   %Set end time

TimeMIN = time(MINstart:MINend);            %time array for UW MIN testing
VInMIN = VInTemp(MINstart:MINend);          %Inlet temp for v-wire section
VOutMIN = VOutTemp(MINstart:MINend);        %Outlet temp for v-wire section
VvelMIN = VVel(MINstart:MINend);            %Vanadium wire section velocity
PlugVelMIN = PlugVel(MINstart:MINend)';     %Plugging meter velocity
PlugTempMIN = PlugTemp(MINstart:MINend);    %Plugging meter temperature
ColdInMIN = ColdInTemp(MINstart:MINend);    %Cold trap isothermal zone inlet
temp
ColdOutMIN= ColdOutTemp(MINstart:MINend);   %Cold trap isothermal zone outlet
temp
ColdVelMIN = ColdVel(MINstart:MINend);      %Cold trap velocity
LoopTempMIN= LoopTemp(MINstart:MINend);     %Loop bulk temperature
LoopVelMIN = LoopVel(MINstart:MINend);      %Main loop flowrate


for i =1:length(TimeMIN)
    plottimeMIN(1,i)=datetime(TimeMIN(i));          %Turns datetime into
something workable
end

figure(11)

plot(plottimeMIN,PlugVelMIN)                        %Plotting plug velocity vs
time
title(TestName+" UW MIN Method PM Velocity Trace")
xlabel('time');
ylabel('Velocity [m/s]');

MINVwireTempAve = mean((VInMIN+VOutMIN)/2)          %Getting representative
stats from vanadium wire section temps, flow
MINVwireTempStd = std((VInMIN+VOutMIN)/2)
MINVWireVelAve = mean(VvelMIN)
MINVWireStd = std(VvelMIN)

MINColdTempAve = mean((ColdInMIN+ColdOutMIN)/2)     %Getting representative
stats from cold trap temps, flow
MINColdTempStd = std((ColdInMIN+ColdOutMIN)/2)
MINColdVelAve = mean(ColdVelMIN)
MINColdVelStd = std(ColdVelMIN)

%% UW Minimum tests

% Each section of 4 lines of code defines start/end times and finds the
% index value associated with those times

minteststart(1)="13:11:13";
mintestend(1)="13:31:27";

minstartindex(1)=find(ismember(TimeMIN(:,:),minteststart(1)),1,"first");
minendindex(1)=find(ismember(TimeMIN(:,:),mintestend(1)),1,"first");
```

```
minteststart(2)="13:31:27";
mintestend(2)="13:54:00";

minstartindex(2)=find(ismember(TimeMIN(:,:),minteststart(2)),1,"first");
minendindex(2)=find(ismember(TimeMIN(:,:),mintestend(2)),1,"first");

minteststart(3)="13:54:00";
mintestend(3)="14:14:00";

minstartindex(3)=find(ismember(TimeMIN(:,:),minteststart(3)),1,"first");
minendindex(3)=find(ismember(TimeMIN(:,:),mintestend(3)),1,"first");

minteststart(4)="16:05:00";
mintestend(4)="16:40:01";

minstartindex(4)=find(ismember(TimeMIN(:,:),minteststart(4)),1,"first");
minendindex(4)=find(ismember(TimeMIN(:,:),mintestend(4)),1,"first");

minteststart(5)="16:40:01";
mintestend(5)="17:03:00";

minstartindex(5)=find(ismember(TimeMIN(:,:),minteststart(5)),1,"first");
minendindex(5)=find(ismember(TimeMIN(:,:),mintestend(5)),1,"first");

minteststart(6)="10:41:00";
mintestend(6)="11:01:00";

minstartindex(6)=find(ismember(TimeMIN(:,:),minteststart(6)),1,"last");
minendindex(6)=find(ismember(TimeMIN(:,:),mintestend(6)),1,"last");

minteststart(7)="11:01:00";
mintestend(7)="11:22:00";

