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Liquid Metal In-Line Impurity Measuring Instruments (Sodium) State-of-the-Art Study

By

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I. SUMMARY

Certain impurities occurring in liquid-metal systems are the cause of objectionable precipitation and damaging chemical and metallurgical effects. The impurities usually of greatest concern are oxygen, hydrogen, carbon, and nitrogen. Several instruments have been developed for in-line service to detect oxygen, hydrogen, and carbon, and to measure their concentration in liquid metal. No in-line method of detecting nitrogen has been developed.

A large number of techniques have been evaluated for possible application to impurity measurement, but only a few have been feasible.

A. PLUGGING METER

The operation of a plugging meter is based upon the temperature/solubility relationship of the impurity in the liquid metal. By cooling the liquid metal, a temperature is reached at which a soluble impurity is precipitated. The operation of the plugging meter is to cool the liquid metal, inducing the precipitation and thereby indicating the temperature at which objectionable precipitation could occur elsewhere in the system. As an indicator of the precipitation temperature, the plugging meter is capable of excellent performance.

Since oxide is the usual precipitant, the plugging meter has often misleadingly been called an oxide meter. It is an oxide meter when no other soluble impurities are present. The plugging meter also responds to hydrides and, when this is the only impurity, a hydride calibration may be used; the meter then functions as a hydride meter. The combination of oxide and hydride may be registered simultaneously under certain conditions.

The performance of a plugging meter is inherently poor at low values of concentration, where the slope of the solubility curve is low. For most designs, the lower limit of good performance is of the order of 10 ppm, although operation at lower values is common. One design uses a variable volume orifice to improve the low-range performance.

The main concept in the operating principle is so readily understood, and the design and construction of a workable model is so simple, that considerable laxity in design and construction is prevalent. Often, the plugging meter is not constructed as a unified instrument, but rather, the essential functions are accomplished by the parts distributed on the loop. The design of a plugging meter does not involve any critical factors. Observance of a few rules regarding the placement of the cooling section, relative to the orifice and the sizing of the orifice, can ensure good performance. The poor performance of several plugging meters has been attributed to improper design of the cooling section and to its being placed too far upstream from the orifice. Recognition of this matter is evident in most recent designs.

The use of a variable orifice has become common in manually operated or programmed plugging meters. There is less tendency to use a variable orifice on automatic continuous plugging meters since complete plugging does not occur in normal operation. However, unusual circumstances or malfunction of the automatic control circuits may result in complete plugging and possibly the formation of an intractable plug. To avoid such an event, a variable orifice should be used in all plugging meters.

The wide variety of designs reported in the literature are evidence of the plugging meter simplicity, as mentioned above, and the fact that in most applications the requirements have not been critical; hence, a less-than-desired performance usually is acceptable. There has been no tendency for a specific design to be copied and become the model or established design. Also, there is no commercial plugging meter. Thus, although for classification purposes the plugging meter has been called an instrument, it actually has been treated as a piece of plumbing. This situation is improving.

B. ELECTROCHEMICAL CELL

The operation of an electrochemical cell is similar to the operation of the common electric power cell (battery). In the electrochemical cell, the liquid metal is one electrode. The voltage produced is a function of the oxygen activity in the liquid metal. The oxygen concentration is related to the activity, and the cell therefore functions as a concentration indicator. The cell response is specific to oxygen and may be correctly considered an oxygen activity, or concentration, indicator.

The electrochemical cell performs in the 1 to 100 ppm concentration range. The cell is temperature-sensitive, but the sensitivity is low enough to be readily accommodated, hence is not a great problem. However, the operating temperature range is limited. The recommended operating temperature is 600°F. The cell may be used uncalibrated with fair accuracy. For monitoring functions to indicate changes in concentration, the uncalibrated cell is satisfactory. A calibration is required for absolute values.

The solid oxide electrode is the "critical" part of the cell. Its development has required significant effort. It is a relatively delicate part and is subject to fracture by thermal or mechanical shock. Somewhat less critical is the reference electrode. In contrast with the plugging meter, the electrochemical cell is not a device readily made in the shop with the readily available materials of construction.

The development of the electrochemical cell has been conducted by only one organization. The instrument has been available commercially "off-the-shelf" for several years and has been subjected to considerable performance evaluation testing. The performance is generally regarded as satisfactory for typical applications.

C. DIAPHRAGM PERMEABILITY SEPARATOR

Several techniques of sensing impurities require the separation of the impurities from the liquid metal. By the use of a diaphragm of suitable material, in contact with the liquid metal, certain impurities may permeate through the diaphragm and register on a conventional instrument. This technique is used to sense hydrogen and carbon, two of the impurities of interest.

Nickel is one of the best materials to use for the separation of hydrogen. It is compatible with the liquid metal and readily passes hydrogen to the exclusion of the liquid metal. Several well established techniques for sensing and measuring the quantity of hydrogen released from the diaphragm have been used.

The design and construction of a diaphragm separator cell is relatively simple. The materials involved are readily available and have not required any special development effort. There are no critical design or material problems. A number of cells have been constructed and tested with generally satisfactory results. One prominent application of a hydrogen detector is as a water-to-sodium leak detector, making use of the fact that hydrogen is released in the reaction. For this function, response time and sensitivity are important qualifications. Tests show that the hydrogen-permeable diaphragm method is satisfactory.

A hydrogen detector is not available commercially off-the-shelf.

To separate carbon from the liquid metal, a diaphragm of iron or nickel may be used. The design and construction of a diaphragm separator cell for carbon is relatively simple. The materials involved are readily available and have not required special development effort. There are no extremely critical design or material problems. Preliminary experiments have demonstrated the feasibility of this method. The development of a cell and a carbon detection device to comprise a carbon meter for liquid metals is in progress. Only one organization is engaged in the development of the instrument. Based on present available data, success seems certain, hence a commercially available off-the-shelf instrument is expected in the near future.

D. RESISTANCE METER

The operation of the resistance meter is based upon the change in resistance of liquid metal as a function of impurities contained. The resistance change occurs as a result of a geometrical change — such as caused by bubbles and particulate matter — and by resistivity change caused by impurities in solution. The resistance change is measured by passing an electric current through the liquid metal. This method of sensing impurities is not specific to any impurity.

The problems in the design and construction of a resistance meter are relatively large. One of the problems involves making electrical contact to the liquid metal. Generally this problem is circumvented by using an inductive coupling technique. This method incurs fabrication and upper temperature limitation problems although these are not formidable. The temperature sensitivity is one of the major problems, since resistivity is a function of temperature as well as impurity concentration, and in the ranges involved in practical applications, an uncompensated temperature-induced change may exceed the impurity-induced change. The development of a suitable temperature compensator has been a significant part of the total development effort.

The development of the resistance meter has been primarily the result of efforts in one organization. A resistance meter, called the Liquid Metal Rhometer has been commercially available off-the-shelf for several years. It has been subjected to a substantial amount of performance evaluation testing. The performance has not been entirely satisfactory for most applications, and a considerable amount of modification work on the commercial models has been done.

Since it is not specific for any impurity, and responds to bubbles and particulate matter as well as soluble impurities, the range of concentration is not conveniently specified. A further problem is the recent discovery that the sensitivity to oxide is low or substantially zero. This matter is presently under review. A high sensitivity to hydrogen has been demonstrated.

Generally this instrument is regarded as of limited application as an indicator of impurities but may be very useful as a void or entrained gas indicator.

A modified method of operation has been considered and additional data recently acquired tend to substantiate the feasibility and superiority of the modified method.

II. INTRODUCTION

A. EFFECTS OF IMPURITIES

The consequences of impurities in the liquid metals, Na and NaK, when used as a heat transfer fluid, are (1) effects on the liquid physical properties, specifically those involved in the heat transfer function, and on the properties involved in the operation of the system and its components, and (2) effect of the liquid chemical properties, specifically those involved in the integrity of the materials contacted by the liquid metal.

B. TYPES AND FORMS OF IMPURITIES

Many impurities have been identified in liquid metal heat transfer systems, but in present technology these occur in very small, usually trace, quantities. Despite the apparent insignificance in terms of quantity, four of the impurities are detrimental even in small quantities. These impurities are oxygen, hydrogen, carbon, and nitrogen. They are carried by the liquid metal in various forms.

Oxygen is carried, (1) dissolved as a gas, but (2) more prevalently, as a compound with the liquid metal or other impurities in particulate form or dissolved according to the prevailing temperature/solubility condition. Reaction of oxygen with sodium is favored by the presence of hydrogen, and/or nitrogen.(1,2)

Hydrogen is carried in the same manner as oxygen. The solubility of hydrogen in sodium is affected by the presence of oxygen according to Reference 3 but according to Reference 1, a reaction is independent of other contaminants.

Carbon is carried (1) as a particulate, (2) dissolved, or (3) as a compound with the liquid metal or other impurities in particulate form or dissolved according to the prevailing temperature/solubility condition. The solubility of carbon is increased by the presence of oxygen.

Nitrogen is carried (1) as a gas by entrainment, (2) as a compound with other impurities, and (3) dissolved, although this form may be less prevalent since the solubility is very low.

The effect of each of these impurity elements depends upon the form in which it exists; the severity of the adverse effects depends upon system operational circumstances.

C. RELATIVE SIGNIFICANCE OF THE TYPES OF IMPURITIES

Plugging of the flow passages — due to the precipitation of excess impurities — and corrosion with the related damaging effects on the containment vessel materials are the main concerns in impurity measurement and control.

Generally the impurity concentration (particularly oxide) is relatively high during the initial operation of a system. The relatively high concentration is due to the "as-received" condition of the liquid metal and to impurities, such as gases and surface contamination, in the containment system. Consequently, the plugging problem must be considered beginning with the filling of the containment system. The severity of the problem during subsequent operation depends upon the effectiveness of the impurity control measures during operation. Generally these are sufficiently effective that, in typical operation, plugging is not an impending threat after the initial "clean-up" or cold-trapping.

In terms of the operating time scale, the damaging effects of the chemical or metallurgical nature, such as corrosion and mass transfer, are different from the plugging effects in that the damage continues throughout the operating time. The damage is time- and temperature-dependent, hence presents no problem during initial operation. Moreover the chemical and metallurgical damage continues at concentration levels below those at which plugging is much of a problem. Another difference is that plugging is a problem in low temperature regions whereas the chemical-metallurgical damage is greatest at the higher temperatures.

The importance of the problem of plugging and chemical-metallurgical damage is dependent upon such factors as the nature of the system, temperature, and required operating lifetime.

Impairment of the liquid metal physical properties, such as reduced thermal and electrical conductivity, is relatively small in the impurity ranges ordinarily encountered, so this aspect of impurity effects is of lesser importance in typical operations. However, the accumulation of impurities to form an "insulating" layer is a significant problem.

Precipitation of impurities, yielding particulate matter, is of concern where sliding mechanisms are involved, as the particulate matter abrasive qualities may damage sliding surfaces, or may prevent movement.

D. APPLICABLE INSTRUMENTS AND TECHNIQUES

The instruments and techniques herein described are those applicable to in-line operation. Methods which require the withdrawal of samples for analysis in the analytical laboratory are discussed in numerous other reports. Generally the in-line instruments are calibrated against the measurements obtained in the analytical laboratory.

In addition to the already-developed instruments described here, several techniques thought to have possibilities for development into practical instruments have been proposed from time-to-time. Most of the ideas which have been examined are discussed in References 4 and 5. Reference 5 is the initial report in a series.

This report provides background information showing the development sequence, development problems, and principles of operation to provide perspective on the state-of-the-art.

III. PLUGGING METER

A. BACKGROUND

Prior to the development of any form of plugging meter, it was observed, during the course of oxide solubility measurements, that oxide precipitated in the throat of the conduction pump used to circulate the sodium.(6) The precipitation restricted the flow and, if allowed to continue, resulted in plugging. The use of cooled copper electrodes on the pump was the factor causing precipitation onto the walls. The effect on flowrate was accentuated by the narrow passage through the pump. It was recognized that the temperature at which the plug formed indicated the oxide concentration. The use of this behavior as a means of determining concentration was not immediately accepted since the difficulty of unplugging made it seem like a "one-shot" measurement. Efforts were made to monitor the presence of oxide crystals by other means, but these showed little promise.

Later, in an application of liquid sodium to cool a reactor, it was decided that particles in excess of 0.05 in. in diameter could not be tolerated in the liquid sodium system. One form of particulate matter was known to be sodium oxide, soluble in sodium at high temperatures but subject to precipitation at low temperatures and, by the formation of particulate matter, capable of plugging the coolant passages.

To monitor the particle size and thereby avoid conditions leading to plugging in the main coolant passages, a plugging meter was developed. The plugging meter consisted of a length of pipe fitted with a flowmeter, a cooling section, and an orifice plate of several holes 0.05 in. in diameter.

The operation of the plugging meter was based upon creating a "worst-case" condition. The holes were sized to provide a more restricted passage than any of the system passages. The intent was to induce precipitation of oxides in the cooling section and, if the particulate matter thus formed was too large to pass through the holes, plugging at the orifice would result. Any particles small enough to pass through the orifice were considered small enough to pass through the remainder of the system without plugging it.

Although there were some uncertainties concerning the nature of plug formation and other aspects of operation, the early plugging meters were constructed according to the concept described. Some discrepancies in performance added doubts about the prevalent concept of design and operation. However, the performance of the plugging meter was sufficiently satisfactory and promising that its use continued and further development followed.

In subsequent studies concerning the nature of precipitate formation in cold traps, it was concluded that "the removal and retention of oxide by a cold trap appears to be due primarily to the mechanism of crystal growth at cooled surfaces rather than by mechanical filtration."(7)

This concept, applied to plugging meters, indicated that the design should be based upon the growth of the plug at the orifice surface rather than the growth in an upstream cooling section. Moreover, the precipitation of oxide in the cooling section has come to be viewed as an objectionable process since any precipitation on the walls is equivalent to a cold trap preceding the orifice which is the oxide detector. A false indication is the consequence. Accordingly, it has become design practice to recognize the need for the minimum temperature at the orifice plate and to avoid precipitation elsewhere.

In early plugging meter operations, unplugging was often a difficult and time-consuming process. To circumvent this problem, a variable orifice concept was introduced to provide a means of breaking the plug and provide a stream of relatively clean hot sodium to flush out the orifice. The popular method of accomplishing this was to form the orifice holes in a valve seat or disc rather than in a fixed plate. In this method, with the valve closed, the sodium passed through the holes in the seat, and plugging action was the same as with the orifice plate. To unplug, the valve was opened, resulting in the mechanical disruption of the plug, and the increased flow of cleaner, hotter sodium which dissolved and flushed away the oxide. Upon completion of the unplugging process, the valve was closed and was ready for the next plugging cycle.

Another way to avoid the difficulty often associated with unplugging has been to control the plug formation so that complete plugging and cessation of flow does not occur. This method of operation can be used when the partial plug and consequent partial flow cessation are sufficient to indicate the plugging temperature.

When a sufficient degree of plugging for measurement is obtained, the cooler is stopped, the heater is activated, and the partial plug is dissolved away.

B. PRINCIPLES OF OPERATION

Liquid metals used in heat transfer systems dissolve certain commonly occurring impurities. The limit to the amount of a specific impurity that can be dissolved in the liquid metal is a function of the temperature and the nature of the impurity and the liquid metal. This limit is the solution saturation, and any excess impurity remains undissolved. An increase in the temperature results in an increase in the saturation limit. The saturation limit is expressed by an equation of the form

$$\log C = A + BT_L^n$$

where C is the saturation limit or concentration, T_L is the temperature, and A, B, and n are constants determined by the materials involved.

This relationship is illustrated in Figure 1. A simplified analysis follows: Assume an initial condition in which all the impurity is in solution. The concentration and temperature values correspond to the region below the curve. Let the point S represent the initial values and assume that the temperature is decreased. The saturation limit is reached at the point L.

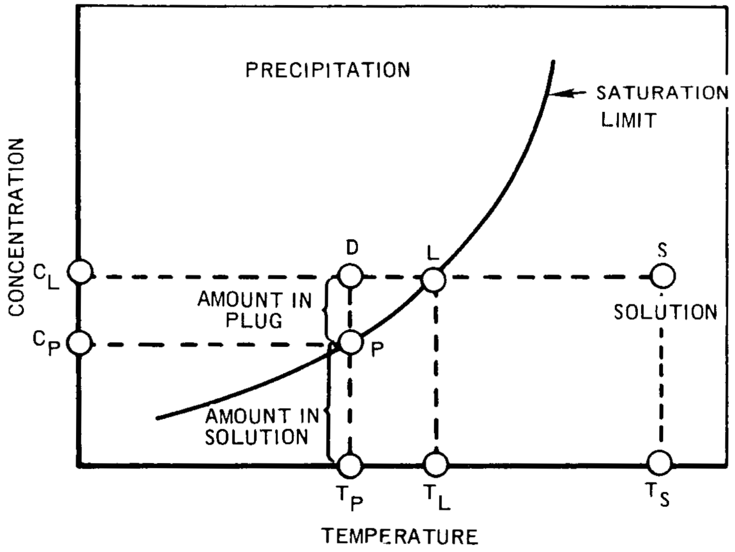

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Figure 1. Solubility Curve Illustrating Plugging Meter Operation

The concentration C_L corresponds to this temperature T_L. However, in the reduction of the temperature from T_S to T_L, nothing occurs to indicate when T_L is reached. To determine the value T_L, it is necessary to reduce the temperature below T_L to cause the precipitation of a detectable amount of impurity. This is represented by the point D, and the temperature at which a sufficient amount of precipitant is formed is T_P. In a plugging meter, a detectable amount of precipitant is the amount required to fill the orifice and thereby stop flow (or plug the orifice). (A modification of this definition is treated later.) Since some of the impurity, initially in solution, is precipitated to form a plug as the means of measurement, the amount of impurity remaining in solution is less, as indicated in the graph at the point P. The corresponding temperature is T_P. This is the temperature indicated by the plugging meter. The corresponding concentration is C_P. This indicated value is lower than the true value C_L. The magnitude of this inherent error is a function of the amount of impurity required to cause plugging. This is a function of the orifice volume and the criterion of plugging as well as the factor relating the proportion of impurity precipitated in the orifice to that precipitated elsewhere. The shape and temperature gradient in the volume preceding the plugging orifice determine the proportion of the precipitant usefully deposited in the orifice, compared to the part deposited on the vessel walls.

The plugging temperature T_P, as determined in the foregoing description, cannot be identical to the solubility limit temperature T_L. However, in the high range, that is, on the steep portion of the curve, these are so nearly identical in value that they may be considered the same for most practical purposes. In the lower range, where the slope of the curve is low, there is a significant difference between these temperatures. Also it should be noted that in the low range, a relatively large amount of liquid metal must flow through the orifice to provide sufficient impurity precipitate volume to plug the orifice. For a given flowrate, this requires a longer time. Since the extent of plugging is limited by the available impurity, the cooling rate must be reduced accordingly so that the precipitation remains controlled by the temperature. For operation in the low concentration range, a small orifice volume is preferred. The limited availability of impurity in relation to the orifice volume to be plugged, and the low slope of the temperature solubility curve in the low region, contribute to measurement difficulties in the low concentration range.

The concept of filling the orifice volume has been used for convenience. Typically, the orifice diameter is at least as great as the length as illustrated in Figure 2. The formation of an impurity agglomerate sufficient to stop flow through the orifice does not require complete filling of the orifice volume. The main factor to consider is the orifice diameter since the volume varies as the square of the diameter and, moreover, the full length of the orifice generally is not filled.

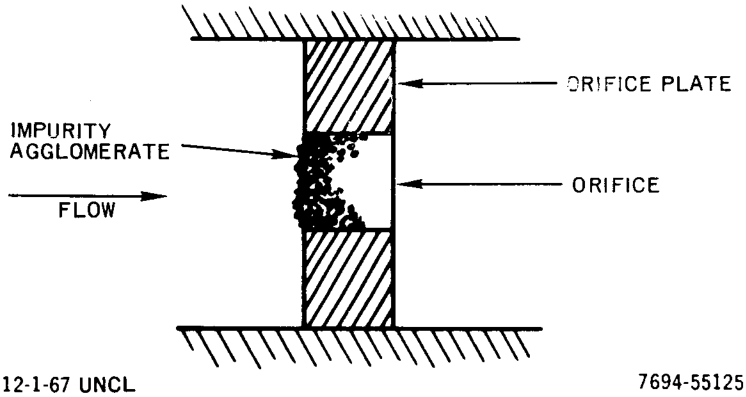

Figure 2. Plugged Orifice

Since the amount of impurity required to plug an orifice increases with its size, the large orifice necessitates a greater difference between plugging temperature and solubility limit temperature. This "overrun" in temperature increases the uncertainty in determining the true value. As the orifice is made progressively smaller, a point is reached at which the most minute excess of precipitate (over that which can be held in solution) is sufficient to fill the volume. This occurs very near the solubility saturation limit line and results in the minimum uncertainty since the required temperature "overrun" is negligible. Since the orifice size satisfying this condition is vanishingly small, the "before-plugging" flowrate is correspondingly small and hence impractical.