minstartindex(7)=find(ismember(TimeMIN(:,:),minteststart(7)),1,"last");
minendindex(7)=find(ismember(TimeMIN(:,:),mintestend(7)),1,"last");

minteststart(8)="11:22:00";
mintestend(8)="11:44:00";

minstartindex(8)=find(ismember(TimeMIN(:,:),minteststart(8)),1,"last");
minendindex(8)=find(ismember(TimeMIN(:,:),mintestend(8)),1,"last");

minteststart(9)="12:13:00";
mintestend(9)="12:34:11";

minstartindex(9)=find(ismember(TimeMIN(:,:),minteststart(9)),1,"last");
minendindex(9)=find(ismember(TimeMIN(:,:),mintestend(9)),1,"last");

minteststart(10)="12:34:11";
mintestend(10)="12:56:00";

minstartindex(10)=find(ismember(TimeMIN(:,:),minteststart(10)),1,"last");
minendindex(10)=find(ismember(TimeMIN(:,:),mintestend(10)),1,"last");
```

```
numtests = length(minteststart);

% Creating blank arrays to hold test data

minpmvel = zeros(2700,numtests);
minpmtemp = zeros(2700,numtests);
mintime = string(zeros(2700,numtests));
fittimeMIN = zeros(2700,numtests);

for i = 1:numtests                                      %This section of code
just fills up the zero arrays created above with relevant data
        sz(i)=minendindex(i)-minstartindex(i)+1;
        minpmvel(1:sz(i),i)=PlugVelMIN(minstartindex(i):minendindex(i));
        minpmtemp(1:sz(i),i)=PlugTempMIN(minstartindex(i):minendindex(i));
        mintime(1:sz(i),i)=TimeMIN(minstartindex(i):minendindex(i));
        plottimeMIN(1:sz(i),i)=datetime(mintime(1:sz(i),i));


end
        testing=smoothdata(minpmvel,1);

for i =1:numtests
        [M(i), I(i)]=min(minpmvel(1:sz(i),i));      %Finds minimum velocity,
along with index
        [M2(i),I2(i)]=min(testing(1:sz(i),i));      %Finds minimum velocity in
smoothed data
        SatTemp(i)=minpmtemp(I(i),i);               %Finds temp associated
with minimum velocity
        SatTempSmooth(i)=minpmtemp(I2(i),i);        %Same but for smoothed
data
        SatTempK(i)=SatTemp(i)+273.15;              %Temp in Kelvin
        SatTempKSmooth(i)=SatTempSmooth(i)+273.15;
        PPM(i)=10^(6.239-(2447/SatTempK(i)));       %Runs saturation
temperature through Eichelberger correlation to get ppm
        PPMSmooth(i)= 10^(6.239-(2447/SatTempKSmooth(i)));

        figure(i+10)                                            %Plotting all
individual UW MIN tests with minimum point marked
        titlestring = string(i);
        f(1)=plot(plottimeMIN(1:sz(i),i),minpmvel(1:sz(i),i));
        hold on
        f(2)=plot(plottimeMIN(1:sz(i),i),testing(1:sz(i),i));
        f(3)=scatter(plottimeMIN(I(i),i),M(i),80,'filled');
        f(4)=scatter(plottimeMIN(I2(i),i),M2(i),80,'filled');
        yyaxis left
        ylabel('Plugging Velocity [m/s]')
        yyaxis right
        f(5)=plot(plottimeMIN(1:sz(i),i),minpmtemp(1:sz(i),i));

        title(TestName+' UW MIN Plugging Test '+titlestring)
        legend(f,'Plug Vel','fit','Minimum Vel','Minimum Vel Smooth','Plugging
Temperature')
        ylim([160 200])
        xlabel('Time')
        ylabel('Temperature [C]')
```