The orifice volume is a compromise between the uncertainty in plugging temperature (a reading always too low) and the practical means of detecting filling of the orifice volume (plugging). The usual method of detecting the filling or plugging is by the decrease of flow through the orifice as indicated by a flowmeter in the line. An electromagnetic flowmeter is typical.

The maximum orifice volume is established by another consideration, the total volume of impurity in the system. If the total volume is less than the required plug volume, plugging cannot occur. To achieve plugging, the required plug volume cannot exceed the volume of the precipitate available, which is the total volume of impurity minus the volume in solution and minus the volume inadvertently precipitated elsewhere.

1. Batch Method

The plugging operation described in the preceding section is characteristic of the batch method. In this method, the total quantity of liquid metal is small enough that, with a reasonable time for measurement, all the liquid metal passes through the orifice and is thus available for precipitation of the impurities in excess of the solubility limit. The batch method is illustrated in Figure 3. The valves are closed prior to initiation of a measurement so that the small volume of the subsystem becomes the batch.

As a consequence of the circulation, the progress of plug growth at the orifice is greatly increased over the rate which could occur in a noncirculating system depending entirely upon diffusion.

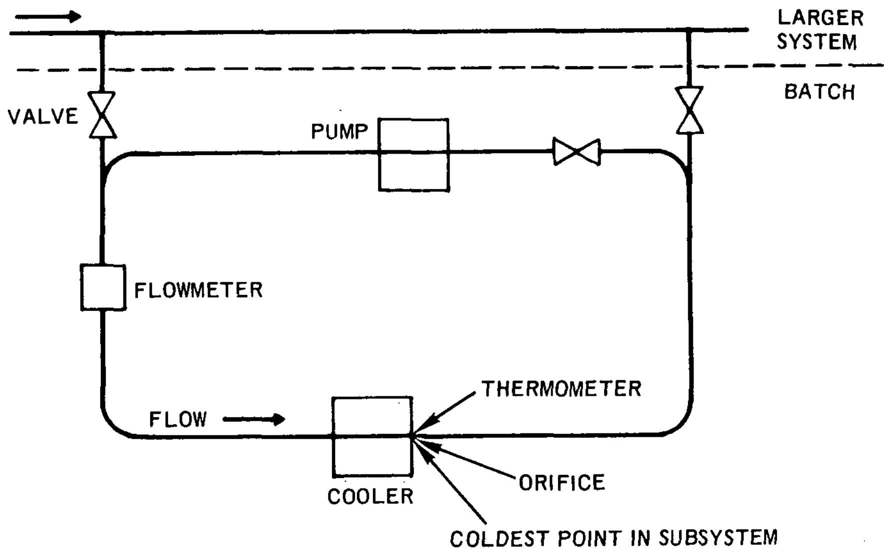

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Figure 3. Plugging Meter Illustrating the Batch Method of Operation

The following approach is used to determine the time factors.

Let

V_T = total liquid volume including impurity

V_{TI} = total volume of impurity

V_{TI}/V_T = system concentration C_T (by volume)

C = solubility limit (by volume), a function of temperature

t = time

V_P = volume of precipitate

V_S = volume of impurity in solution

Now,

$$V_{TI} = V_P + V_S \, .$$

At saturation and below,

$$V_S = V_T \cdot C$$

$$V_P = 0 \, .$$

Beyond saturation, that is below saturation temperature,

$$V_S = V_T \cdot C$$

$$V_P = V_{TI} - V_T \cdot C \, .$$

By making no allowance for diffusion, it will be assumed that each elemental volume of liquid metal must pass through the orifice and deposit in the orifice the excess impurity (the impurity in excess of the solubility limit at the temperature in the orifice region) until the orifice is filled (or plugged).

Let

V_O = orifice volume

Q_I = precipitation formation rate.

In a time t, at a rate Q_I, a volume V_P is produced. Thus

$$V_P = Q_I t \; .$$

In a sufficient period of time, the volume of precipitate V_P reaches the orifice volume V_O (or the orifice is filled). Then $V_O = Q_I T$ where T is the time required for filling.

Since

$$Q_I = \frac{V_P}{t} \; ,$$

then

$$V_O = \frac{V_P}{t} \, T \quad \text{or} \quad \frac{V_P}{t} = \frac{V_O}{T} \; .$$

But it was shown that

$$V_P = V_{TI} - V_T \cdot C \; ,$$

and dividing through by t gives

$$\frac{V_P}{t} = \frac{V_{TI} - V_T \cdot C}{t} \; .$$

So

$$\frac{V_O}{T} = \frac{V_{TI} - V_T \cdot C}{t}$$

and

$$V_O = \frac{V_{TI} - V_T \cdot C}{t} \cdot T \; .$$

Since V_{TI} is the total volume of impurity and V_T is the total volume of liquid metal, the total concentration C_T is given by

$$C_T = \frac{V_{TI}}{V_T} \quad \text{or} \quad V_{TI} = V_T C_T \; .$$

Using this value of V_{TI} we have

$$V_O = \frac{V_T C_T - V_T \cdot C}{t} \cdot T = \frac{V_T(C_T - C)}{t} T .$$

Since $V_T/t = Q$, the total flowrate

$$V_O = Q(C_T - C)T$$

or

$$T = \frac{V_O}{Q(C_T - C)} ,$$

which is the time to "fill" the orifice.

The cooling rate is not critical but should be fast enough that the liquid metal makes more passes through the orifice than is otherwise required to deposit the excess impurity. However, the rate should not exceed the limit imposed by a limited precipitation rate such as discussed on Page 20 .

The total volume V_T of the liquid metal in the batch must be large enough to provide sufficient impurity precipitant V_P, so the minimum volume system is

$$V_T = \frac{V_O}{(C_T - C)} .$$

2. Bypass Method

In the bypass method, the valves shown in the illustration are not closed, hence the system liquid metal flows continuously through the loop. The pump shown may not be necessary since the system pressure may be large enough to maintain an adequate circulation. A valve in the pump line may be used to adjust the pressure across the plugging meter.

The principles of operation of the bypass method are the same as those described for the batch method. Substitution of expressions for volumetric flowrate and time in place of the volume as in the foregoing analyses shows that the same results are obtained.

Experimental data(7,8) show the results are the same by both methods.

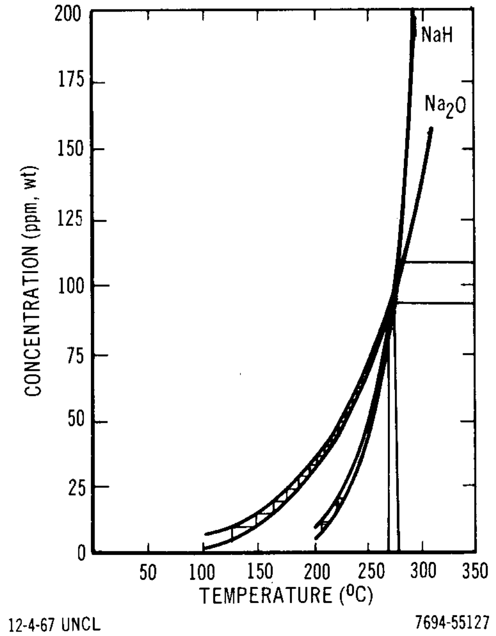

Figure 4. Solubility of NaH and NaO_2 as a Function of Temperature

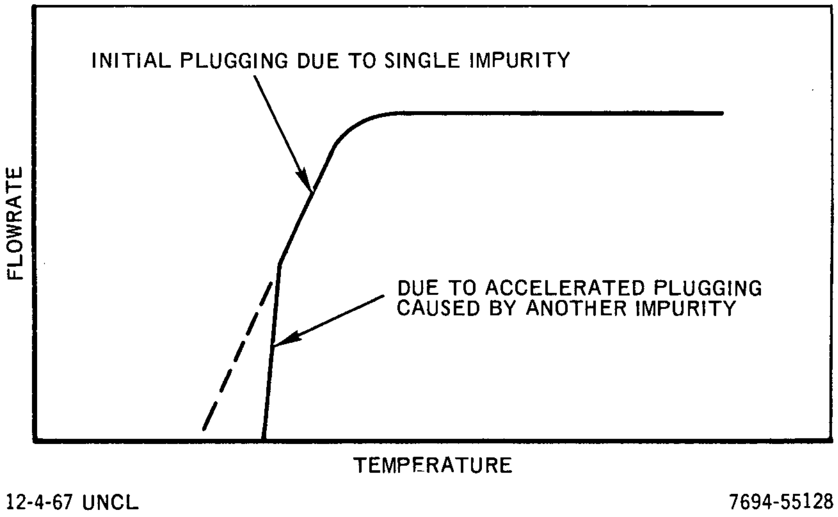

Figure 5. Plugging Curve Illustrating the Effect of a Second Impurity

3. Multiple Impurities

The situation involving several impurities having different solubility/temperature relationships is illustrated in the following discussion for a typical case, sodium monoxide (Na_2O) and sodium hydride (NaH) in liquid sodium. Figure 4 shows the typical temperature solubility relationships for these materials in the range of interest. The curves shown illustrate the relationships and are not necessarily exact. The numerical values used in this discussion are approximate accordingly.

The analysis is similar to that presented for the case of one impurity. Again it is emphasized that, for a plugging meter to function, there is a minimum amount of impurity which must be precipitated; hence while the temperature is decreasing, the solubility limit must be exceeded by an amount determined by the design and operating features. The amount by which the solubility limit curve must be exceeded is illustrated in Figure 4.

As the temperature is decreased, approaching about 275°C, the Na_2O curve must be crossed first. This means that if the Na_2O concentration is higher than about 97 ppm, the plugging will be initiated by the Na_2O. Moreover, at levels above about 107 ppm the plugging is determined entirely by the Na_2O and the NaH cannot be detected regardless of its concentration. If the Na_2O concentration is below about 97 ppm, any NaH present will initiate the plugging. Below about 92 ppm the plugging is determined entirely by the NaH and any Na_2O of a lower concentration cannot be detected.

In the region between concentration values of 107 and 92 ppm, and the corresponding temperature range 270 to 280°C, both impurities contribute to plugging. This results in plugging occurring sooner, and at a higher temperature, than when only one impurity contributes to the plugging. In this region, the plugging curve has the appearance illustrated in Figure 5. The plugging curve "break" of the type illustrated is relatively rare, and a consideration of the factors which cause it shows why it is unusual. If the amount of precipitated impurity required to cause plugging is vanishingly small, as would be the case for a vanishingly small orifice, the width of the bands shown in Figure 4 would shrink to the lines representing the solubility limit. Then the lines would cross at a point, and the common region would be zero. Consequently the plugging would be initiated and completed by one impurity only. In practical designs the amount required is not vanishingly small, but a small volume of precipitate is sufficient. The amount determines the width of the band, hence the size of the common region is a function of the amount of precipitant required. For the case of Na_2O and NaH in sodium, considered in the example, the region is very small and extends over a concentration range of 92 to 107 ppm. The simultaneous occurrence of these two impurities within this range would be required to produce a plugging curve break of the type shown in Figure 5.

In the previous paragraphs, the effect of multiple impurities was shown to contribute to an accelerated plugging curve when the concentrations of the impurities involved were of the same order of magnitude.

A more commonly observed break is one of the form shown in Figure 6. The inflection indicates that, after plugging has been initiated, the plugging action is retarded prior to completion of the plugging and the flowrate remains nearly constant, or does not decrease as rapidly, even though the temperature continues to decrease. In some instances the plugging action is resumed and continues until plugging is complete or until another retarding range is reached. There are a number of conditions which could cause this behavior. It is conceivable that, as the plug is formed and the flow progressively decreases, a point is reached in which the mechanical forces – the fluid flow pressure or erosion – retards further plug development. Precipitation of impurities in a

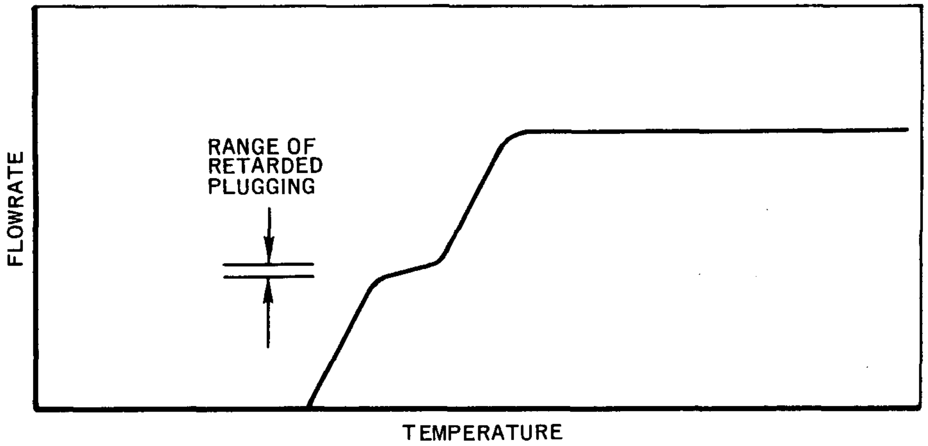

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Figure 6. Plugging Curve Showing an Arrested Plug Growth

cooling section upstream, thereby passing on relatively pure liquid metal to the orifice with the consequent retarding of plug development, may occur in some designs. Also a reduction in cooling rate can retard the plugging rate.

4. Criteria of Plugging

In the discussion of plugging, the detectable amount of precipitant was defined as the amount required to fill the orifice, or, as illustrated in Figure 2, the amount required to stop the flow. This concept was presented to facilitate development of the equations and describe the operation. It is obvious that the plugging process need not proceed to the point of complete cessation of flow. Moreover, complete plugging is generally undesirable since unplugging is difficult in some instances, and the total time required is greater. Also, as shown, the temperature at the point of complete plugging is always lower than the solubility limit temperature, hence any interpretation in terms of concentration level is subject to the correspondingly reduced value. For reasons such as these, the plugging temperature is ordinarily taken to be the temperature at which plugging begins. This is easily determined when the flowrate decreases linearly with temperature as illustrated in Figure 7. A curve with a well-defined beginning of plugging is not always obtained. Often, random disturbances cause a distribution of data points as illustrated in Figure 8. In such cases it is customary to draw straight lines through the points as shown and define the point of intersection as the plugging temperature.

In either case, the plugging need proceed only as far as required to establish the point at which plugging begins. This depends upon the characteristics of the random fluctuations. It is possible to pass the flow signal through suitable control circuits which enable the temperature to be oscillated about the temperature at which plugging begins under the overall control of the flowrate signal, so that this point is automatically and continuously determined.

It is evident that, when plugging temperature is defined as the temperature of incipient plugging, the equations presented require a reduced value for the orifice volume V_O. This reduced value, corresponding to partial filling, may be designated v_o. The numerical value of v_o is related to the quality of the plugging curve, that is, a sharp definite break as shown in Figure 7, or a slightly

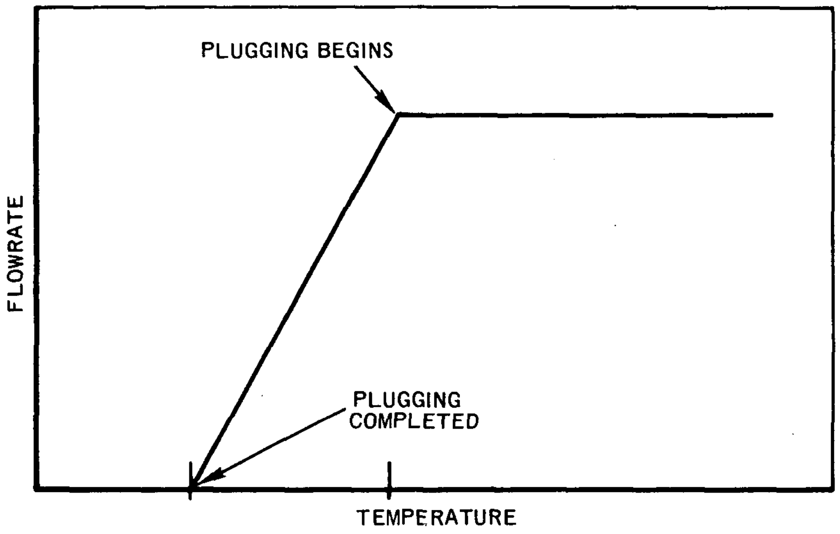

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Figure 7. Plugging Curve Showing a Well-Defined Break

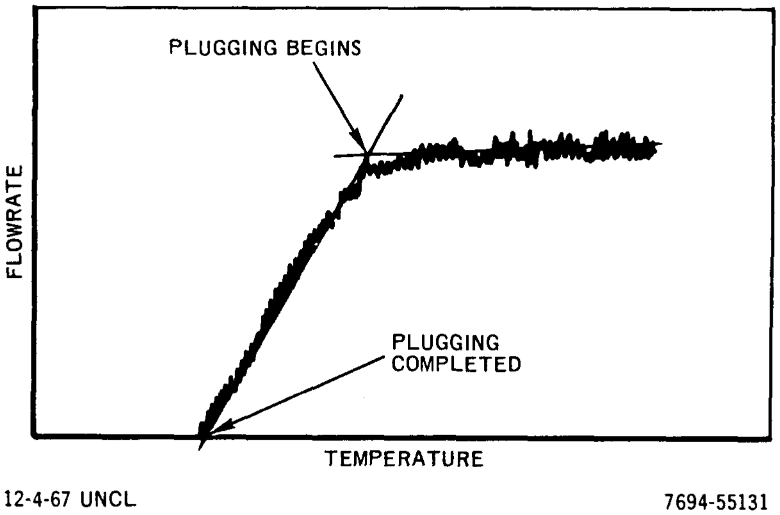

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Figure 8. Plugging Curve Illustrating a Poorly Defined Break

irregular case as shown in Figure 8, or a much poorer curve as occurs in some cases. The volume v_o may be estimated as some fraction of V_O, a tenth to a half, subject to experimental confirmation.

5. Operating Method

The operating methods may be categorized as (1) manual, (2) programmed, and (3) automatic. A further operational feature involves the extent of plugging.

a. Manual

In manual operation the "plugging run" consists of actuating the cooler and observing the resultant flow vs temperature relationship. Temperature is measured at the plugging orifice. The cooling may be continued to the point of complete plugging or may be stopped during partial plugging at the operator's choice. Interpretation of the data, i.e., determination of the plugging temperature, is subject to the choice of criteria used by the analyst (see Part B-4, above, Criteria of Plugging).

The method of cooling may be as simple as removing the thermal insulation from a section of pipe upstream from the orifice. Usually that section of pipe is finned to improve heat dissipation. A blower also is used when a higher cooling rate is desired or when a lower minimum temperature is needed. In nearly all cases, air is used for cooling. The rate and ultimate temperature are determined by the capacity of the cooling system in relation to the heat load and is otherwise uncontrolled. Upon completion of a plugging run, the cooler is deactivated, heat is applied, and, if a variable orifice is used, it is opened. Opening of the variable orifice permits a high flowrate of relatively pure hot liquid metal to flush out the plugs and restore the meter to the initial condition for another plugging run. If a variable orifice is not used, the dissolving of the plug proceeds at a slower rate, limited by the rate at which heat from an external source can be applied. Dissolving is facilitated by flow through the orifice, hence it is advantageous to operate so that the orifice is never completely plugged.

b. Programmed Operation

In programmed operation, the cooling rate is regulated by a control mechanism and the temperature lower limit is determined by a control actuated by a flowrate signal. Plugging is determined by a limit switch on the flowmeter set so that, when the flow is a predetermined fraction of the nominal unplugged rate, a signal operates the cooler control. The plugging temperature may be taken as that at which the flow drops to the predetermined fraction or may be determined as discussed in Part 4 above. Recycling, i.e., unplugging and restoring the operating condition for another plugging run, is accomplished by the programmer operating the control devices. The advantage of the programmed operation over the manual is that operation is unattended and, by better control of the operating variables, the data may be more repeatable. The disadvantage is the increased complexity of control apparatus. However, such apparatus is well developed and these methods are widely used in the process instrumentation field.

c. Automatic Operation

The automatic operation is similar to the programmed operation except that the operating cycle is determined by the operating conditions rather than by a fixed, predetermined program. The operation is more characteristic of a closed loop servo system and as such can be set to determine the point of incipient plugging and provide an essentially continuous indication of plugging temperature.