```
        annotation('textbox',[0.15, 0.1, 0.1, 0.1],'String',"Sat temp is
"+SatTemp(i)+"C")
        annotation('textbox',[0.15, 0.2, 0.1, 0.1],'String',"Conc.
is"+PPM(i)+" ppm")


end
```

RDT VWE PROCEDURE

12. DETERMINATION OF OXYGEN ACTIVITY IN SODIUM BY THE EQUILIBRATION METHOD USING VANADIUM WIRES

12.1 PRINCIPLE

A vanadium wire is immersed in sodium for a time sufficient to establish equilibrium with respect to oxygen. Subsequent measurement of the oxygen concentration in the wire is related to an oxygen activity in sodium by means of the distribution coefficient.

12.2 SENSITIVITY AND PRECISION

This procedure is applicable in the range of 10 to 1000 μg of oxygen in vanadium (0.1 to 15 ppm of oxygen in sodium with the amount of vanadium wire sample usually available). The range can be extended down to 0.003 ppm of oxygen in sodium if vanadium wire samples ≥ 0.1 g are available.

12.3 APPARATUS

Specimen Equilibration Device Options. Fig. 12-1 is a schematic drawing of the Specimen Equilibration Module for use on reactors and large sodium systems. Fig. 12-2 is a schematic drawing of a typical Specimen Equilibration Device for use on small experimental systems. These modules shall conform to the requirements of RDT C 8-8. Fig. 12-3 shows a typical basket-type specimen holder and a second specimen equilibration device. The basket-type holder may be used with either an equilibration device or an equilibration module. A typical sample holder that may be used with static pots that have access ports and inert gas locks above the sodium is shown in Fig. 12-4. A holder of similar design may also be used with modular- or device-type apparatus.

Electropolishing Apparatus. This apparatus consists of a 3- to 4-cm-diameter by 7-cm-long hollow platinum or tantalum cathode and a 6.0- to 7.5-V low-impedance dc power supply.

Oxygen Determination Apparatus. This apparatus must be capable of determining 0.1 to 1.5% oxygen in vanadium metal by an inert-gas or vacuum-fusion technique. A LECO RO-16 Oxygen Determinator, manufactured by the Laboratory Equipment Company, has been used successfully by the originator of this method.

Magnetic Stirrer, with Teflon-coated stirring bars.

Forceps, self-locking type.

12.4 MATERIALS AND REAGENTS

Oxygen Standards. Approximately 100 and approximately 300 ppm oxygen in steel. LECO Oxygen Standards, Stock Numbers 501-645 and 501-646 have been found satisfactory.

Lintless Tissue. Cel-Fibe Wipes No. 1745, or equivalent.

Acetone. Technical grade.

Ethanol. Technical grade.

Electropolishing Solution. This solution is composed of 80 vol % absolute methanol-20 vol % concentrated sulfuric acid.

High-Purity Vanadium Wire. Annealed, 0.25 mm (0.010 in.) or 0.50 mm (0.020 in.) diameter with a tolerance of 0.005 mm (0.0002 in.). Typical impurity concentrations are: <300 ppm total metallic impurities (Ti + Zr + Hf shall be <20 ppm), <300 ppm total of oxygen, nitrogen, hydrogen, and carbon (none of which shall be >150 ppm). The wire surface shall be smooth and free of scale, showing only fine drawing marks. This surface must also be free of galling and pitting marks. Ductility and surface condition of the wire must be such as to permit bending the wire 180° about its own diameter without surface cracking. The ductility of the wire shall be sufficient to withstand, without fracture, six bends about its own diameter under the conditions described in paragraph A2.8 of ASTM A 510, which states in part:

> "One end of the specimen is clamped in a vise or bending machine, the jaws of which are rounded to a specific radius; and the wire is bent back and forth at a uniform rate through a total of 180°. Each 90° movement in either direction is counted as one bend."

12.5 PROCEDURE

12.5.1 Wire Preparation and Equilibration

1. Cut the high-purity vanadium wire into 9- to 10-cm lengths and straighten the pieces. Measure and record the length of wire to be equilibrated.

2. Holding the wire with clean dissecting forceps, carefully degrease the lengths of wire with lintless tissue moistened with acetone. (After degreasing, the wire must be handled only with the forceps.)

3. Insert the wires into the appropriate wire holder. If a basket-type holder is used, bend each wire into an equal-armed U and drop it into the basket with the bend toward the wire-mesh bottom. If a holder like that in Fig. 12-4 is used, fix the wires in place by bending their ends around the holder.

4. Insert the sample holder into the sodium system.

5. Choose an equilibration time from Table 12-1 and find the minimum-flow-rate parameter for the estimated concentration of oxygen in the sodium. (If no reliable concentration estimate is available, assume 0.01 ppm.) The equilibration time for 0.25-mm-dia. wires must be in the range of 4 to 30 hr. The equilibration time for 0.50-mm-dia. wires must be in the range of 16 to 120 hr.

6. Find the minimum sodium flow rate by multiplying the length of the wire sample (in cm) by the minimum-flow-rate parameter.

7. Establish at least the minimum sodium flow rate through the equilibration device and equilibrate the wires at 750 ± 5 C for the chosen time.

Table 12-1. Flow-Rate Parameter for Vanadium Wire Equilibration

	Equilibration Time for 0.25-mm Wire, hr				
	4	5	10	20	30
Oxygen Concentration in Sodium, ppm	Equilibration Time for 0.50-mm Wire, hr				
	16	20	40	80	120
	Minimum-Flow-Rate Parameter, gal/min per cm of wire				
10.	1.5×10^{-4}	1.2×10^{-4}	6.0×10^{-5}	3.0×10^{-5}	2.0×10^{-5}
1.	7.4×10^{-4}	5.9×10^{-4}	3.0×10^{-4}	1.5×10^{-4}	1.0×10^{-4}
0.1	2.2×10^{-3}	1.8×10^{-3}	9.2×10^{-4}	4.4×10^{-4}	2.9×10^{-4}
0.01	3.3×10^{-3}	2.6×10^{-3}	1.3×10^{-3}	6.6×10^{-4}	4.4×10^{-4}

12.5.2 Post-Equilibration Treatment

12.5.2.1 Procedure for Non-Radioactive Systems

1. Shut off sodium flow by closing inlet and outlet valves.

2. Pressurize the equilibration device with inert gas, open the drain valve, and drain the sodium from the equilibration device. (If drainage at 750 C is prohibited by local safety practices, cool the sodium in the device at a rate of at least 50 C/min down to 500 C before draining the sodium. Cooling may be accomplished, for example, by turning off the heaters and flowing cool sodium over the wires.)

3. Shut the drain valve and inert gas inlet valve.

4. Cool the equilibration device to a convenient tempature no less than 110 C.

5. Pull the wire holder from the equilibration device. Insert a holder to close the device.