The advantage of automatic operation over the programmed operation is in the possibility of higher accuracy, improved repeatability, and continuous data display. The higher accuracy is possible since the operation depends upon cycling around (above and below) the incipient plugging temperature, thus minimizing the effect of exceeding the solubility limit and incurring the resulting errors previously discussed. The additional complexity due to the automatic control equipment may be a disadvantage. However, the type of control equipment used is well developed and used widely in other process instrumentation applications.

6. Type of Orifice

The foregoing discussion has shown that the problem of unplugging, to enable repeated plugging measurements, has engendered the development of the variable orifice design in addition to the original fixed orifice design. The advantage of the variable orifice design is that it can always be unplugged. It may be operated in the manner of a fixed orifice design, with the variable orifice feature used only when the plug is intractable.

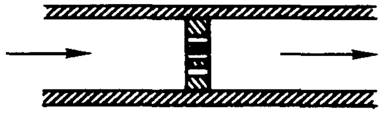
In systems in which the liquid metal is relatively pure, and when the plugging meter operation is based upon partial plugging only, unplugging may not be a problem, and during such operation the fixed orifice design may be satisfactory. However, during initial operation of a liquid metal loop, and in the event of containment vessel leak or failure of the plugging meter cooling control, the ideal conditions may not be maintained and an intractable plug may be formed in the plugging meter. In such cases, the variable orifice design provides a simple solution. Figure 9 shows the various forms of orifices reported in the literature on plugging meters.

7. Sensitivity

The sensitivity of an instrument is defined as the smallest change in the value of a variable to which the instrument will respond. Several aspects of sensitivity in plugging meters have been discussed. One of these is the quantity of precipitate required to produce a detectable flow reduction. Since flow is the result of a pressure difference, the discussion of flow reduction requires a consideration of the pressure, P, vs volumetric flowrate, Q, of the pressure source (pump) and hydraulic load (plugging meter).

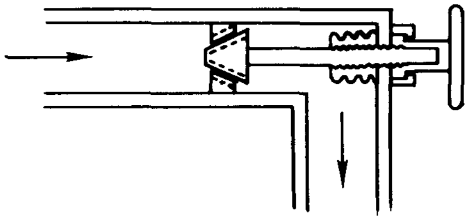
The P vs Q relationships involved are shown in Figure 10. The plugging meter is the same in the two cases shown. The difference in the two cases is in the pressure source (pump) characteristic. The word "pump" is used here to indicate any source of pressure. It may be a pump in the plugging meter circuit, or it may be a pressure drop in the system to which the plugging meter is connected. The optional arrangements are illustrated in the plugging meter shown in Figure 16, for example.

The pumps in the graphs A and B of Figure 10 have the same power. They differ only in the P vs Q characteristic or slope. The flowrate prior to any plugging is shown as Q_u. As the orifice becomes plugged, the plugging meter hydraulic characteristic changes from the curve labelled "unplugged" to a curve of steeper slope such as that labelled "partially plugged." This curve represents



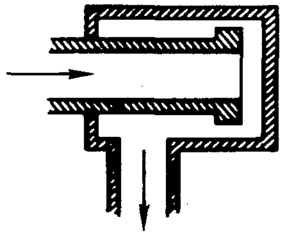
(A) FIXED ORIFICE:

A PERFORATED PLATE PLACED IN A PIPE. IT WAS THE FIRST TYPE USED, BUT PROBLEMS WITH UNPLUGGING HAVE LIMITED ITS USEFULNESS.



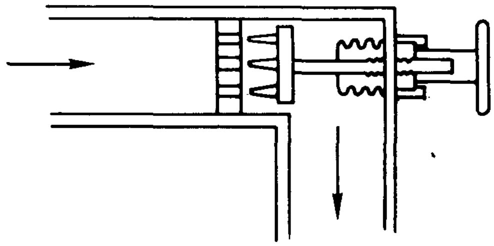
(B) VALVE ORIFICE:

CONSISTS OF SLOTS IN THE VALVE SEAT OR IN THE VALVE PLUG. IT IS BECOMING WIDELY USED TO FACILITATE UNPLUGGING.



(C) ANNULAR ORIFICE:

THE ORIFICE IS THE ANNULAR CLEARANCE BETWEEN TWO CONCENTRIC TUBES.



(D) VARIABLE ORIFICE:

A PERFORATED PLATE AND A PLUG, CONSISTING OF TAPERED PINS MOUNTED TO PARTIALLY CLOSE THE HOLES IN THE PERFORATED PLATE. THE OBJECT IS TO PROVIDE A VARIABLE AREA ORIFICE TO MATCH THE IMPURITY CONCENTRATION LEVEL.

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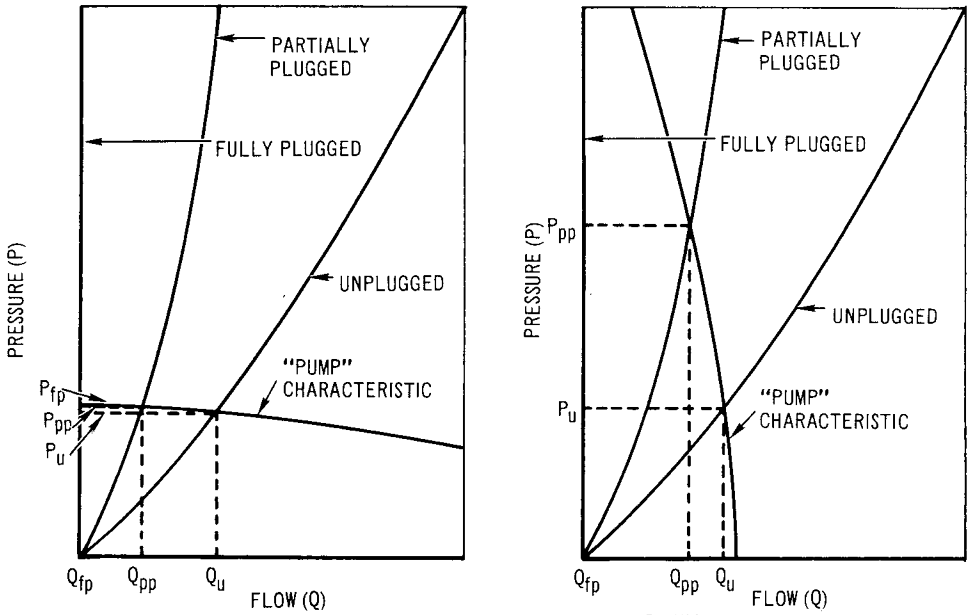
Figure 9. Various Forms of Orifices



A. LOW IMPEDANCE HYDRAULIC POWER SOURCE (PUMP)

B. HIGH IMPEDANCE HYDRAULIC POWER SOURCE (PUMP)

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Figure 10. Pressure vs Flow Curves to Show the Effect of "Pump" Characteristics on Plugging Meter Sensitivity

a particular extent of plug formation and is the same in both cases. As the extent of plugging proceeds, the slope becomes steeper and the limit approaches the vertical axis as shown.

Graph A shows the flow values for the case of a low impedance pump. As plugging proceeds, the flow decreases from Q_u to Q_{pp} and to Q_{fp} or zero if the process is continued. Graph B shows the flow values for the case of a high impedance pump. Comparison of these two graphs shows that the flow reduction in the case of a low impedance pump is much greater than in the case of a high impedance pump for the same extent of partial plug formation. It is evident, that for a given amount of impurity to initiate plugging, a flowrate decrease is more readily discernible in the case of the low impedance pump, hence this case has the higher sensitivity.

To achieve suitable hydraulic impedance relationship, bypass flow lines are used in some installations.

The high impedance pump method may be objectionable since, in its use, the maximum pumping power, $(PQ)_{(max)}$ is less than the power at incipient

TABLE 1

PLUGGING METERS DESCRIBED IN THE LITERATURE

Place of Use	Description							Reference No.	Figure No.	Remarks
	Flowrate (cm^3/sec)	Cooling Rate (°C/sec)	No. Holes	Hole Shape	Hole Size (cm)	Orifice Type	Effective Orifice Area (cm^2)			
Rapsodie (Fr.)	27.8	0.083	12	R	0.1	P	0.094	9	11	Type 1, manual, plug and unplug easy, operation satisfactory.
Rapsodie (Fr.)	55.6	0.083	50	R	0.1	-	0.493	9	12	Type 2, manual, plug easy, unplug diff., onset of plugging unclear, operation unsatisfactory.
Rapsodie (Fr.)	41.7	0.083	12	S	0.1 x 0.1	P	0.120	9	13	Type 3, manual, plug and unplug easy, operation very satisfactory.
Rapsodie (Fr.)	18.9	0.083	12	R	0.1	-	0.0943	9	-	Type 1A, discontinuous automatic, not entirely satisfactory.
Rapsodie (Fr.)	41.7	~0.083	12	S	0.1 x 0.1	-	0.120	9	14	Type 3A, very satisfactory.
MSA (USA)	63.3	-	16	R	0.127	P	0.203	10	15	-
MSA (USA)	-	-	15	R	0.127	P	0.190	6	16	Manual, satisfactory operation.
ORNL (USA)	6.33	-	4	1/2 R	0.094	V	0.028	11	18	Manual, fluid NaK, satisfactory.
ORNL (USA)	5.67	0.371	4	1/2 R	0.094	V	0.028	11	-	Manual, fluid NaK, satisfactory.
Hallam (USA)	63.3	0.046	-	-	-	P	-	12	20	Programmed, plug and unplug easy, very satisfactory.
P.F.R. (UK)	-	-	-	-	-	A	-	13	23	Automatic, used special pressure regulator, operation satisfactory.
ANL (USA)	7.1-16.2	0.055-0.358	10	S	0.081 x 0.040	-	0.0328	14	24	Satisfactory, range of flow and cooling rate had no effect.
AI (USA)	6.33	0.464	4	1/2 R	0.127	V	0.048	16	26	Manual, satisfactory, range of flow and cooling rate had no effect.
- (USSR)	-	0.005-0.618	16	S	0.10 x 0.10	-	0.160	17	28	-
- (USSR)	-	0.005-0.618	16	S	0.10 x 0.10	-	0.160	17	28	-
- (USSR)	-	0.005-0.618	34	S	0.05 x 0.05	-	0.085	17	28	-
JEARI (Japan)	26.9	0.005	17	R	0.12	VP	0.127	19	32	Manual, plug and unplug easy, very satisfactory operation.
SRE (USA)	63.3	0.046-0.371	-	-	-	-	-	20	34	Manual, operation satisfactory.
KAPL (USA)	31.6	0.00093-0.046	8	R	0.127	P	0.102	7	36	Manual, plug and unplug easy, operation satisfactory.
KAPL (USA)	50.6-95.0	0.0093-0.185	16	R	0.127	P	0.203	7	38	Manual, plug and unplug easy, operation satisfactory.
MSA (USA)	-	0.00093-0.093	1	R	0.127	P	0.013	6	17	Manual, used to study effect of cooling rate.
KAPL (USA)	19	0.046-0.092	17	R	0.117	P	0.137	11	40	Manual, prototype of model used in USS Seawolf.
KAPL (USA)	63.3	-	21	R	0.127	P	0.268	14	42	Manual, used in early cold trap studies.

NOTES:
R – Round
S – Square
1/2 R – Half-Round
P – Plate
V – Valve
A – Annular

plugging, hence the pumping power increases during incipient plugging. This increase in pumping power would seem to hinder the aggregation of precipitates within the orifice by causing them to be pushed out and washed downstream. This action prevents or delays plugging. This effect is unevaluated and may be negligible in practical cases.

While the reduction in flowrate is the usual indicator of plugging, the rise in pressure could be used. Graph B shows that, for a high impedance pump, the change in pressure is relatively great as plugging proceeds. In a system having a high impedance pump, the pressure indicator method provides a higher sensitivity.

C. PLUGGING METER DESIGNS USED ON VARIOUS PROGRAMS

The design features and performance of various plugging meters as reported in the literature are summarized in Table 1. A more detailed description and schematic illustrations are presented in the following paragraphs. An extensive collection of descriptions and illustrations is presented to show the variety of designs and the range of design and operating features. This matter is of interest in view of the various (sometimes conflicting) statements made regarding criticalness of some design and operating features.

The plugging meter illustrated in Figure 11 was designated Type I in the Rapsodie test program.(9) A simple disc containing 12 holes 0.1 cm (0.0394-in.) in diameter constitutes the plugging orifice. The sodium passes through an economizer and then through a finned air-cooled tube prior to entering the orifice plate. The cooling rate is 0.083°C/sec (9°F/min). A thermocouple at the orifice exit indicates the temperature. Flow is indicated by the electromagnetic flowmeter. The flowrate is of the order of 27.8 cm^3/sec (0.441 gpm). The operation is satisfactory and unplugging is easily accomplished by reheating. This plugging meter has been adapted to discontinuous automatic operation (programmed). An adjustable contact on the flow recorder controls the operation of the cooler so that, when the flow decreases as the result of plugging, to an established lower limit, the cooler is turned off and the partial plug is dissolved. When the nominal flowrate is again attained, and a programmed 10-minute delay to ensure complete unplugging has occurred, the cooling and consequent plugging

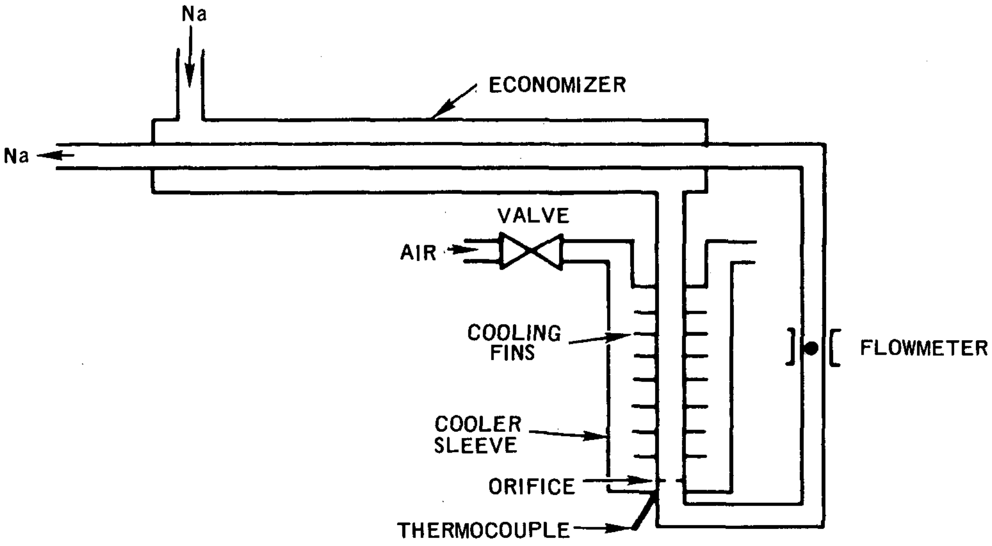

Figure 11. Type 1 Plugging Meter (Rapsodie)

cycle are resumed. The experimentally chosen cooling rate of 0.083°C/sec is a compromise between the requirement for a high rate to shorten the cycle time and a low rate to enable precise determination of the start of plugging.

The plugging meter designated Type 2 in the Rapsodie test program$^{(9)}$ is illustrated in Figure 12. The orifice is in the form of a check valve containing 50 holes 0.1 cm (0.0394-in.) in diameter. The flowrate used was 55.6 cm^3/sec (0.88 gpm). The cooling rate was 0.083°C/sec (9°F/min). The performance of this plugging meter was not satisfactory. Due to thermal inertia, the valve's response to cooling was sluggish. Part of the oxide was deposited in the cooling coil. The onset of plugging was not clearly defined; also unplugging was difficult.

Figure 13 shows the design designated Type 3 in the Rapsodie test program.$^{(9)}$ The orifice consists of a cap having 12 notches 0.1 x 0.1 cm (0.0394 x 0.0394-in.) at the base of the economizer. The economizer is finned and air-cooled at the plugging orifice end. The flowrate was of the order of 41.7 cm^3/sec (0.66 gpm) and the cooling rate was 0.0833°C/sec (9°F/min). With this configuration, the manual operation was very satisfactory and unplugging was a achieved simply by reheating. A plugging temperature accuracy of ±5°C was obtained.

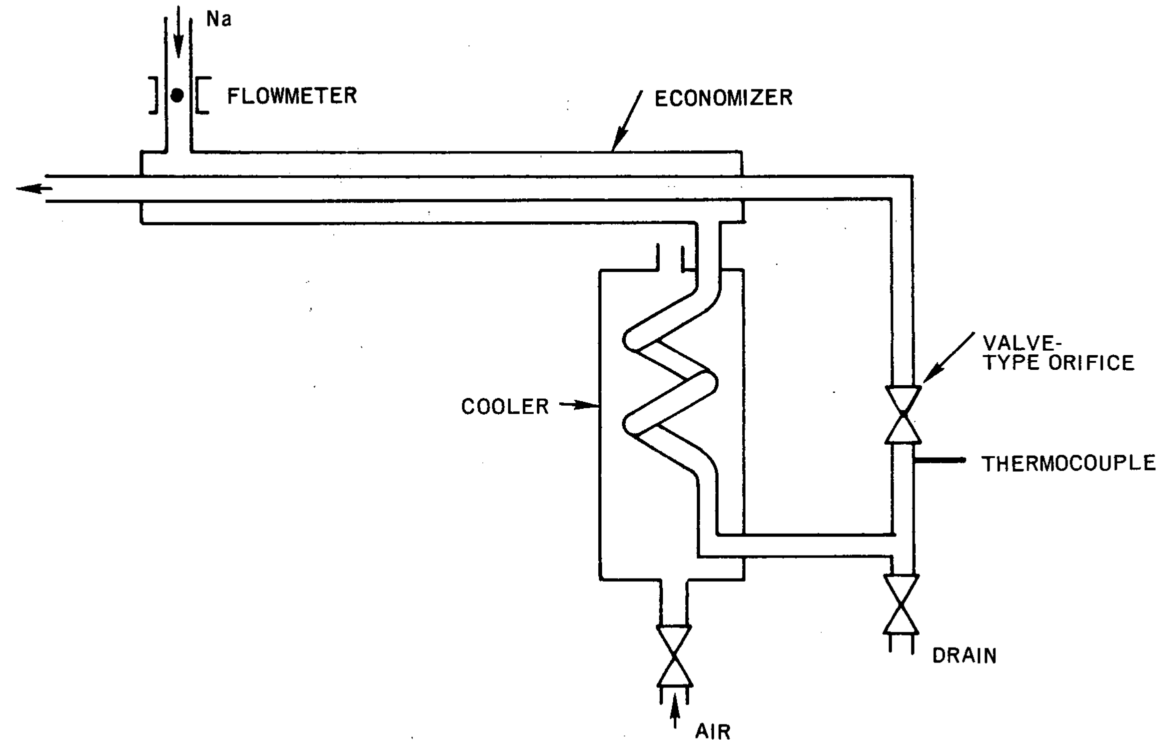

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Figure 12. Type 2 Plugging Meter (Rapsodie)

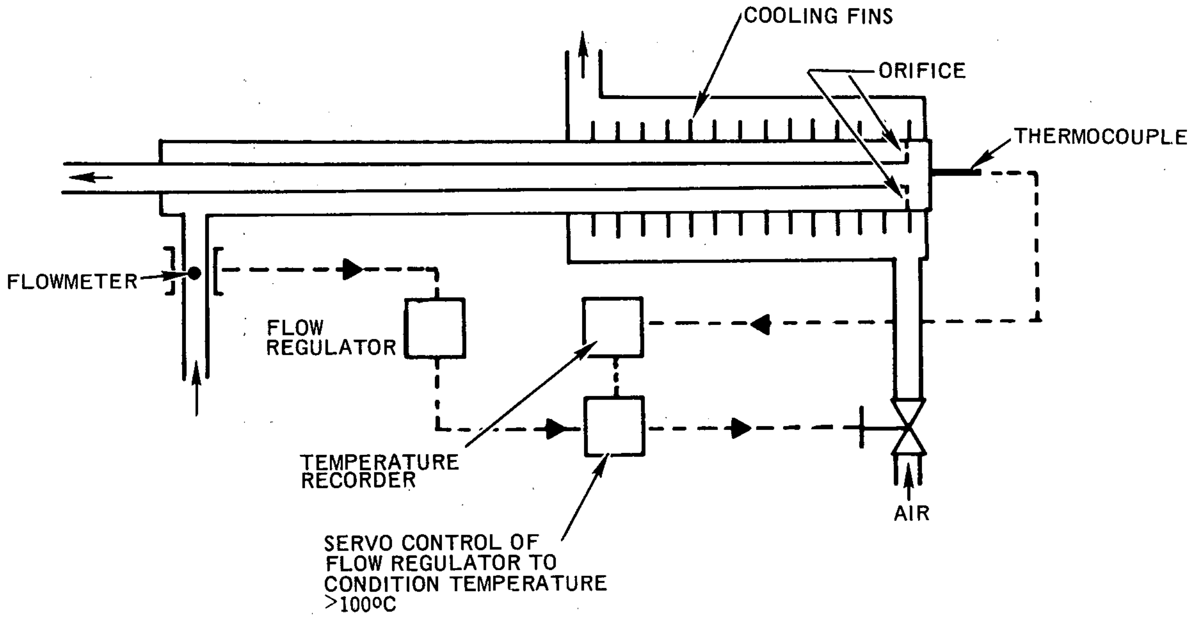

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Figure 13. Type 3 Plugging Meter (Rapsodie)

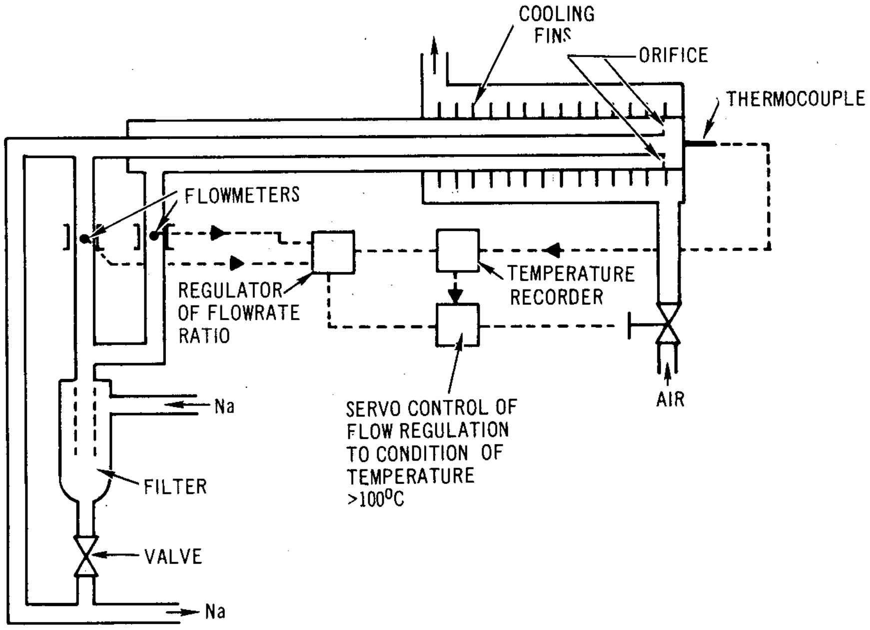

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Figure 14. Differential Automatic Plugging Meter (Rapsodie)

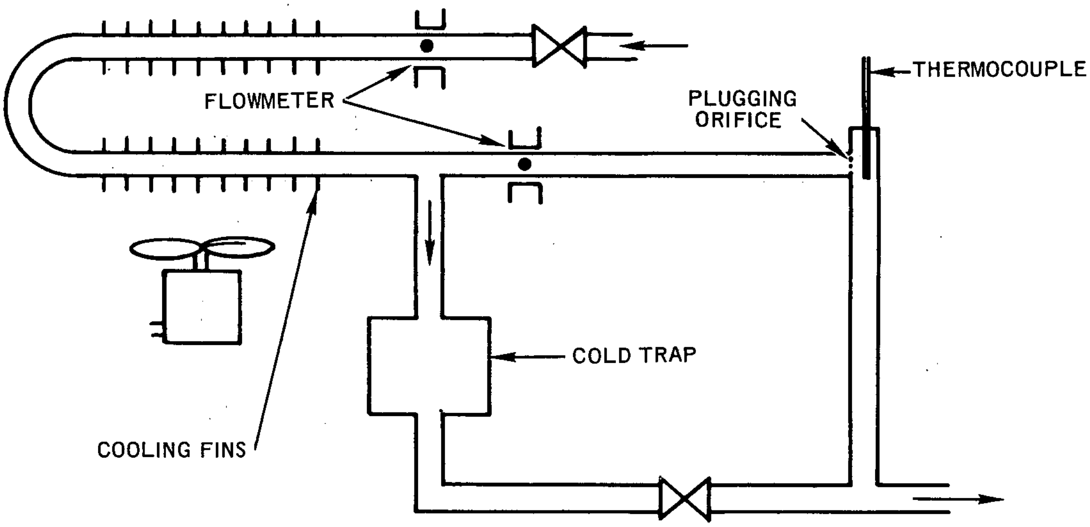

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Figure 15. Plugging Meter Used in a Component Development Project (MSA)

The plugging meter shown in Figure 14 was designated Continuous Automatic in the Rapsodie test program.(9) This plugging meter was made from the Type 3 basic unit described above, with automatic control apparatus added. The cooling is servo-controlled by the sodium flowrate so that the flow is maintained at a constant value corresponding to a partial plugging of the orifice. Under this condition a solution equilibrium exists between the precipitation and the impurity-saturated sodium. The temperature is measured at the orifice. The regulation is accomplished by first establishing the flowrate at some definite value below the unplugged value; then the regulator controls the cooler to maintain this assigned flowrate. During operation, if the impurity content of the sodium decreases, the temperature at the orifice is higher than the saturation temperature, and the impurity precipitated in the orifice begins to dissolve. This dissolution enlarges the flow passage, permitting an increased sodium flowrate. The regulator, sensing the increased flowrate, operates the cooler to decrease the sodium temperature. The temperature decrease results in the precipitation of impurities, thereby decreasing the flow-path area through the orifice, and resulting in a decreased flowrate. This process of "hunting" continues about the set value of flow, and a "steady operation" condition is attained. The automatic operation was very satisfactory. The accuracy of determining plugging temperature was ±1°C. Experimental work on this instrument showed that an excessive pressure caused flowrate instabilities. This was attributed to the mechanical instability of the oxide deposit when the upstream pressure was greater than about 4.9×10^5 dynes/cm^2 (7.1 psi).

The plugging meter illustrated in Figure 15 was used in a liquid metals component development test program.(10) The plugging orifice consisted of a plate containing 16 holes 0.127 cm (0.050-in.) in diameter. Reference 10 and other reports available in the series gave no information on operation.

Figure 16 shows a plugging meter consisting of an economizer, a cooling section, a flowmeter, and a plugging plate 1/16-in. thick with fifteen 0.127 cm (0.05 in.) diameter holes in the periphery.(6) Little operational data were given, but the report stated that the meter is very sensitive and provides excellent reproducibility, though some care in operation is required to avoid complete plugging.

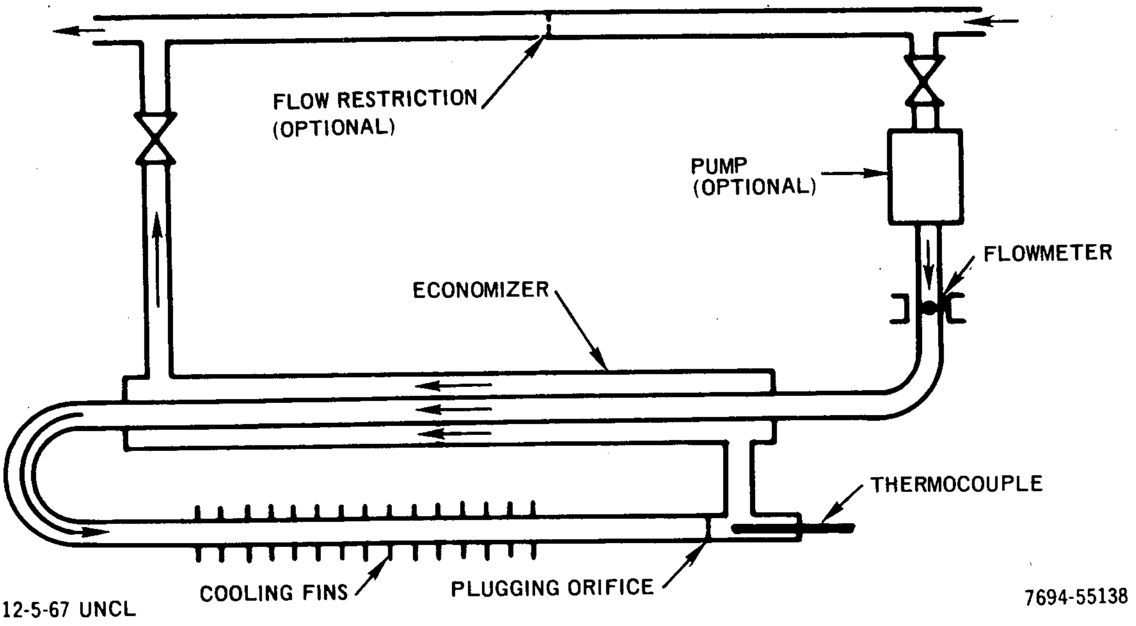

Figure 16. Plugging Meter Designated for "Normal" Use (MSA)

The plugging meter represented in Figure 17 was constructed for experimental purposes.(6) It was installed in a small loop (20 lb of sodium having an oxide content of 0.06 wt %). The orifice plate had only one hole, 0.127 cm (0.050-in.) in diameter. The object of this design was to study the effects of precipitation onto the cooling surface. The tests showed a slight decrease in flow when the system was cooled at a rate of 0.92°C/sec (100°F/min), and no fluctuations were evident when the system was slowly cooled (1°F/min). Two possibilities were indicated: (1) the oxide crystals were too small to plug the hole, or (2) some oxide plated out onto the cold surfaces. Since widely different

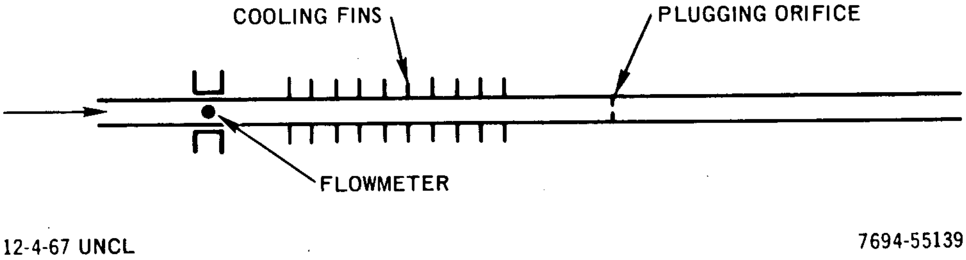

Figure 17. Plugging Meter Used to Study the Effect of Cooling Rate (MSA)

cooling rates were used, it was believed more probable that the oxide plated out on the colder surfaces of the cooling section. Faster cooling caused formation of a sufficiently thick deposit on a short section of the cooler to cause some flow fluctuations. At the slower cooling rate, oxide was probably more evenly plated out over a longer section and presented less resistance to flow. This limiting condition was considered nonexistent in a large system, where relatively large amounts of oxide are available at the same concentration and cooling runs are made under the proper conditions. It was assumed that the plating phenomena could cause a lag in plugging meter response, thereby indicating a plugging temperature below the actual saturation temperature. This problem was considered especially significant at low concentrations. The experiments in this program included various sizes and numbers of holes as well as the location of the orifice plate relative to the cooler. The location affected the response to some extent. Based on the results of these tests, the plugging meter such as that described in the previous paragraph, and illustrated in Figure 16, was considered a good design for general purposes.

One of the plugging meters used in the SNAP 8 corrosion loop tests is illustrated in Figure 18.(11) The liquid metal used in these tests was NaK. The plugging orifice was fabricated from a modified 1/2-in. bellows sealed valve.

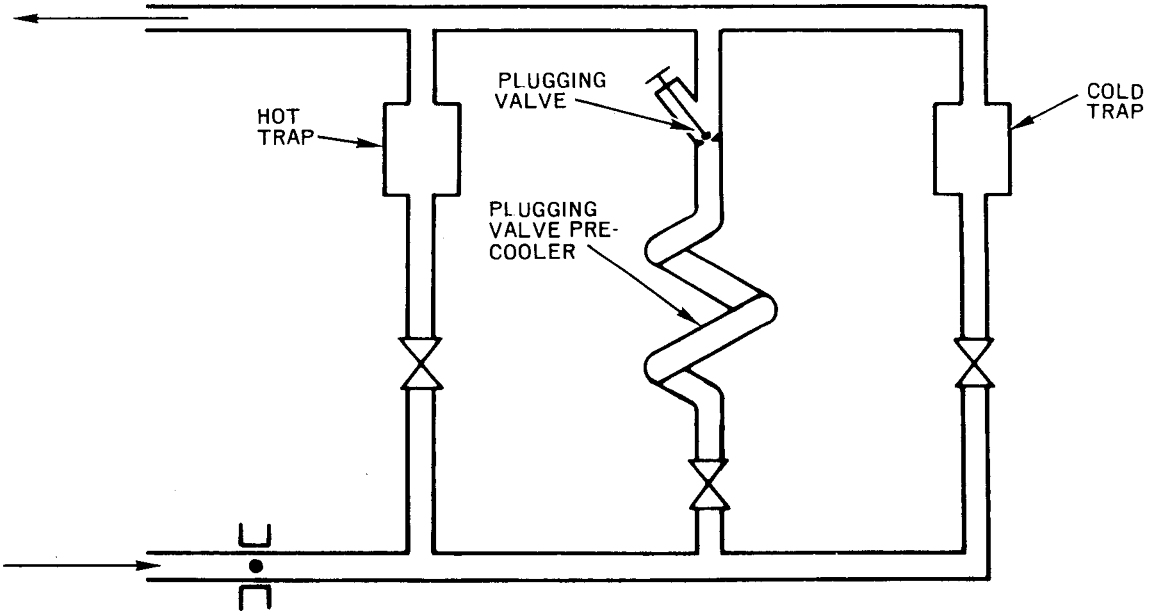

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Figure 18. Plugging Valve and Related Components Used in a Corrosion Test Loop (ORNL)

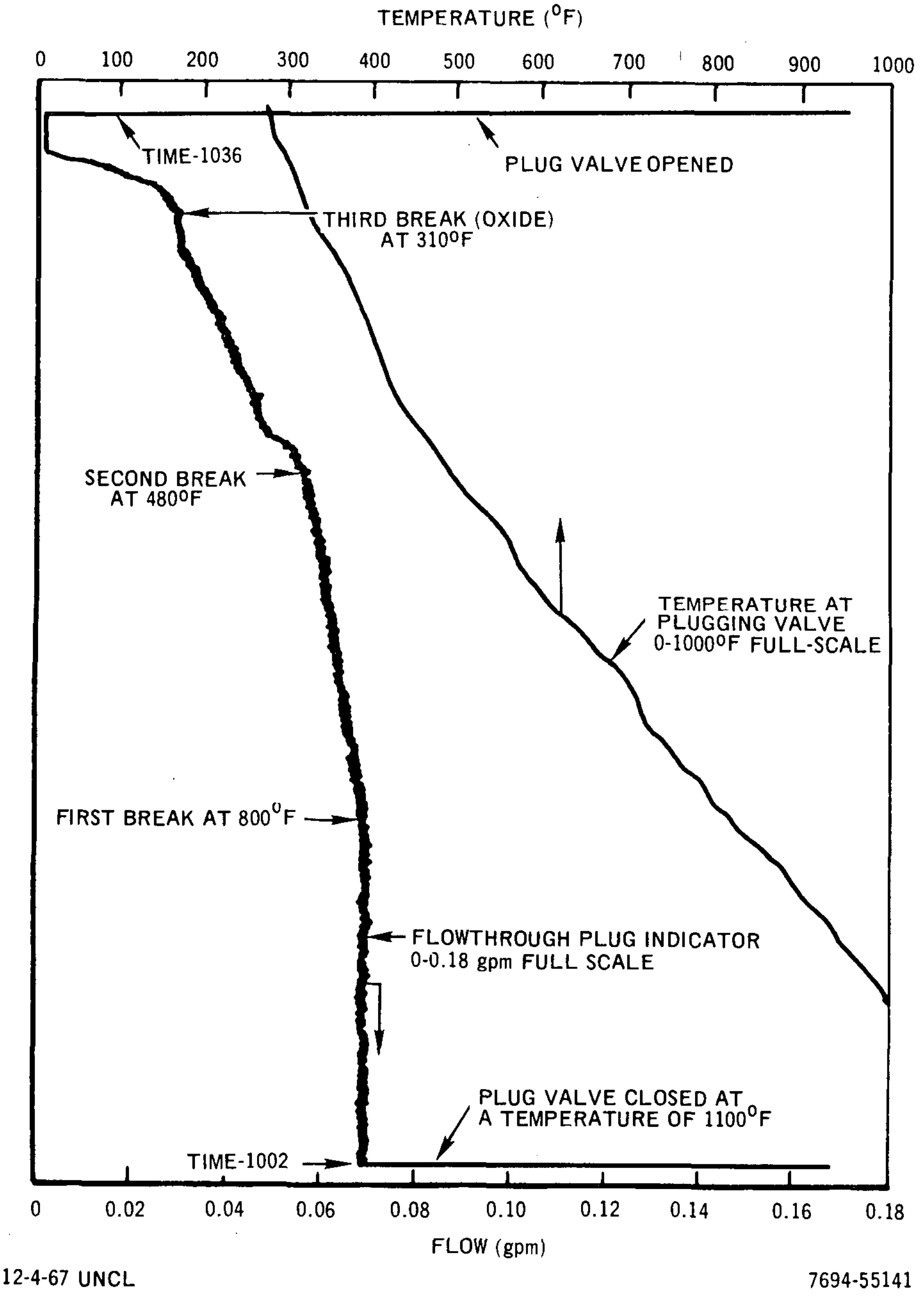

Figure 19. Typical Three-Break Plugging-Indicator Curve

The plugging orifices were machined into the valve poppet and consisted of four grooves at 90° whose cross-section was half-circular with a radius of 0.047 cm (0.0185 in.). The stainless steel sheathed thermocouple was inserted into the valve body to measure the NaK temperature immediately upstream from the plugging orifices. The design flowrate through the orifices was 6.33 cm^3/sec (0.1 gpm). The precooler upstream of the plugging valve was a vertically mounted 16-ft-long coil of 1-in. stainless steel pipe cooled by natural convection. This plugging indicator was considered satisfactory when used on the loop having low oxide concentration. However, it was not considered satisfactory for the "high oxide" loops because it was difficult to preheat the uninsulated natural-convection-cooled precooler to a high temperature prior to a plugging test, and because the NaK volume in the precooler was large compared to the loop and created a large dilution effect when the plugging meter circuit was operated. A small (2-$in.^3$ volume) forced-convection plugging meter was designed for the "high oxide" test loop and was used on all loops subsequently constructed. The plugging valve was essentially the same as on the larger plugging meter described above. The flowrate through the orifices was 5.67 cm^3/sec (0.09 gpm), and the cooling rate was about 0.37°C/sec (40°F/min). During the course of the operation of the corrosion test loops about 500 plugging meter "runs" were conducted. One problem which received considerable attention was the multiple breaks in the plugging meter curve. A typical three-break curve is shown in Figure 19. A relatively detailed account of the problems is contained in the progress reports and summarized in the Summary Report, Reference 11.