NOTE: If withdrawal of wires at temperatures ≥110 C is prohibited by local safety practices, omit steps 4 and 5 and substitute steps 4a and 5a.

4a. Cool the equilibration device to ambient temperature.

5a. Pull the wire holder from the equilibration device. If the wire holder does not pull free easily, reseal the equilibration device, reheat it to about 150 C and repeat steps 2 through 5a. Finally, insert a spare holder to close the device.

6. Dissolve the sodium adhering to the holder in about 1000 ml of technical grade ethanol. (The large volume of ethanol prevents excessive heating of the wires.)

7. Rinse holder and wires with distilled water and allow the wires to dry.

NOTE: For the rest of the procedure, the wires must be handled with forceps.

8. Remove the wires from the holder. Only straight portions of the wire are used for analysis. Make cuts, as necessary, at least 3 mm from each bend.

9. Separate the wires for archival storage from those for immediate analysis.

10. Store the archival wires in a capped vial that is properly marked for identification.

11. Set the electropolish solution container on the magnetic stirrer and adjust the stirring rate to keep the solution moving steadily. Electropolish the wires for analysis to remove approximately 0.01 mm (0.0004 in.) from the surface. (An electropolishing current, 0.2 to 0.5 amp, should flow for about 30 sec total, 15 sec for each end.) Rinse with distilled water, then with methanol.

12. Determine the oxygen content of the wire by a standard inert-gas fusion or vacuum-fusion technique (e.g., by ASTM Method E 146, or if a LECO RO-16 Oxygen Determinator is used, by the procedure described in Section 12.5.3 below).

12.5.2.2 Procedure for Radioactive Systems

1. Shut off sodium flow by closing inlet and outlet valves.

2. Pressurize the equilibration device with inert gas, open the drain valve, and drain the sodium from the equilibration device. (If drainage at 750 C is prohibited by local safety practices, cool the sodium in the device at a rate of at least 50 C/min down to 500 C before draining the sodium. Cooling may be accomplished, for example, by turning off the heaters and flowing cool sodium over the wires.)

3. Shut the drain valve and the inert gas inlet valve.

4. Cool the equilibration device to a convenient temperature no less than 110 C.

5. Wait until activity has decayed to a tolerable level.

6. Pull the wire holder from the equilibration device. Insert a holder to close the device. Follow local radiation safety practices during this operation.

NOTE: If withdrawal of wires at temperatures ≥110 C is prohibited by local safety practices, substitute steps 4a, 5a, and 6a for steps 4, 5, and 6.

4a. Cool the equilibration device to ambient temperature.

5a. Wait until activity has decayed to a tolerable level.

6a. Pull the wire holder from the equilibration device. If the wire holder does not pull free easily, reseal the equilibration device, reheat it to about 150 C and repeat steps 2 through 6a. Finally, insert a spare holder to close the device. Follow local radiation safety practices during this operation.

7. Fasten the wire holder into a metal test tube carrier with a matching coupling at its open end.