The plugging meter designed for use in a sodium cooled reactor (HNPF) is shown in Figure 20.(12) The plugging valve is of special design. The valve body is made from 2-in. Schedule 40 pipe and 2-in. pipe fittings. To conform to a proven plug and seat design, the plug and seat are of a 1-in. design with the plug slotted to provide an orificed flow through the valve. To provide remote electrical control of the valve a movable core of a solenoid enclosed within the valve body is connected to the plug by a rod. A positive spring return is provided to close the valve when the solenoid is de-energized. A variable speed blower is used to force nitrogen over the finned surface of the cooler. In operation, a bypass flow is taken from the main sodium stream, passed through a

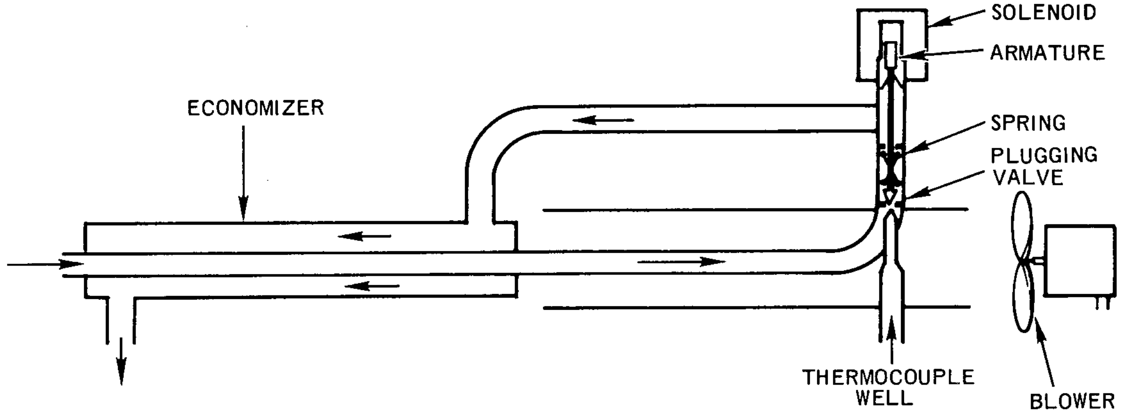

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Figure 20. Plugging Meter Used at Hallam Nuclear Power Facility (AI – Hallam)

flowmeter, the economizer section, the nitrogen cooler, and the plugging valve, and then back through the economizer to the main sodium stream. With the plugging valve "closed" the flow is 63.3 cm^3/sec (1 gpm) and the blower control is adjusted to provide a cooling rate of 0.046°C/sec (5°F/min). When plugging begins, the flow decreases to 0.6 of the initial value, the cooler is turned off, the heaters are turned on, and the solenoid is activated to remove the plug and prepare for another plugging cycle. The sequence is programmed as illustrated in Figure 21. Curves traced during a laboratory test are presented in Figure 22. This plugging meter was used in the Hallam Nuclear Power Facility and its performance was described as entirely satisfactory.

An experimental design of a continuous automatic plugging meter is shown in Figure 23.(13) No orifice dimension, flowrate, or cooling rate data were provided in the reference. The operation was described in some detail. The sample flow is divided between the fixed flow restrictor and the plugging annulus. Upon cooling below the impurity saturation temperature, the annulus begins to plug, causing a reduction in flowrate. The control system is designed to maintain the annulus flow at a small value, equivalent to a partially-plugged condition by adjusting the flow of cooling air. At the controlled equilibrium

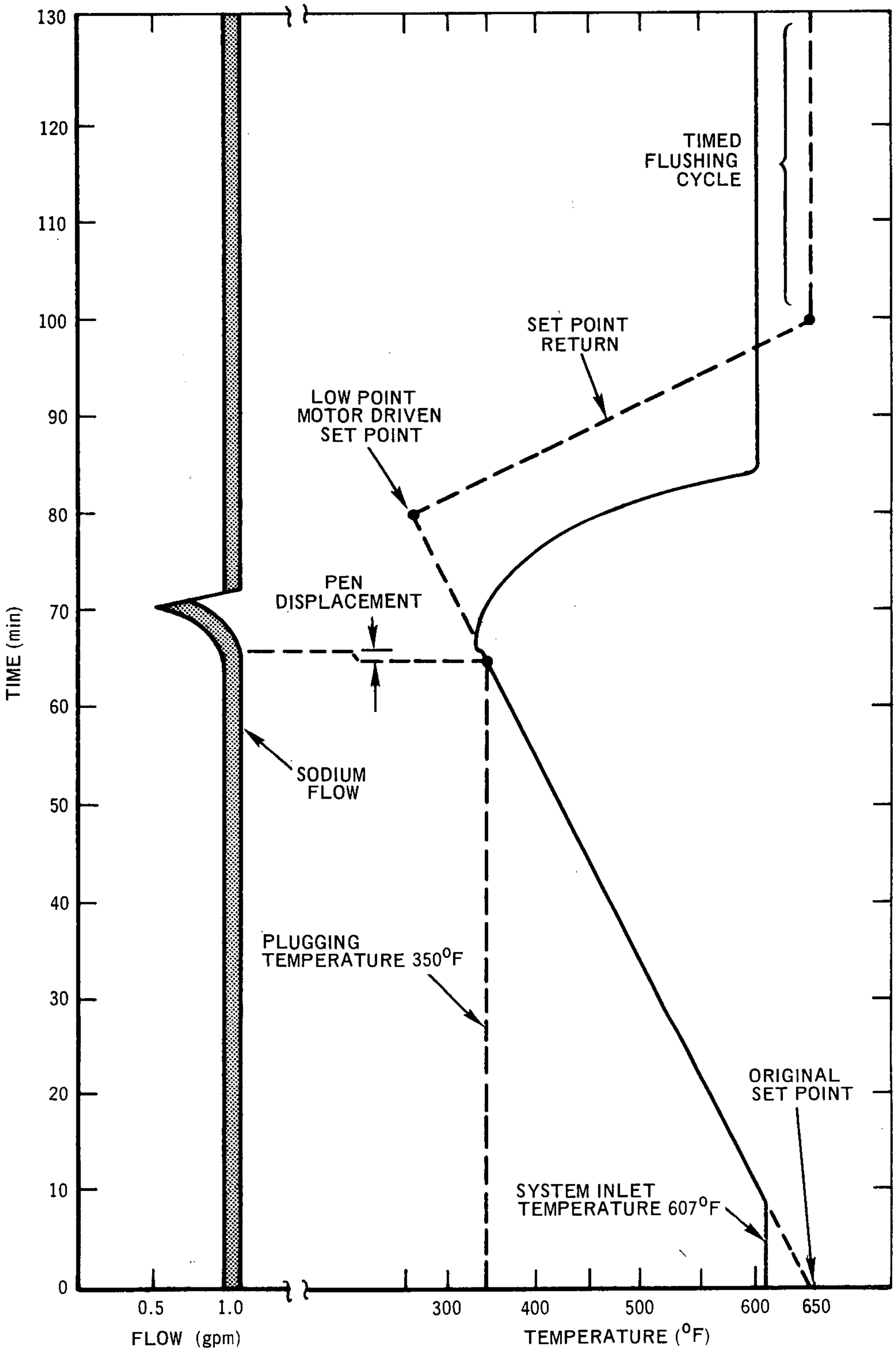

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Figure 21. Two-Pen Recording of Plugging Determination

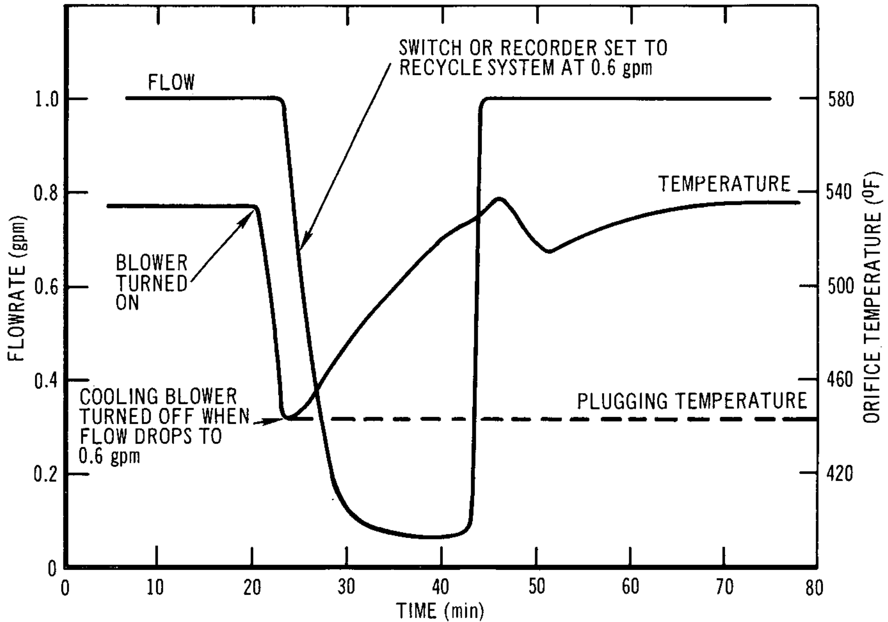

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Figure 22. Flow and Orifice Temperatures at HNPF Plugging Meter (Laboratory Test Data)

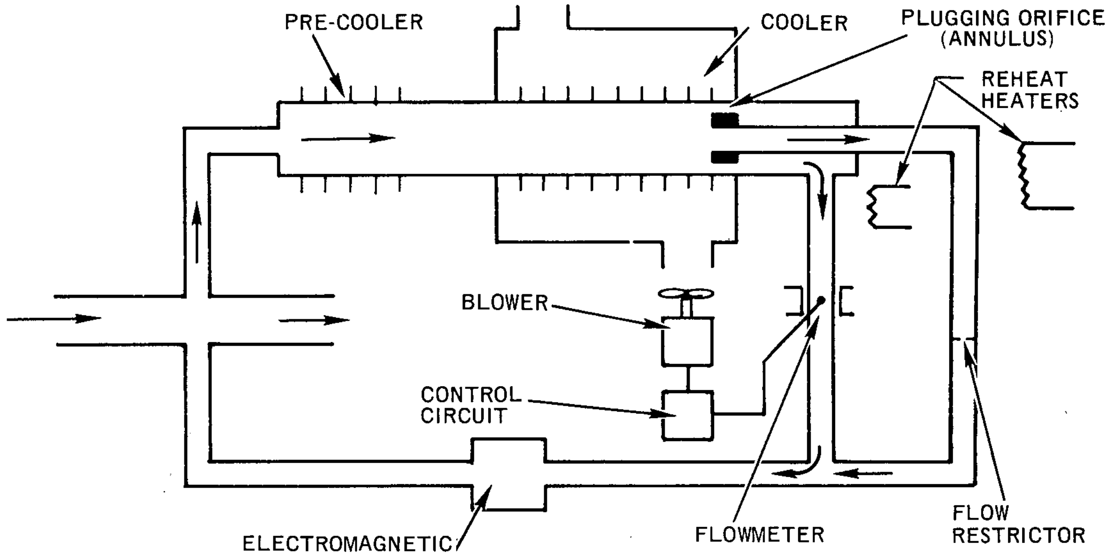

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Figure 23. Experimental Design of a Continuous Automatic Plugging Meter (PFR)

(i.e., with the establishment of the partially-plugged condition) the annulus temperature coincides with the saturation temperature, which is measured and indicated as the output signal. The constant pressure auxiliary pump avoids the need to measure flow ratio and also allows the meter to be independent of flow changes in the sampled circuit. The flow-sharing principle is used, not only to give good sensitivity for a given mass of precipitated impurity, but to provide an adjacent continuous flow into which an accidental total plug of the annulus can redissolve with reasonable ease. This meter has operated satisfactorily with indicated plugging temperatures from 250 to 125°C.

The plugging meter used in a test facility sodium quality control loop is illustrated in Figure 24.(14) The plugging valve shown in some detail in Figure 25 is a modified 1/2-in. glove valve with a cone-shaped stem fitted into a cone-shaped seat. The sodium bypass through the valve consists of 10 slots in the stem cone 0.032-in. wide by 0.016-in. deep. A similar valve is shown in detail in Reference 15. The plugging loop contained a flowmeter (not shown in the diagram). The cooling was accomplished by a fan blowing room air over the entire plugging loop. This plugging meter was operated over a range of: oxide concentrations, 3 to 37 ppm; flowrates 7.1 to 16.2 cm^3/sec (0.112 to 0.256 gpm); and cooling rates giving plugging times of 6 to 39 min when the loop temperature varied from 204 to 339°C (399 to 642°F). Based upon the observations under the variety of conditions the reported(14) conclusion was that "...within the limits of the experiments, variations in sodium flow, time of cooling, concentration of oxygen, and sodium inlet temperature made no difference in the behavior of the plugging valve as a means of oxygen-in-sodium analysis."

The plugging meter shown in Figure 26 was an experimental model used initially to test some concepts used in the HNPF design.(16) It was later used in hydride detection experiments in the SNAP program. In this design the economizer, cooling section, and plugging valve comprise a single unit. The cooling air is directed onto the plugging-orifice end of the economizer so that the oxide concentration is greatest in the vicinity of the plugging orifice. The diameter of the central hole in the plate is 1/8-in., and the diameter of each of the adjacent holes is 0.05 in. In normal operation, the central hole is covered

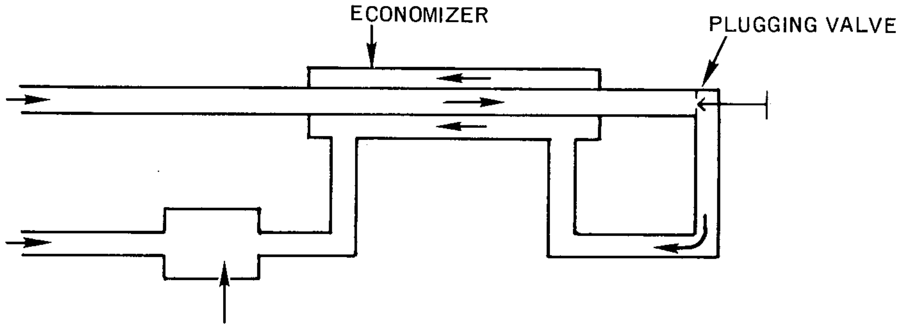

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Figure 24. Schematic Diagram of a Plugging Meter Used in a Sodium Quality Control Loop (ANL)

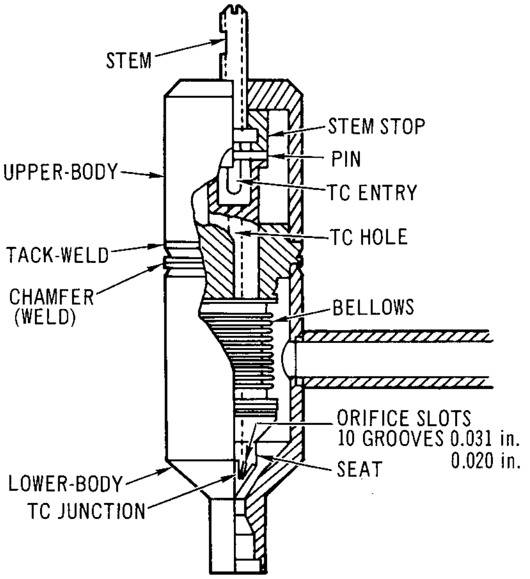

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Figure 25. Details of a Plugging Valve

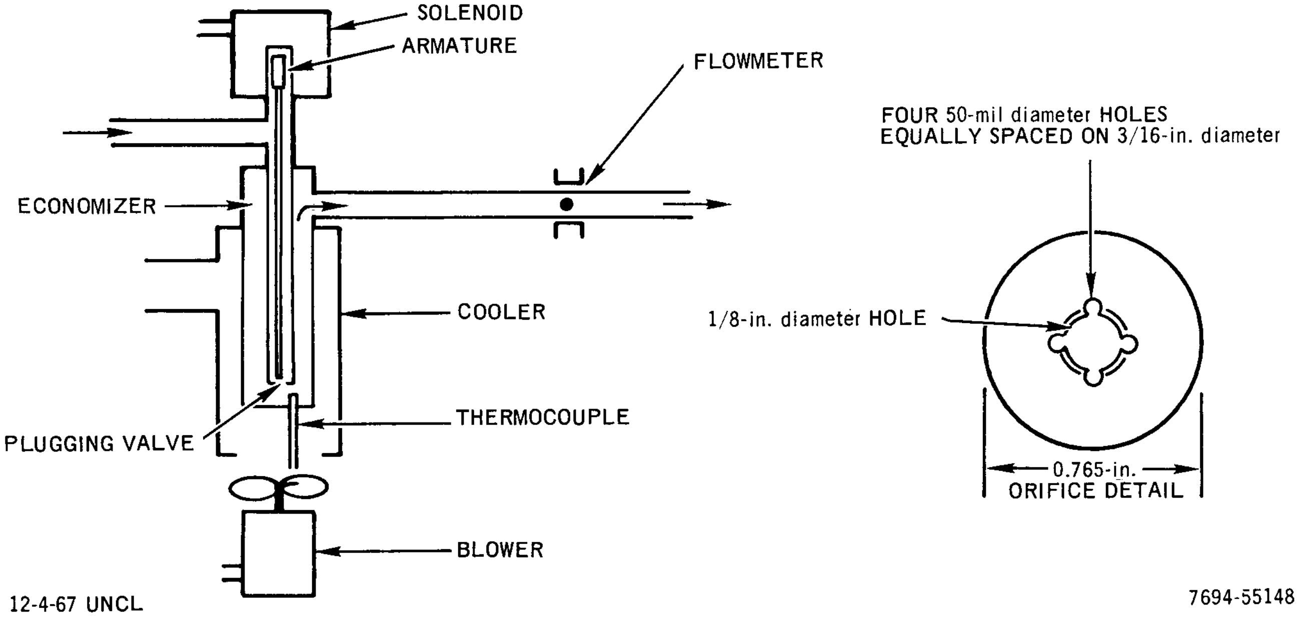

Figure 26. Laboratory Development Plugging Meter (AI)

by the cone-shaped point of the central rod so that sodium passes through the outer four holes only. When the temperature is lowered and precipitation occurs, the four small holes become plugged. Unplugging is accomplished by turning off the cooler, turning on electric heaters surrounding the economizer, and withdrawing the central rod by means of the solenoid. When the rod is withdrawn a fraction of an inch, the plug is mechanically disturbed and the opening of the central hole permits a high flowrate of relatively hot, clean sodium to flush away the precipitate. Approximately 200 plugging tests were conducted on this plugging meter under a variety of conditions. The operation was considered to be very satisfactory and capable of very rapid unplugging. A typical recorder display is shown in Figure 27. The usual flowrate was 6.33 cm^3/sec (0.1 gpm) and the cooling rate was 0.464°C/sec (50°F/min). A variation of these rates over a 3-to-1 ratio did not significantly change the plugging characteristics.

Figure 28 shows a plugging meter used in experimental work.(17) A valve-type orifice was used to facilitate washing out of the oxides from the holes after plugging. In the experimental designs, the number and size of holes and the heat exchanger size were varied to determine the effect on performance. The

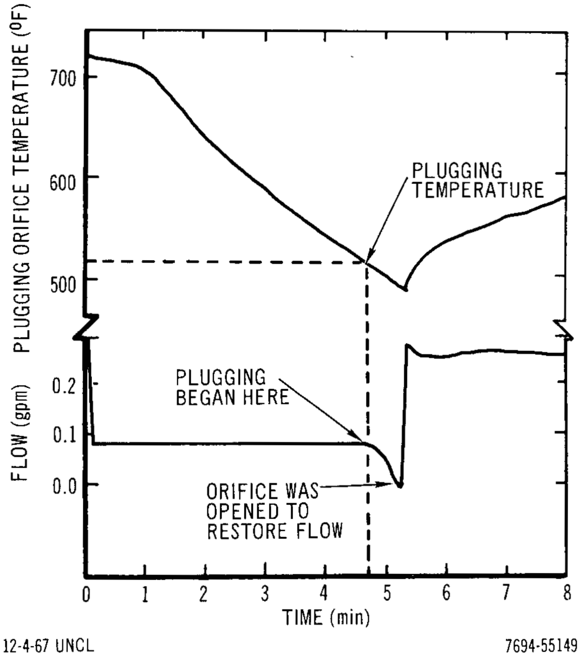

Figure 27. Recorder Display of Temperature and Flow in the Plugging Orifice Region

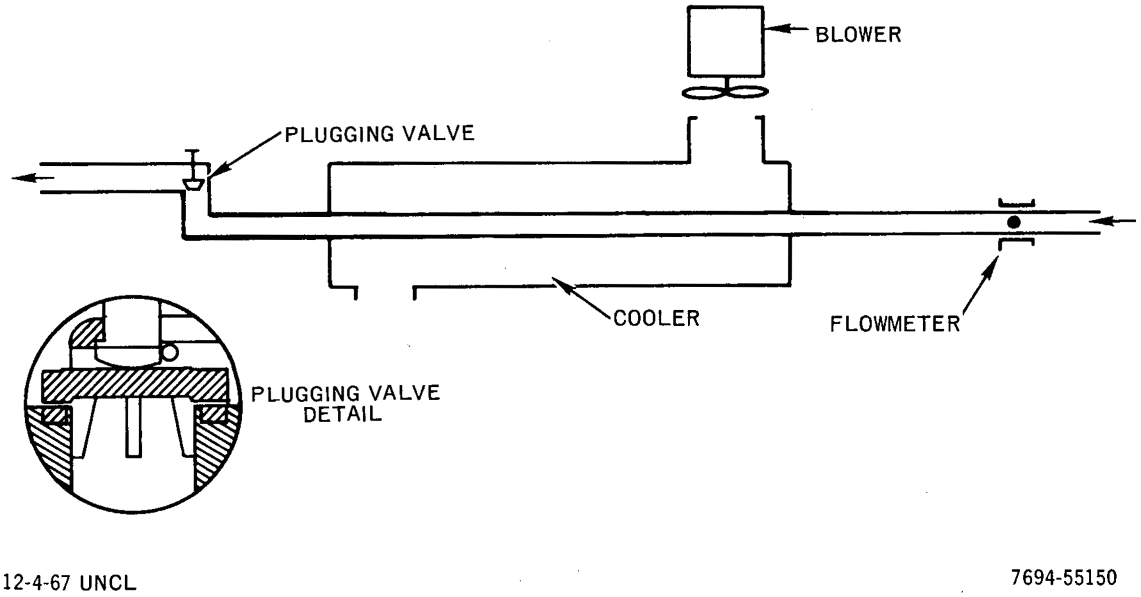

Figure 28. Plugging Meter Used in Experimental Investigations (USSR)

variations are indicated in the table below.