8. Transport the protected wire holder to the laboratory.

9. Dissolve the sodium adhering to the holder in about 1000 ml of technical grade ethanol. (The large volume of ethanol prevents excessive heating of the wires.) Perform this operation in a hood or hot cell and according to local radiation safety practices. If alcohol is not appropriate for removal of the sodium (in a hot cell, for example) mercury may be used instead of alcohol.

10. Rinse the holder and wires with distilled water and allow the wires to dry.

NOTE: For the rest of the procedure, the wires must be handled with forceps.

11. Remove the wires from the holder. Only straight portions of the wire are used for analysis. Make cuts, as necessary, at least 3 mm from each bend.

12. Separate the wires for archival storage from those for immediate analysis.

13. Store the archival samples in a capped glass or metal vial that is properly marked for identification.

14. Set the electropolish solution container on the magnetic stirrer and adjust the stirring rate to keep the solution moving steadily. Electropolish the wires for analysis to remove approximately 0.01 mm (0.0004 in.) from the surface. (An electropolishing current, 0.2 to 0.5 amp, should flow for about 30 sec total, 15 sec for each end). Rinse with distilled water, then with methanol.

15. Determine the oxygen content of the wire by a standard inert-gas fusion or vacuum-fusion technique (e.g., by ASTM Method E 146, or if a LECO RO-16 Oxygen Determinator is used, by the procedure described in Section 12.5.3 below).

12.7 DISCUSSION

This entire procedure, excluding the equilibration time, requires approximately 3 to 4 hr.

Table 12-2 was calculated by using the following equation applicable to the equilibrium oxygen distribution between vanadium and sodium at 750 C.

$$\ln \frac{N_{\underline{O}_V}}{N_{\underline{O}_{Na}}} = -28.22 + 39.42\ (1 - N_{\underline{O}_V})^2$$

where

$N_{\underline{O}_V}$ = atom fraction of oxygen dissolved in vanadium

$N_{\underline{O}_{Na}}$ = atom fraction of oxygen dissolved in sodium

While the general procedure does not require a specific oxygen analyzer, the current or planned use of the LECO RO-16 Oxygen Determinator in a majority of the laboratories in the sodium technology community made it desirable to describe precautions and deviations from the recommended procedure that experience dictates are required for successful operation with this instrument. Because a step-by-step method was deemed to be the best way of highlighting potential operational problems and of presenting precautionery measures, a detailed procedure has been given in Section 12.5.3. Even this approach, however, has not proven satisfactory to identify all potential difficulties and their solution. Two additional problems are as follows:

1. Successful operation requires that both a "purge" and a "measure" pressure be approximately 12 psig and that they be equal within 0.1 psig.

2. Effective operation requires the maintenance of a fixed nitrogen purge rate of 0.8 to 2.0 liters/min. To prevent blockage of the purge gas exit orifice by particulates, the instrument is equipped with a paper filter in the line. This filter may become plugged and will require removal and replacement. The revised LECO instruction manual (1972) covers this maintenance step.

REVISED VWE PROCEDURE

Determination of Oxygen Concentration in Sodium by the Equilibration Method Using Vanadium Wires

Principle

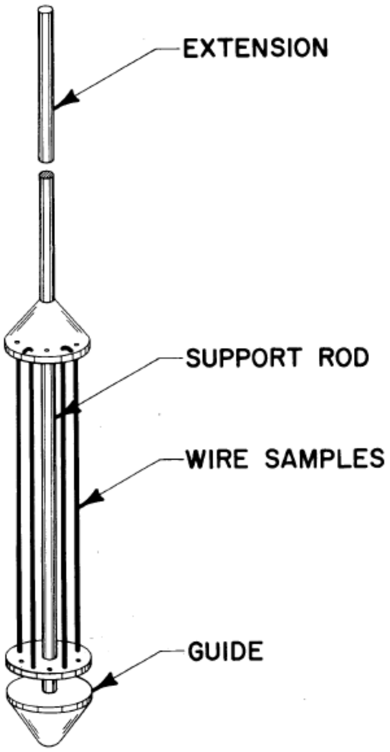
A vanadium wire is immersed in sodium for a time sufficient to establish equilibrium with respect to oxygen. Subsequent measurement of the oxygen concentration in the wire is related to oxygen concentration in sodium by means of an empirical correlation.

Sensitivity and Precision

This procedure is applicable in the range of 2 to 12 ppm of oxygen in sodium.

Apparatus

Specimen Equilibration Device Options. The figure below is a schematic drawing of a typical Specimen Equilibration Device for use on small experimental systems. The Specimen Equilibration Device should have a shroud of 200-size SS mesh protecting and retaining the wire specimens.



Electropolishing Apparatus. This apparatus consists of a 7.5cm long by 3.5cm wide by 0.5mm thick tantalum cathode and a digital DC power supply.

Oxygen Determination Apparatus. This apparatus must be capable of determining 0.5 to 1.5% oxygen in vanadium metal by an inert-gas or vacuum-fusion technique.

Magnetic Stirrer, with Teflon-coated stirring bars.

Forceps, self-locking type.

Materials and Reagents

Oxygen Standards. LECO shit, have to figure out what Anderson uses.

Lintless Tissue. Kimwipes or equivalent.

Acetone. Technical grade.

Ethanol. Technical grade.

Electropolishing Solution. This solution is composed of 80 vol% absolute methanol-20 vol% concentrated sulfuric acid.

High-Purity Vanadium Wire. Annealed, 0.25 mm (0.010 in.) diameter with a tolerance of 0.005 mm (0.0002 in.).

Latex Examination Gloves. Gloves should be free of powder or other coatings.

Procedure

Wire Preparation and Equilibration

1. Cut the high-purity vanadium wire into 10-cm lengths and straighten the pieces. Two lengths of wire constitute one sample for analysis.

2. Set the electropolish solution container on the magnetic stirrer and adjust the stirring rate to keep the solution moving steadily. Submerge the tantalum cathode in the electropolishing solution and connect the DC power supply’s positive output to the body of the locking forceps. Using the locking forceps, fully submerge the wires for equilibration in the electropolishing solution for 15 seconds at 0.3 amp polishing current. If the wire cannot be submerged fully in the electropolishing solution, grasp the midpoint of the wire with locking forceps and submerge each half of the wire for 15s. Rinse wires with distilled water, then dry using lintless wipes.

   [Following this step, wires should be handled only with forceps]

3. Insert the wires into the wire holder.

4. Insert the sample holder into the sodium system.

5. Establish a flow rate corresponding to Re = 2500 through the equilibration device and equilibrate the wires at 750 ± 3 C for 4 hours.

Post-Equilibration Treatment

1. Shut off sodium flow by closing inlet/outlet valves.

2. Drain the sodium from the equilibration device. Depending on the device/system used, this may be accomplished by pressurizing with inert gas and opening a drain valve or withdrawing the sample holder into an inert gas space. If drainage/withdrawal is prohibited by local safety practices or