Design Characteristic	Modification A	 B	 C
Number of Grooves in Valve	16	16	34
Dimensions of Grooves (cm)	0.1 x 0.1	0.1 x 0.1	0.1 x 0.1
Heat Exchanger Tube Diameter (cm)	2.5	4.9	4.9
Heat Exchanger Area (cm^2)	4500	7200	7200

During the tests, the oxygen content of the sodium was varied from 0.002 to 0.1 wt %, and the temperature of the sodium was varied from 110 to 550°C. The relationships between the readings and the flowrate at two different oxygen concentration levels were determined for each modification. The temperature at which the holes became plugged was constant for flowrates of 2.5 to 14 m/sec. At low flowrates, the plugging temperature was lower than at higher flowrates. The relationship is shown in Figure 29. When the hole size was increased from 0.05 x 0.05 to 0.1 x 0.1 cm, the plugging temperature was reduced by 2.5%. A sufficiently large number of grooves (10 to 15) was considered necessary to minimize the effect of adventitious plugging of a hole, such as by a steel particle. The plugging temperatures were independent of the rate of cooling within the range of conditions: (1) oxygen concentration 0.008 to 0.02 wt %; (2) flowrate 2.5 to 13 m/sec; and (3) cooling rate as measured at the orifice of 0.005 to 0.617°C/sec. A cooling rate of more than 0.167°C/sec was considered undesirable since it increased the difficulty of determining the plugging temperature. A plugging curve is shown in Figure 30. A comparison of the plugging meter indications with chemical analyses showed good agreement. Another report(18) by the same authors, and apparently describing the same plugging meter, stated that the design of a plugging meter was not as simple a task as was presumed, and further investigation was found necessary. The additional investigation involved variations in flowrate, hole dimensions, heat exchanger design, and oxygen concentration levels. As shown in Figure 31 for one of the plugging meters, cell designs showed a sensitivity to flowrate as a function of oxygen concentration. Also, the increase in orifice dimensions from 0.03 x 0.03 to 0.08 x 0.08 cm caused an increase in the flowrate at which the plugging temperature begins to decrease. In tests under constant conditions, except variable

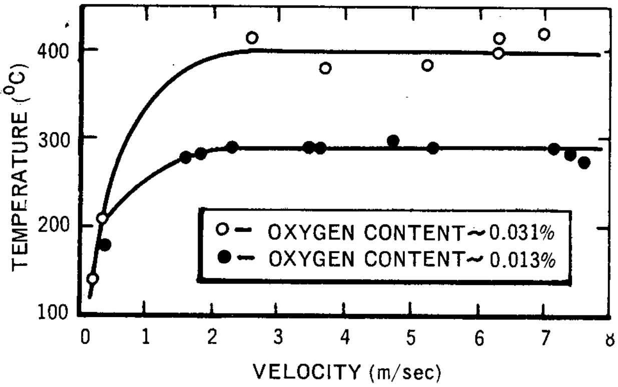

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Figure 29. Relationship Between Temperature of Blockage of Holes in the Oxide Indicator and Rate of Flow in Holes

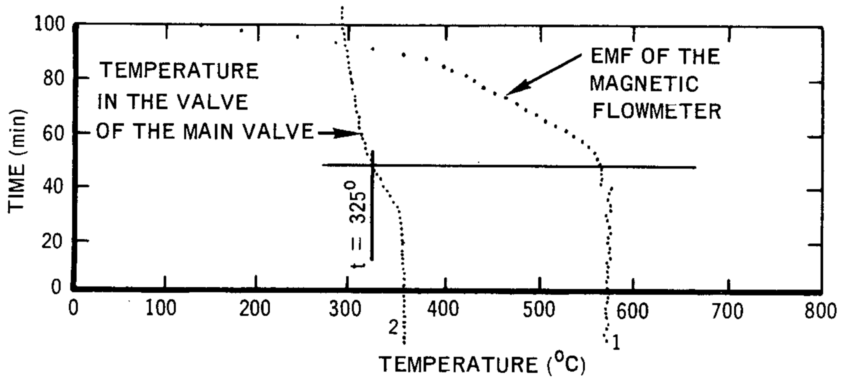

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Figure 30. Examples of Curve Recording of Flow and Temperature of Sodium in Secondary Apparatus of Oxide Indicator

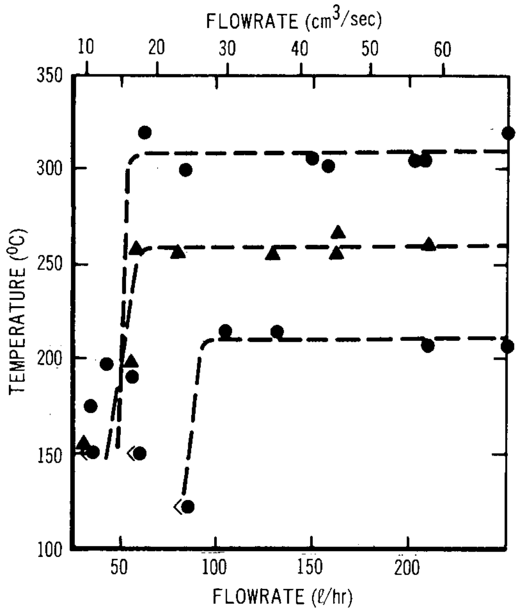

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Figure 31. Relationship of Plugging Indicator Readings with Flowrate and Contamination Level of Sodium

orifice dimensions, the plugging temperature decreased with increased dimensions. For 0.01 x 0.01 cm grooves, the plugging temperature was 8.5% lower than for 0.03 x 0.02 cm grooves. For an optimum design plugging meter, the determination of plugging temperature to a precision of ±10°C was considered practical. The report stated that the range of stable operation must be determined experimentally for each new design.

The plugging meter shown in Figure 32 was used in test loops.(19) The plugging orifice design is unique since it provides a variable volume orifice to permit use of an optimum size for the concentration level. The orifice plate is 0.45-cm thick and contains 17 holes 0.12-cm in diameter. A similar plate containing 0.07-cm diameter pins is placed so that the pins may be inserted in the orifice plate holes. At low plugging temperatures the pins are inserted to decrease the orifice volume, and at higher temperatures they are withdrawn to an appropriate position. This variable feature also facilitates unplugging. With the pins completely inserted and the flowrate adjusted to 33.3 to 50.0 cm^3/sec (0.53 to 0.79 gpm), and the cooling rate at 0.005°C/sec, a plugging temperature as low as 110°C was possible. The time required for one measurement was about 30 min. Figure 33 shows a plugging curve made with this instrument. The report(19) gives an estimated plugging temperature measurement accuracy of 1°C. High accuracy is attributed to the use of low flowrate and cooling rate and prevention of precipitation in the cooler rather than in the orifice.

The plugging meter used at the SRE is shown schematically in Figure 34.(20) The plugging orifice is mounted in a 1-in. "Y"-pattern valve body. The disc contains 16 grooves, each 0.1 x 0.1 cm (0.04 x 0.04 in.). The operating experience has demonstrated results reproducible to within 2.8°C (5°F). A plot of a typical measurement is shown in Figure 35. The standard cooling rate was 0.046°C/sec (5°F/min) although the rate shown was slightly higher. The original SRE plugging meter was cooled by tetralin since it was available as a service coolant. When the use of tetralin in the SRE was discontinued, the cooling section was modified for use with gas (nitrogen).

Figure 36 shows a plugging meter used in a test facility. This was called the "batch type" since it consisted of a pumped loop, and, by means of inlet and

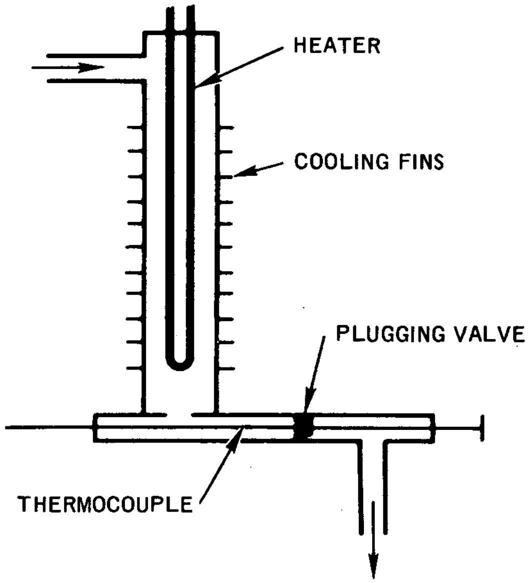

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Figure 32. Plugging Meter Using Variable Volume Orifice (JEARI)

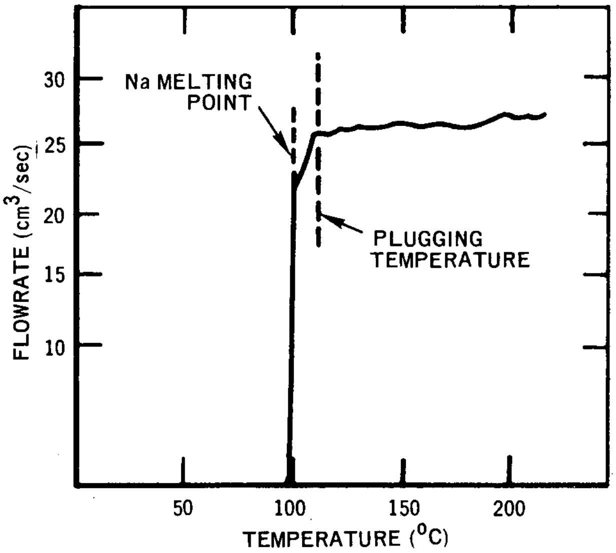

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Figure 33. Plugging of Variable Volume Orifice Plugging Meter

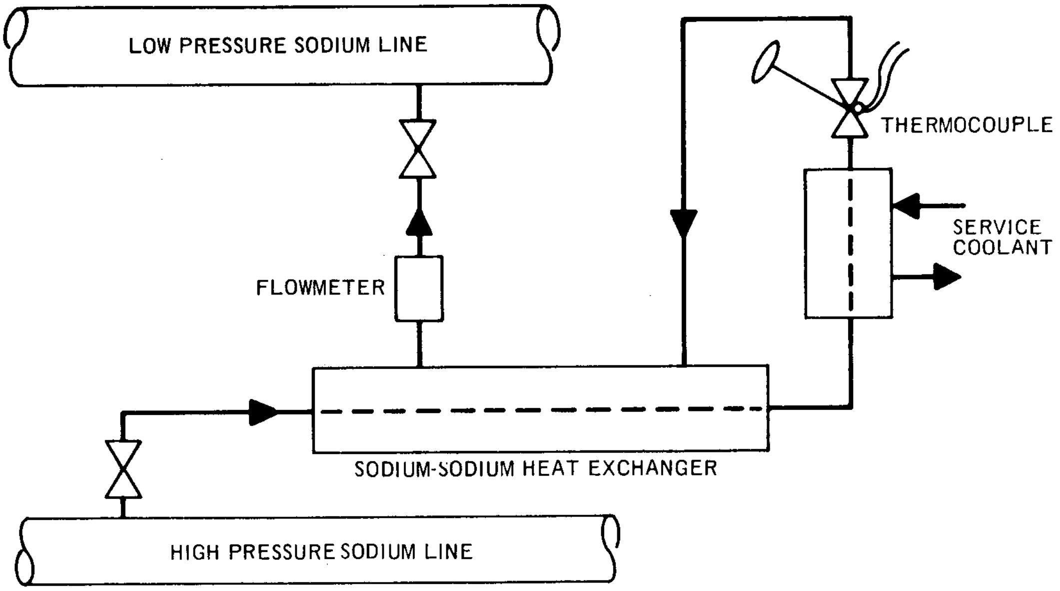

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Figure 34. Plugging Meter Used at SRE (AI)

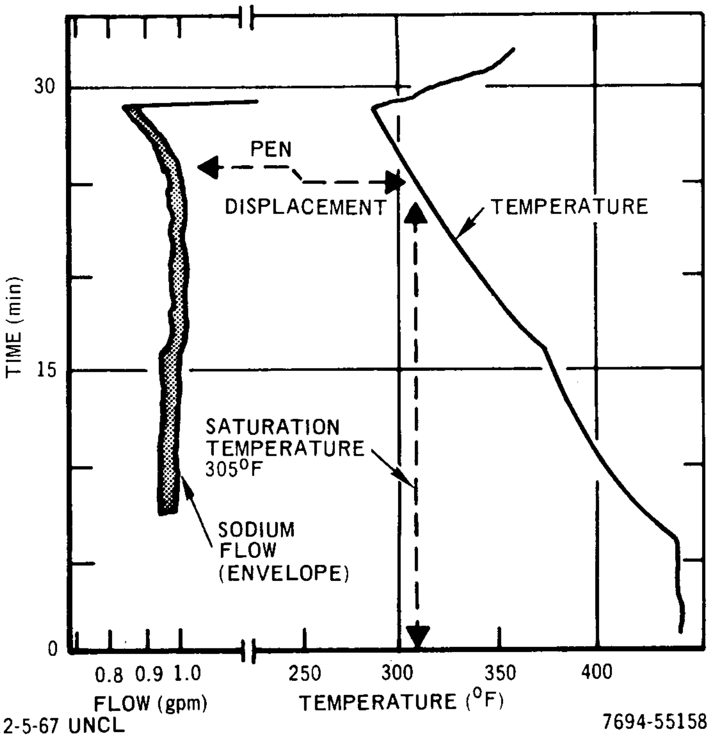

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Figure 35. Typical 2-Pen Recording of Plugging Determination at SRE

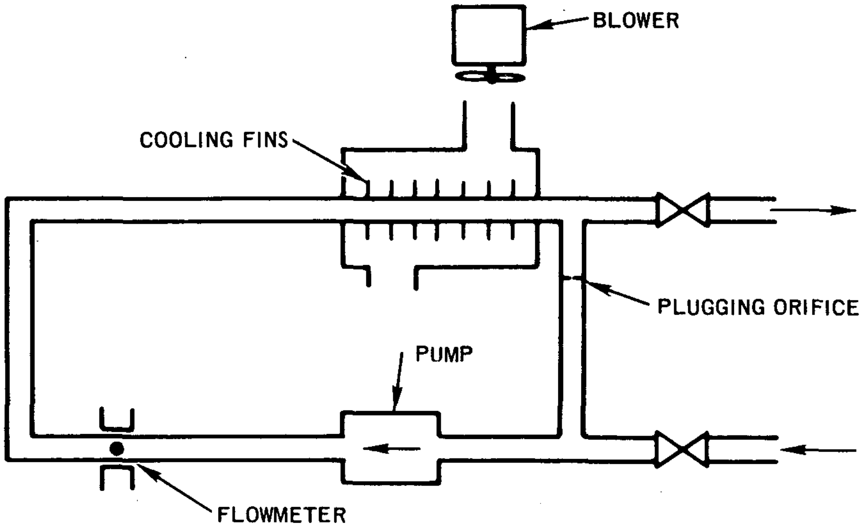

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Figure 36. Type I, Batch Plugging Meter (KAPL)

outlet valves, a batch of liquid metal was separated from the system, and the measurement was made on the batch. In this plugging meter, the orifice consisted of an 1/8-in. thick disc containing eight 0.127-cm (0.05-in.) diameter holes. In the operation of this plugging meter, the loop was maintained at a temperature well above (~50°F) the "saturation temperature" to prevent unintended precipitation in the loop while the region of the orifice plate was maintained 10°F below the loop temperature. With the valves closed to isolate the loop from the larger system, the loop flowrate was adjusted to 31.6 cm^3/sec (0.5 gpm). While maintaining the 10°F-lower orifice temperature, the entire loop temperature was reduced to induce precipitation in the orifice. Various cooling rates from 0.00093 to 0.046°C/sec (0.1 to 5°F/min) were used. Typical plugging curves are shown in Figure 37.

An alternative to the batch method described in the preceding paragraph is the "bypass" method used in the same facility.(7) The bypass plugging meter is illustrated in Figure 38. The "bypass" nomenclature was given the design since the meter was connected as a bypass circuit in the system and, as contrasted with the batch method, was not arranged to permit the formation of a separate isolated loop. The plugging orifice was an 1/8-in. thick plate containing

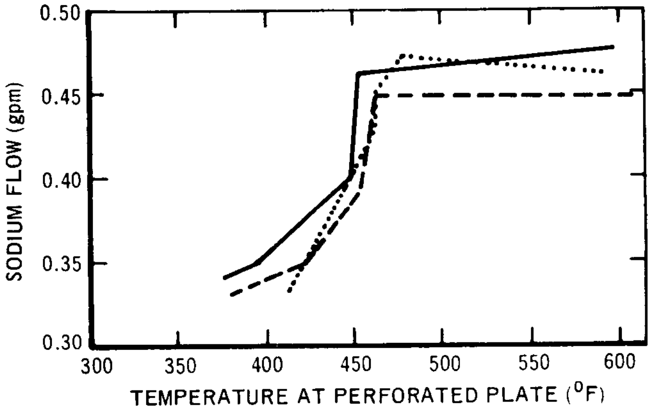

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Figure 37. Type I Plugging Indicator Typical Runs

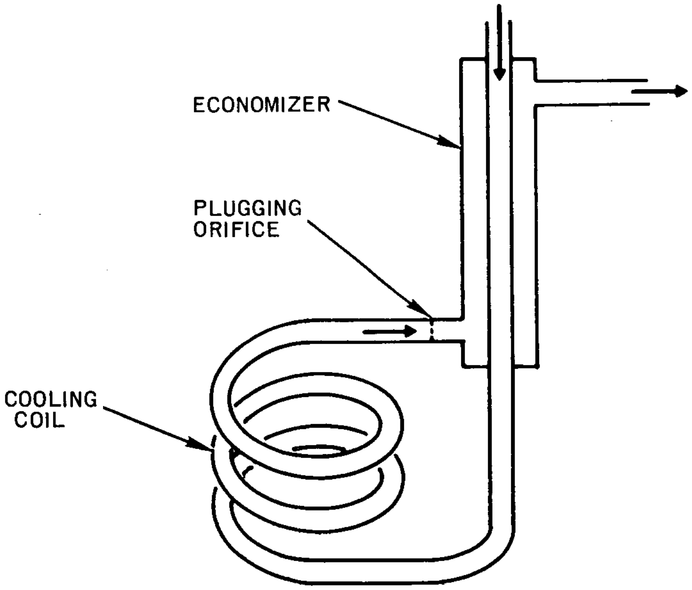

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Figure 38. Type II, Bypass Plugging Meter (KAPL)

sixteen 0.127-cm (0.05-in.) diameter holes. The air cooler consisted of nine turns of 1-in. tubing coiled on a 6-in. diameter. In operation, the system temperature was held at 28°C (50°F) above the "saturation temperature" and the desired bypass flowrate of 50.6 to 94.8 cm^3/sec (0.8 to 1.5 gpm) was established. Cooling was accomplished by removing insulation from the cooler coil and blowing air over the coil. Cooling rates varied from 0.00925 to 0.185°C/sec (1 to 25°F/min). Typical plugging curves are shown in Figure 39. In a test sequence of 21 consecutive plugging runs, the plugging temperatures were within an 8.3°C (15°F) band where the average temperature was 218°C (425°F). A comparison of the "readings" provided by the bypass method with those obtained by the batch method described in the previous paragraph shows negligible difference between the results of the two methods.

Figure 40 illustrates the plugging meter used in Mark A, SIR.(21) The orifice consisted of a thin plate with 17 holes, each 0.117 cm (0.046 in.) diameter. The flowrate was 19 cm^3/sec (0.3 gpm) and the cooling rate was 0.046 to 0.092°C/sec (5 to 10°F/min). A typical plugging curve obtained with this instrument is shown in Figure 41. The plugging temperature could be determined to within 19.5°C (35°F).

Figure 42 illustrates the plugging meter used in experimental loops in cold trap experiments.(22) The plugging meter was described as a "...perforated plate containing twenty-one 50-mil diameter holes in the cold zone to simulate restricted passages at the SIR inlet." Some plugging curves obtained are shown in Figure 43.

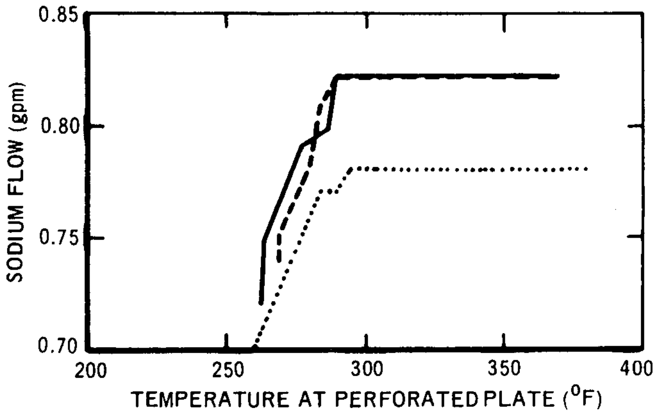

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Figure 39. Type II Plugging Indicator Typical Runs

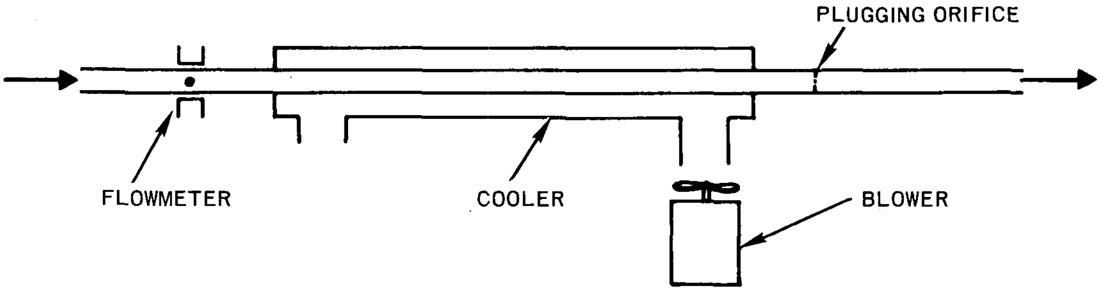

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Figure 40. Schematic Diagram of a Mark A Plugging Indicator (KAPL)

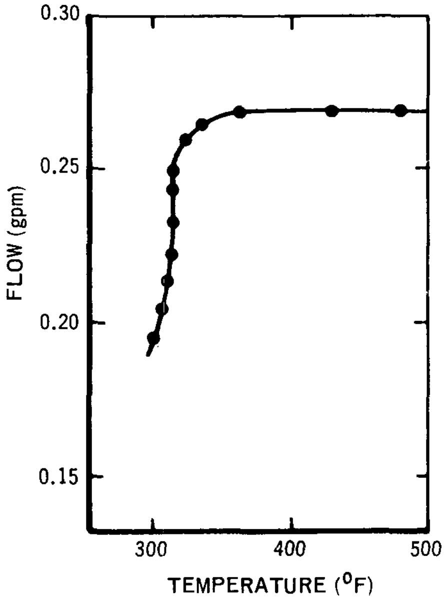

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Figure 41. Typical Plugging Curve of a Mark A Plugging Indicator

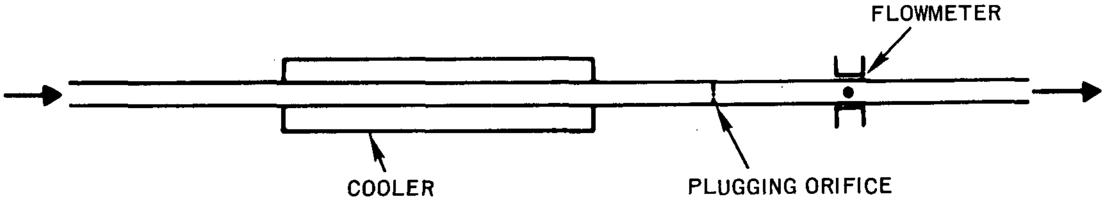

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Figure 42. Plugging Meter Used in Cold Trap Experimental Loops (KAPL)

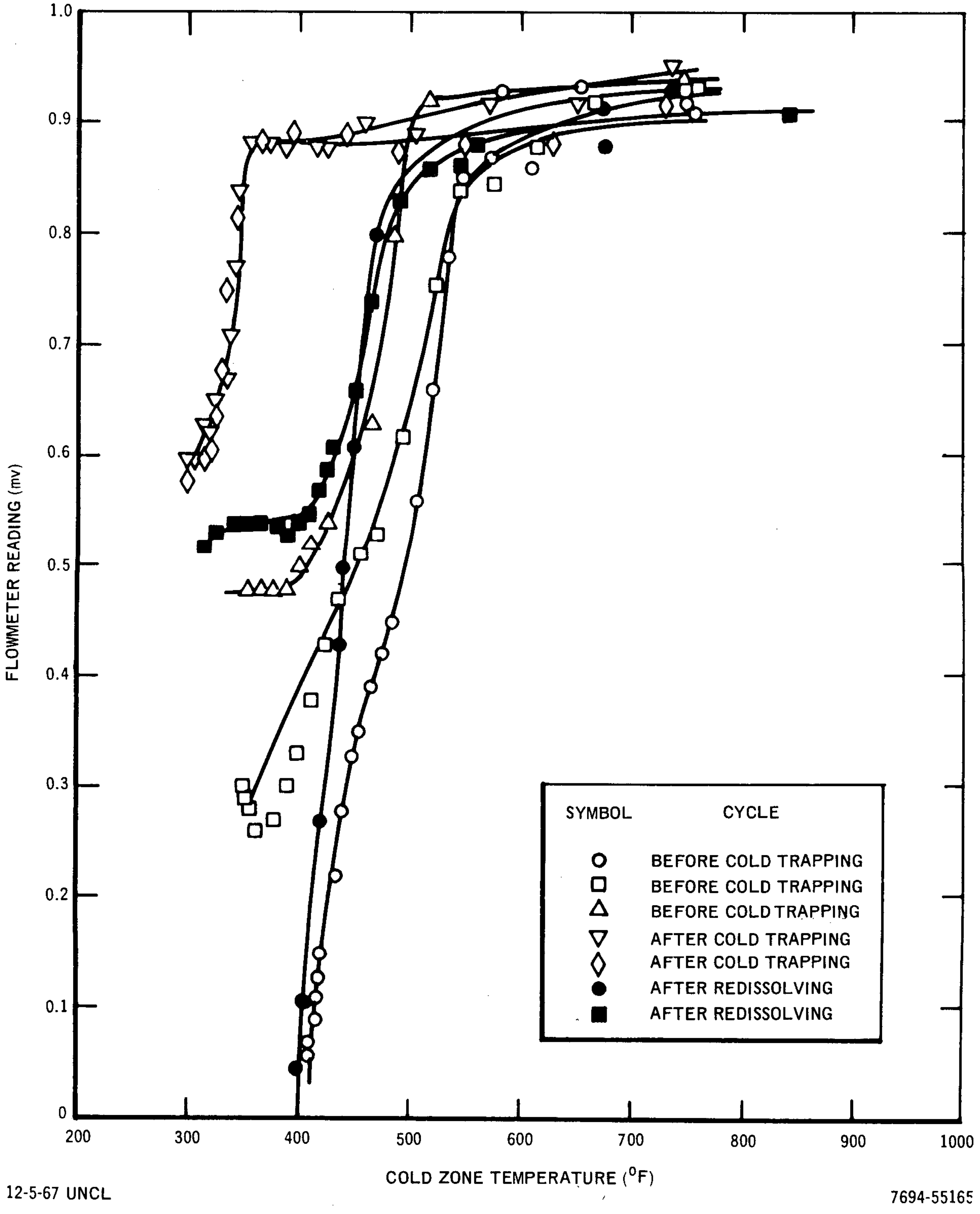

Figure 43. Plugging Curves Obtained with Plugging Meter Shown in Figure 42

D. DISCUSSION AND EVALUATION

Plugging meters have not attained the status of being available commercially off-the-shelf. A British report,(23) describing an automatic plugging meter compared its performance to a "commercially-produced version." This is the only reference to commercial production found in this review of plugging meter literature. A few organizations having experience in liquid metal technology may design and construct plugging meters on a special order basis. However, most plugging meters in use today have been designed and constructed on an "as needed" basis by the group or organization using them.

Often in applications where requirements are not stringent or where time and funding impose limitations, plugging meters are treated as a part of the system piping and constructed accordingly with relatively little design regarding its performance as an instrument. Thus, the piping is arranged to contain the basic components, a flowmeter, a cooler, and a plugging orifice. Often this method is satisfactory. In applications having more stringent requirements the basic components are integrated and the design and construction is more nearly like that of an instrument – a separate device having definite performance characteristics as an instrument.

The great diversity of designs is shown in the collection of plugging meter descriptions presented in this report. In a few cases the variations were a part of the experimental development to determine the effect on performance.

However, most of the diversity may be ascribed to the "homemade" aspect. Certainly the diversity is not due to diversity in basic requirements.

Most aspects of plugging meter design and operation had been studied experimentally by the mid-1950's. The nature of some installations and methods was not conducive to the production of reliable design data. Some installations produced and published very useful information. However, generally the pieces of information remained isolated and no general unified body of design concepts developed. Thus some plugging meters were made during the late 50's and early 60's without the use of design advice available in the earlier literature.

No published reports of analytical studies of plugging meter characteristics were found. One advantage of the analytical approach is to provide a model which serves as a means of unifying the concepts and as a reference for experimental data comparisons. For example, recently two conflicting views have been expressed regarding the effect of cooling rate on plugging meter performance. One report(14) states that the performance was unaffected by cooling rate variations, while another report(24) indicates that the plugging temperature can be depressed by increasing the cooling rate. Conflicting observations regarding the effect of flowrate have been reported.(14,16,17,18,19) It is of interest to observe that about 60% of installations reporting satisfactory performance operated at flowrates in the region designated in one report as unsatisfactory. To provide a better understanding of this matter, a rough analysis was made and included in this report. An analysis of several other aspects of design and operation has been made and included here to enable understanding some of the data reported and some design features not adequately explained in the various reports.

Within recent years interest in establishing a standard plugging meter has been developing. No design has been fixed although some tentative design value are under consideration. The slotted valve type plugging orifice such as described in this report is the tentative selection for an orifice. The development of automatic continuous plugging meters is under consideration. Such instruments have been developed and tested by the French and British. A Japanese report expressed automatic plugging meter development intentions. The USSR literature discussed manually operated plugging meters in some detail but made no mention of automatic operations.

IV. ELECTROCHEMICAL CELL

A. BACKGROUND

The electrochemical cell has been known in the field of electrochemistry as a galvanic cell and, more specifically when used in the manner considered here, is often called a "concentration cell." As such, the theory was well-developed and applied long before the development of liquid metal technology. Early in the development, the use of the concentration cell principle for determining oxide concentration was proposed. On each occasion, a brief consideration revealed formidable materials problems, so the electrochemical cell development lagged that of other seemingly more promising methods.

The concept of the electrochemical cell for measuring oxide concentration in sodium involved, (1) a reference electrode consisting of a metal-metal oxide enclosed in, (2) a solid electrolyte in the form of a tube, which immersed into (3) the sodium containing oxide as the sample electrode.

The status in 1959 is shown in a theoretical study released in 1961(25) in which the following conclusion was reported:

"If other monitoring methods for oxygen in sodium in the concentration range 1 to 10 ppm are found to be inadequate, this galvanic cell may be worth investigating. However, it will require development of a suitable electrolyte and even then it will only be useful if the activity of the dissolved oxygen varies sufficiently with changes in its concentration."

The major problem was to obtain a solid electrolyte which would be nonporous, compatible with the conditions of the liquid metal environment, and have a high ratio of ionic-to-electronic conductivity. Previous work on solid electrolytes had been primarily directed toward providing thermodynamic data.(26) The materials considered in the earliest studies were unsatisfactory.

The problem was reviewed and a development effort was begun late in 1961(27) using calcia-stabilized zirconia as the electrolyte. In the initial experiment, the cell consisted of zirconium metal chips as one electrode, packed inside a calcia-stabilized zirconia closed end tube as the electrolyte, and the tube immersed into liquid sodium as the second electrode. The voltage produced was measured by a potentiometer. In the exploratory experiments, the voltage decreased with time. This was attributed to progressive shorting by sodium. In subsequent experiments the performance was impaired when the cell was operated at temperatures in the range 900 to 1190°F, due to a reaction between sodium and the calcia-stabilized zirconia tube. A temperature of 560°F was satisfactory. Several different reference electrode materials were evaluated also.(28) Cells with a $Cu\text{-}Cu_2O$ reference electrode were the most stable and yielded the most reproducible results.(29) The time response of the cell was relatively long, of the order of an hour. Slow, and sometimes erratic, drift in output voltage was observed in some instances particularly when the cell had been subjected to relatively high temperatures. An explanation given(30) was that, above 750°F, the zirconia reacts with sodium to form an oxygen-deficient surface layer. The surface layer delays the cell response. Post-test examination supported this explanation. Another problem with the zirconia tubes was that they were too fragile for non-laboratory use.

Subsequent development resulted in a satisfactory instrument which is described in Section IV-C.

B. PRINCIPLE OF OPERATION

A net change in potential energy is the result of a chemical reaction. In some reactions, the energy change may appear as an electrical energy change. Thie type of energy conversion provides a means of determining impurity concentration in liquid metals.

The case of main interest is oxygen as the impurity and sodium as the liquid metal. The objective is to form a galvanic cell so that the sodium-sodium oxide is one electrode. A metal-metal oxide of suitable composition is the other electrode, and a solid oxide electrolyte is interposed.

The galvanic cell may be represented as:

$$\text{Na}, \text{Na}_2\text{O}_D \,\|\, \text{Solid Electrolyte} \,\|\, \text{M}, \text{MO}$$

where M refers to a metal and MO refers to its oxide. The subscript D indicates that the Na_2O is dissolved. The oxidation potential of sodium is high and most metals which may be used for the other electrode have lower oxidation potentials (are more electronegative). If M is an element more electronegative than sodium, the cell reaction is

$$2Na + MO = Na_2O_D + M \ .$$

To elicit the concept of electrical energy conversion, this relation is expressed as two half-reactions,

$$O^= + 2Na = Na_2O_D + 2e^-$$

and

$$MO + 2e^- = 2M + O^= \ .$$

The electric charge is transported through the electrolyte by the $O^=$ ions. This form of conduction, ionic conduction, is the objective. Any electronic conduction is detrimental. Since the materials are chosen for a high ratio of ionic to electronic conduction, and this objective is achieved in practice, the effects of electronic conduction are neglected at this point in the discussion.

The relation between the quantity of electricity and the quantity of oxygen ions is given by the Faraday Constant, F, which in cgs units is 9652 emu/mole. Since the potential difference, E, is the amount of energy required to transport a charge from one point to another, (or energy per unit charge), the relationship between the free energy ΔG per mole and the potential difference is,

$$\Delta G = 2EF$$

where E is in emu. The factor 2 accounts for the double charge on the oxygen ion. Rewriting the above expression,

$$E = \frac{\Delta G}{2F} \ .$$

It is necessary to obtain an expression relating activity, a, to free energy ΔG. This may be accomplished by the introduction of two definitions and mathematical manipulation as follows.

Fugacity, f, is defined(31)

$$RT\,d\,\ell n\,f = dG$$

where R is the gas constant and T is the temperature.

The activity of a substance is defined(31)

$$a = \frac{f}{f^\circ}$$

where the superscript (here and later) indicates the standard state.

Since f° is constant at constant temperature, and a° is by definition unity, integration of the above relation from the standard state to an arbitrary state gives

$$RT\,\ell n\,a = G - G^\circ .$$

The free energy change is the algebraic sum of the free energies of the components, so designating the components with subscripts, the equation may be written,

$$\Delta G^\circ - \Delta G = RT\,\ell n\,\frac{\left(a_M^2\right)\left(a_{Na_2O_D}\right)}{\left(a_{Na}^2\right)\left(a_{M_2O}\right)}$$

and

$$\Delta G = \Delta G^\circ - RT\,\ell n\,\frac{\left(a_M^2\right)\left(a_{Na_2O_D}\right)}{\left(a_{Na}^2\right)\left(a_{M_2O}\right)}.$$

Using this value for ΔG in the equation for the potential difference is,

$$E = \frac{\Delta G^\circ - RT\,\ell n\,\dfrac{\left(a_M^2\right)\left(a_{Na_2O_D}\right)}{\left(a_{Na}^2\right)\left(a_{M_2O}\right)}}{2F}.$$

The free energy in standard state ΔG° is the algebraic sum of the free energy of formation of the constituents Na_2O and M_2O so the general equation is

$$E = \frac{\left(\Delta G_{M_2O} - \Delta G_{Na_2O}\right) - RT\ln\frac{\left(a_M^2\right)\left(a_{Na_2O_D}\right)}{\left(a_{Na}^2\right)\left(a_{M_2O}\right)}}{2F}.$$

The emf E is a measure of the thermodynamic activity of the oxygen in sodium. This equation expresses E as a function of activity. So far as corrosion and similar phenomena are concerned, the activity is the factor of concern. However, it is customary to describe the impurity level in terms of the concentration, C, rather than the activity, so the relationship between activity and concentration must be expressed. This relationship is expressed as:

$$a = \gamma C$$

where γ is the activity coefficient (defined as the ratio of the activity to the mole fraction), and C is the concentration. The activity coefficient is unity for the a's except $a_{Na_2O_D}$. The activity of Na_2O in saturated sodium solution is unity, so

$$\gamma = \frac{1}{C_o}$$

where C_o is the concentration at saturation. Upon substituting the values into the general equation, the equation for emf as a function of concentration is obtained:

$$E = \frac{\left(\Delta G_{M_2O} - \Delta G_{Na_2O}\right) - RT\ln\frac{C}{C_o}}{2F}$$

Upon specifying the composition of the electrode represented by M_2O, the value of its free energy of formation and the value for Na_2O is obtained from available thermodynamic data.(32)

Thus, for a given cell,

$$E = E_o - \frac{RT}{2F} \ln \frac{C}{C_o}$$

where E_o, the standard potential, is given by the relation,

$$E_o = \frac{\Delta G_{M_2O} - \Delta G_{Na_2O}}{2F}.$$

Since E_o and R are constants, the emf, E, is a function of temperature and of the logarithm of the ratio of the concentration to the maximum concentration. The value of maximum concentration has been the subject of many investigations. The numerous measurements of the solubility as a function of temperature have been reviewed and the overall correlation of values has yielded the equation,(33)

$$\log_{10} y = 1.21 - \frac{1777}{T}$$

where y is the weight percent of oxygen in sodium assumed to be Na_2O. Changing the base and using C' to indicate concentration in weight percent, gives the final equation,

$$E = E_o - \frac{RT}{2F}\left[\ln C' - \left(2.79 - \frac{4080}{T}\right)\right].$$

C. DESCRIPTION OF THE ELECTROCHEMICAL CELL

The energy conversion method of measuring oxygen activity in sodium, based upon the electrochemical cell described, has been developed by the United Nuclear Corporation. A survey of published literature and other information sources has shown no other organizations engaged in electrochemical cell development for alkali liquid metal applications, though a considerable amount of related work has been done by others. Some studies have been conducted on other liquid metals.(34,35) Solid electrolytes, and factors affecting their performance, are discussed in References 36 and 37.

The following excerpts from the Operating Manual(38) describe the instrument which has been developed and is available commercially off-the-shelf.

"The Electrochemical Oxygen Meter is an on-line device for measuring oxygen activity in sodium. It is installed directly in an operating sodium system and provides continuous indication of changes in oxygen activity without necessity for sampling and chemical analysis. It is intended for operation in the range from less than 1 ppm to about 100 ppm of oxygen. The sensing element of the Electrochemical Oxygen Meter is a galvanic cell employing a ceramic oxide solid electrolyte. The cell develops a voltage which is dependent upon the oxygen content of the sodium.