undesired, cool the sodium in the device at a rate of at least 50 C/min down to 500C before draining the sodium. Cooling may be accomplished, for example, by turning off the heaters and flowing cool sodium over the wires.

3. Cool the equilibration device to ambient temperature under cover of inert gas.
4. Remove the equilibration device from sodium loop/inert gas cover.

5. Dissolve the sodium adhering to the holder in at least 1 liter of technical grade ethanol. (The large volume of ethanol prevents excessive heating of the wires.)

6. Rinse holder and wires with distilled water and allow the wires to dry.

   Note: For the rest of the procedure, the wires must be handled with forceps

7. Remove the wires from the holder. Only straight portions of the wire are used for analysis. Make cuts, as necessary, at least 3mm from each bend.

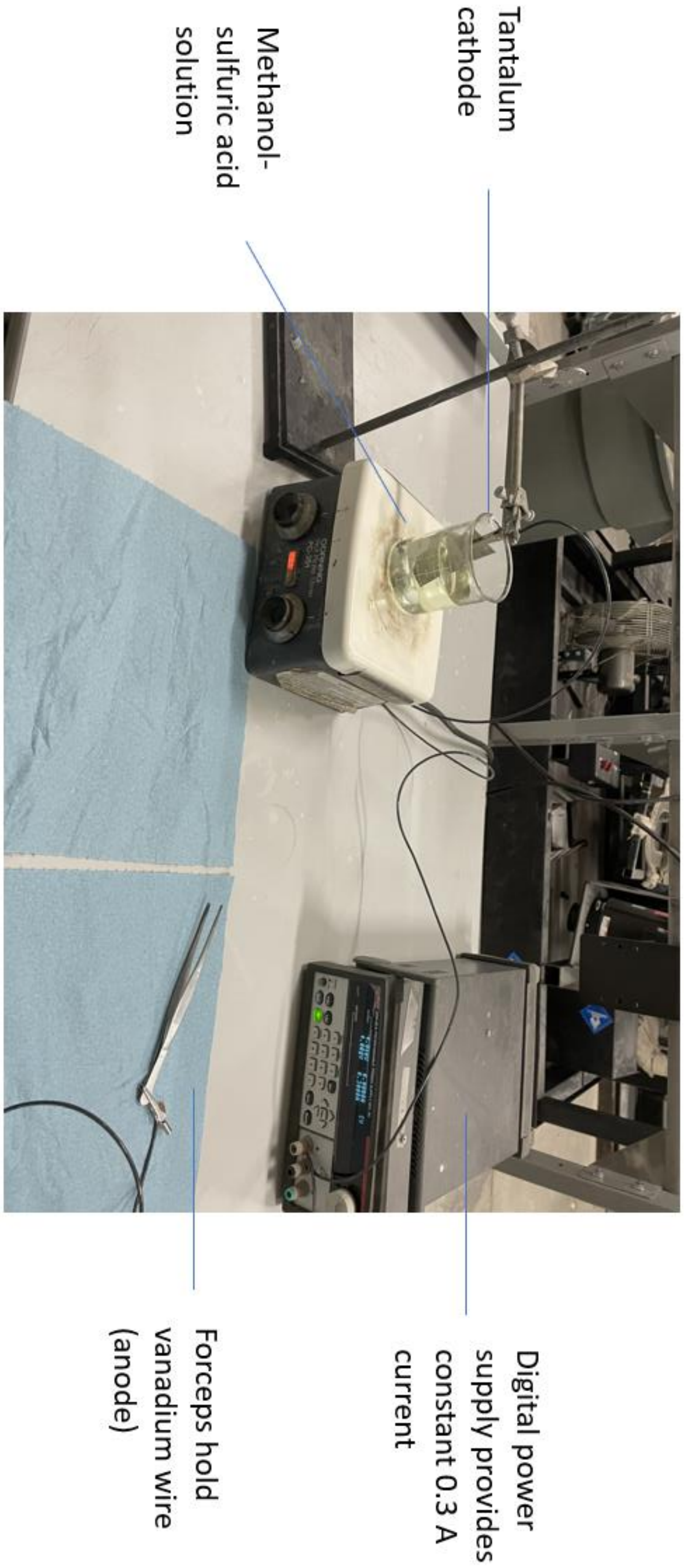
8. Separate the wires for archival storage from those for immediate analysis.

9. Store the archival wires in a capped vial/jar that is properly marked for identification.

10. Set the electropolish solution container on the magnetic stirrer and adjust the stirring rate to keep the solution moving steadily. Submerge the tantalum cathode in the electropolishing solution and connect the DC power supply’s positive output to the body of the locking forceps. Using the locking forceps, fully submerge the wires for equilibration in the electropolishing solution for 15 seconds at 0.3 amp polishing current. If the wire cannot be submerged fully in the electropolishing solution, grasp the midpoint of the wire with locking forceps and submerge each half of the wire for 15s. Rinse wires with distilled water, then dry using lintless wipes.

11. Determine the oxygen content of the wire samples by a standard inert-gas fusion or vacuum-fusion technique.

ELECTROPOLISHING APPARATUS



Appendix B: Accomplishments

Journal Papers:

A. C. Napora, R. L. Belgarde, T. A. Moreira, and M. H. Anderson, “Analysis of plugging meter measurement techniques for oxygen concentration determination in liquid sodium,” *Nuclear Engineering and Design*, vol. 421, p. 113112, May 2024, doi: 10.1016/J.NUCENGDES.2024.113112.

A.C. Napora, R.L. Belgarde, T.A. Moreira, and M.H. Anderson, “Assessment and correction of the vanadium-wire technique for oxygen measurement in sodium,” *Nuclear Engineering and Design*, publication pending.

J. Jacob, A. Napora, M. H. Anderson, and S. T. Sanders, “Molten Sodium Impurity Detection: Investigation of a Fiber-Optic Sensor as a Plugging Meter Alternative,” *IEEE Sens J*, Apr. 2024, doi: 10.1109/JSEN.2024.3362315.

M. T. Farmer *et al.*, “Development of a Sodium Fast Reactor Cartridge Loop Testing Capability for the Versatile Test Reactor,” *Nuclear Science and Engineering*, vol. 196, no. sup1, pp. 148–164, Oct. 2022, doi: 10.1080/00295639.2022.2052552.

Conference Paper:

J. Larson, J. Rein, M. Anderson, M. Weathered, and A. Napora, “Redevelopment of Vanadium Wire Sodium Oxygen Measurement Technique and Correlation to Plugging Meter for VTR Applications,” in *Transactions of the American Nuclear Society - Volume 123*, AMNS, 2020, pp. 1851–1854. doi: 10.13182/T123-33437.