"The cell consists of a reference electrode and solid electrolyte immersed in the liquid sodium (as shown schematically in Figure 44). The solid electrolyte is a gas- and sodium-tight thoria-15 wt % yttria tube. This material has a crystal structure containing oxygen ion vacancies, and conducts electricity, predominantly* by migration of oxygen ions via the vacancies. Within the tube is a reference electrode of copper-cuprous oxide. The reference electrode makes electrical contact with the inside surface of the electrolyte and establishes a constant oxygen activity at this surface. The liquid sodium which contains dissolved oxygen forms the second electrode of the cell. It makes electrical contact with the outside surface of the electrolyte and establishes oxygen activity

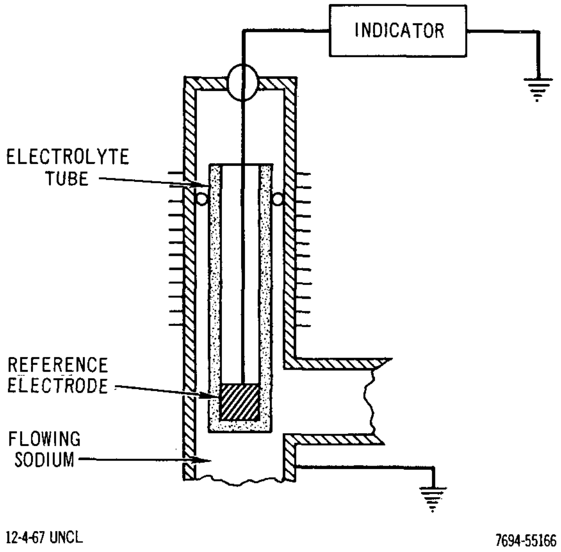

Figure 44. Schematic Diagram of Electrochemical Oxygen Meter

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*The degree of ionic conduction is measured by the ionic transport number, which is the ratio of ionic conductivity to total conductivity of the electrolyte. Predominant ionic conductivity is assumed if $t_{ion} > 0.99$.

at this surface. The oxygen activity at the outer surface will vary with the oxygen content of the sodium.

"The galvanic cell which is created is:

$$\mathrm{Na, Na_2O_{(Na)}} \| \mathrm{ThO_2 - 15\ wt\ \%\ Y_2O_3} \| \mathrm{Cu, Cu_2O}$$

where $Na_2O_{(Na)}$ represents oxygen dissolved in sodium. The spontaneous cell reaction is:

$$2Na + Cu_2O \rightarrow Na_2O_{(Na)} + Cu \ . \qquad \ldots(1)$$

"An electromotive force is developed between the sodium and reference electrode as a result of the difference in oxygen activity at the two electrolyte-electrode interfaces. Assuming predominantly ionic conduction in the thoria-yttria electrolyte, the cell emf is given by:

$$E = E_T^\circ - \frac{RT}{2F} \ln [Na_2O_{(Na)}] \qquad \ldots(2)$$

where

E_T° = standard electrode potential in volts at T, °K

T = cell temperature, °K

F = Faraday constant, 23,065 cal/volt-g-equivalent

R = gas law constant, 1.987 cal/g-mole, °K

$[Na_2O_{(Na)}]$ = activity of oxygen dissolved in sodium.

"In engineering systems, the use of oxygen concentration rather than activity is more convenient. By Henry's law, at the low concentrations which exist in practical sodium systems, the oxygen activity may be expressed in terms of oxygen concentration. The relationship then is given by:

$$E = E_T^\circ - \frac{RT}{2F} \ln \frac{C}{C_0} \qquad \ldots(3)$$

where C is the actual oxygen concentration, and C_0 is the solubility at temperature of the cell.

"For a given cell at constant temperature, cell voltage varies only with oxide concentration. Changes in cell voltage accurately reflect changes in oxide concentration. The change in cell emf for a given change in concentration is given by:

$$\ln \frac{C_1}{C_2} = (K)(E_1 - E_2) \qquad \ldots(4)$$

where K is an experimentally determined constant.

"In practice, it is found that the cell emf is generally lower than the theoretical values predicted by Equation 3. However, the change in emf for a given change in concentration is reproducible, and is in good agreement with the theoretical behavior indicated by Equation 4. At the 95% confidence level the value of K is -36.1 ± 5.4 volt^{-1}, compared to a theoretical value (2F/RT) of -39.5 volt^{-1}. (Figure 45 shows the relation between the voltage change as a function of concentration ratio.)

"The body of the sensing element is a 1/2-in. OD by 1/16-in. wall by 8-in. long thoria-15 wt % yttria tube. The tube is closed at one end. Within the tube at the closed end is the reference electrode, consisting of a mixture of equal volumes of sintered copper and cuprous oxide powders. Electrical contact is made to the reference electrode by means of a spring loaded copper contact assembly. The contact is brought out through an intermediate insulated support and hermetically sealed triaxial connector in the upper housing. The connector mates with the plug on the instrument package input cable." Figure 46 shows the functional block diagram.

D. DISCUSSION AND EVALUATION

A number of Electrochemical Oxygen Meters have been produced. Some of these have been placed into operation in typical applications and others have been subjected to performance evaluation in various laboratories.

The object in developing an electrochemical oxygen meter for use in liquid metal systems was to provide an in-line instrument for continuously measuring oxygen concentration in the low concentration region, down to 1 ppm. This

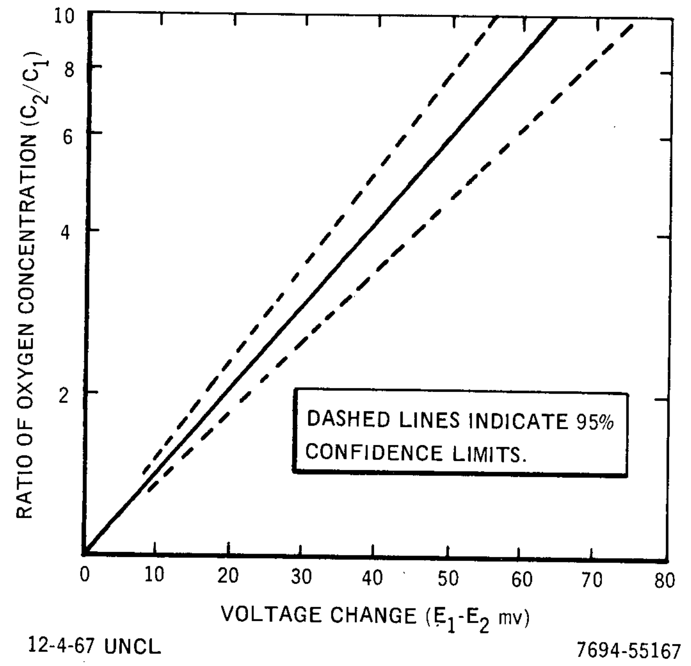

Figure 45. Voltage Change vs Oxygen Concentration Ratio at 600°F

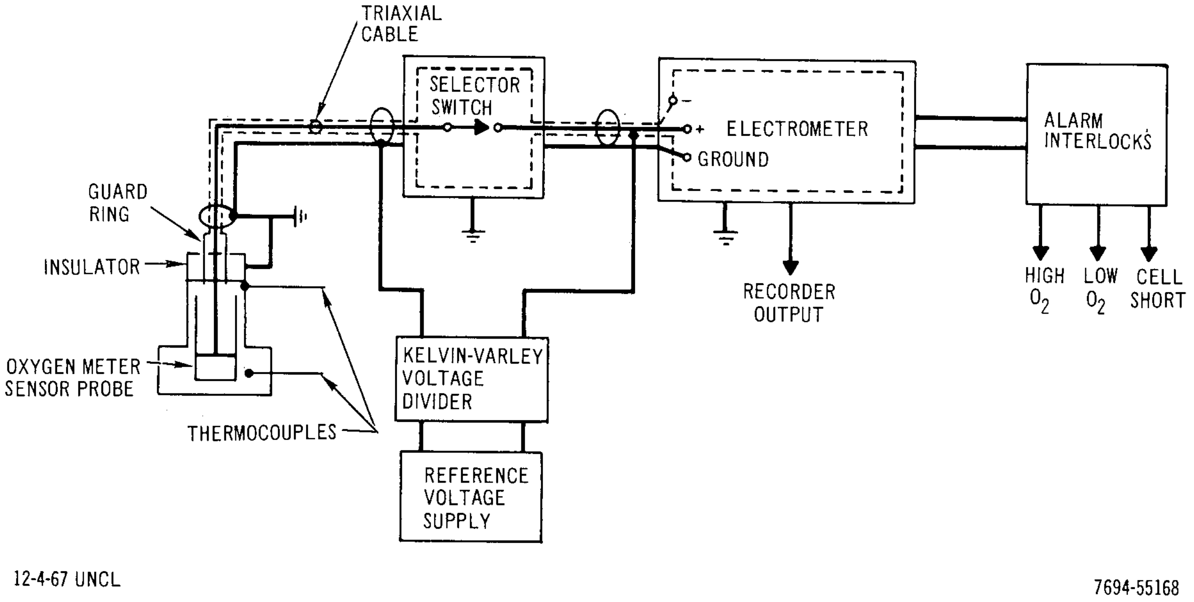

Figure 46. Functional Block Diagram of Instrumentation

objective has been met. However, there are other requirements pertaining to practical applications and some of these have not been met as satisfactorily as desired.

1. Operating Characteristics and Limitations

a. Temperature

The temperature operating range is relatively narrow with a recommended value 315°C (600°F).(38) At temperatures significantly above this value the solid electrolyte is chemically reduced by sodium.(39) Operation has been satisfactory at a temperature as high as 1000°F.(39) However, the lower temperatures permit a longer operating life. At temperatures much below 500°F the resistance of the reference electrode is too high for satisfactory operation.(38)

The solid electrolyte tubes are sensitive to thermal shock, a general characteristic of ceramics. Several have been fractured from this cause. No specific values of shock, found to be damaging, have been reported.

b. Accuracy

The accuracy of calibrated instruments has been given as ±10% in the range 1 to 30 ppm oxygen.(35) Indications based upon the theoretical predictions may be in error by as much as 30%.(40) Factors to consider in relation to accuracy are:

(1) Stabilization

The cell voltage drifts gradually during the first 24 hours of operation at the recommended operating temperature 315°C (600°F).(38) During this initial period of stabilization, an equilibrium is attained between the cell and the sodium. This limits practical use of the instrument to the period after stabilization.

(2) Temperature Sensitivity

The cell is sensitive to temperature changes of the liquid metal in which it is immersed and changes in the ambient air temperature around the meter housing. The recommended value of liquid metal temperature is 600 ± 50°F.(38)

According to the theoretical equation for the emf, the temperature coefficient is a function of oxygen concentration. The theoretical values range from -0.036 mv/°C to +0.126 mv/°C. Experimental data show that the coefficient is independent of concentration over the range of interest and has the value +0.938 mv/°C, according to the manufacturer,(39) and for two instruments tested independently, the values 1.15 mv/°C and 1.05 mv/°C were obtained.(40) Using the highest value, a 10°C temperature change results in a 11.5 mv cell emf change which corresponds to an equivalent oxygen concentration change of approximately 36%.

The effect of ambient air temperature is very noticeable. In one evaluation(40) the ambient air temperature fluctuated by as much as ±17°C, resulting in emf fluctuations as much as ±8 mv. This range corresponds to ±30% fluctuations in indicated oxygen concentrations.

(3) Calibration

The theoretical values are based upon several assumptions not necessarily realized in practice. One of these is the assumption that the conduction through the cell is ionic. Any electronic conduction, effectively, places a load on the generator thereby reducing the terminal voltage below the open circuit emf. The electronic conduction has been blamed for the discrepancy in temperature coefficient(39) and the lower voltage.(40) Another assumption to consider is the dependence of the theoretical relationship on measured values of solubility as a function of temperature. In a recent (1965) survey of solubility determinations, the following statement was made "...At present, over the temperature range 100 to 500°C, considering all the data and ignoring any adjustments by the original authors, the solubility cannot be estimated to an accuracy of better than ±50%."(33) Moreover, discrepancies are greatest in the concentration range in which this instrument operates. The situation may not be as bad at the present time as indicated by the ±50% value, since improvements are being made and higher accuracies are claimed.

Calibration is accomplished after stabilization by cold-trapping at a temperature below about 150°C (300°F) until the voltage is constant to within ±5 mv and the plugging meters or other indicators show a constant impurity content over a period of several hours. Additional calibration points are obtained by repeating the process at a series of cold-trap temperatures. This requires that the cold trap have sufficient oxide in it to saturate the sodium in the loop at the selected cold-trap temperatures. The equivalent oxide concentration is obtained by assuming oxide saturation at the cold-trap or plugging temperature or by chemical analysis of sodium samples. The emf follows a relation of the form

$$\ell n\, C = I - 36.1E$$

where I is an empirically determined intercept on a semilog plot.(38) This calibration procedure requires a solubility determination and is therefore subject to the well-known problems indicated above.

Selected data for four meters are presented in Figure 47.(39) The calculated theoretical performance is also shown. The band representing the theoretical performance is the result of uncertainty in the solubility of oxygen at the recommended operating temperature, 315°C (600°F).

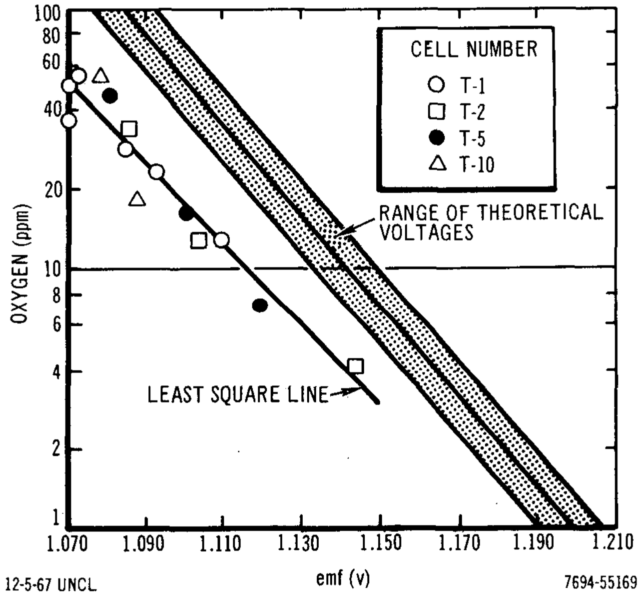

Figure 47. Typical Calibration of emf vs ppm Oxygen in Sodium ‖ ThO_2 - 15 wt % Y_2O_3 ‖ Cu, Cu_2O Cells at 600°F

Values of accuracy as a function of operating time have not been reported. However the various data available suggest that the initial accuracy is maintained for a period of at least 2 months. The cell operating life sometimes is not much longer, although operation for a year has been reported.(3) The short-term stability is unsatisfactory. The conclusion reached in one study(3) stated that "...the cells are generally unreliable on a day-to-day basis because of the short-term, temporary changes in calibration."

The performance as a function of liquid flowrate has been evaluated for flowrates of 15.8 to 190 cm^3/sec (0.25 to 3 gpm). No effect upon calibration or response to changes in oxygen concentration was apparent.(39)

(4) Selectivity

The emf of the electrochemical cell provides a measure of the thermodynamic potential of oxygen dissolved in sodium. Under equilibrium conditions, the measure is independent of the form of the oxygen, provided it is in solution, and is independent of other impurities. The electrochemical cell is considered to measure concentration by virtue of Henry's Law, which relates concentration to activity, a function of thermodynamic potential. Henry's Law is obeyed approximately. Moreover, the activity of dissolved oxygen may be affected by other impurities. Consequently, under some circumstances, the indicated value of concentration may not bear the expected or intended relation to the thermodynamic potential. While this would result in an error in expressing the oxide impurity concentration for general measurement purposes, the indication is correct as a measure of thermodynamic activity, and this is the quantity of interest in assessing chemical and metallurgical effects in containment materials. Hence, the effective oxygen content indicated is the equivalent concentration of dissolved sodium oxide which would exhibit the same activity or chemical potential.

As an example, the impurities which will alter the relationship between total oxygen content and activity are OH, CO_3, and $(Na_2O)_2 \cdot FeO$.(38) It has been found that the addition of carbon to sodium is without effect upon the cell.(41) Hydrogen in the gas above the sodium may be troublesome if it can diffuse to the cathode and interact with the metal oxide.(41)

(6) Response Time

Measurements of response time have been made using a change in cold trap temperature to change the oxide concentration.(39,40) The instrument "followed" the changes but, since the changes by this method occur so slowly (hours), the results do not provide a suitable measure of response time. The "tea-bag" method of adding oxide was used and the initial response was observed within 5 minutes. The full response required about 3 hours but this length of time was attributed to the solution rate.(39)

c. Environment

The temperature as an aspect of environment has been discussed on Page 75. The electrolyte is a ceramic tube and, compared to other components of liquid metal systems, it is fragile. No quantitative data on the susceptibility to damage by mechanical forces have been reported. Preliminary tests to determine the effect of radiation indicated that the response of the cell is affected by exposure to radiation.(42)

V. PERMEABLE DIAPHRAGM

A. BACKGROUND

The techniques of sensing impurities while they are in the liquid metal is limited by the adverse or interfering effects of the liquid metal on the sensor. However, the separation or extraction of impurities from the liquid metal enables the use of several additional detection and measuring methods.

The only method which has received extensive attention is the method of selective diffusion through a diaphragm. In the case of hydrogen detection the technique is based upon first extracting the hydrogen from the liquid metal by the use of a membrane and then sensing the gas in a convenient environment by any of several well-established gas detectors.

The permeation of a substance through a metal membrane has been the subject of scientific investigations for many years. Accordingly, a substantial body of knowledge related to this subject has been developed.

The use of this method as a basis of impurity detection in liquid metals was evaluated early in the liquid metal technology development, primarily as a means of detecting a sodium-to-water leak in a heat exchanger.(43) The feasibility of detecting the hydrogen was demonstrated and further development followed.(44)

A number of instruments to detect hydrogen, using nickel and nickel-plated palladium as membrane materials, have been made and tested. One of these has been developed to the point of an established design with engineering drawings.(44) However, none are available commercially. An instrument for detecting carbon using an iron membrane is under development. Upon successful completion of the development, production as an off-the-shelf commercial instrument is to be expected.

B. PRINCIPLE OF OPERATION

When two dissimilar substances are placed in contact, the atoms of each may migrate across the interface and diffuse through the other substance. This phenomenon is not detectable in most solid-solid contacts, but occurs obviously in most gas-gas contacts. The occurrence in the various contact combinations of liquids, solids, and gases depends upon a number of factors.

Here, interest is in a membrane which will contain the liquid metal on one side while permitting the passage of an impurity to the opposite side, where it actuates a sensor. The impurities of interest have been identified as oxygen, hydrogen, nitrogen, and carbon.

The permeability of a membrane is a function of complex processes. The process depends upon the behavior in the three regions listed below.

1) Entrance surface involving adsorption, dissociation, and solution
2) Bulk diffusion
3) Exit surface involving desorption and recombination.

It has been found that in all instances of permeability, the material permeating the metal is soluble in the metal. It is therefore concluded that solubility is an entrance requirement. There is evidence to show the adsorption and dissociation also are requirements.

The rate of diffusion within the membrane is proportional to the concentration gradient as expressed by Fick's first law

$$J = -D\frac{\partial C}{\partial x}$$

in which J is the flux or quantity of diffusing substance which passes per unit time through a unit area of a plane at right angles to the direction of diffusion; C is the concentration; x is a distance in the direction of diffusion; and D is a proportionality factor known as "diffusivity" or "coefficient-of-diffusion."

Under steady-state conditions when the amount entering the membrane equals the amount leaving, the concentration gradient is constant. Then the equation can be written

$$J = -D\frac{C_o - C_i}{X}$$

where the subscripts indicate "in" and "out," respectively and X represents the membrane thickness. In dealing with gas, it is convenient to express the concentrations in terms of pressure. For diatomic gases the relationship is expressed by Sievert's law

$$C = \sqrt{kP}$$

where k is the mass law constant and P is the gas pressure. Use of this relationship in the equation for flux gives

$$J = -\frac{D\sqrt{k}}{X}\left(\sqrt{P_o} - \sqrt{P_i}\right).$$

The rate is a function of temperature as expressed by the relationship due to Arrhenius,

$$K = a\,e^{-Q/RT}$$

where K is the reaction rate constant, a is a constant, Q is the energy or heat of activation, R is the gas constant, and T is the temperature.

Using this factor, the flux is expressed as

$$J = -\frac{D\sqrt{k}}{X}\left(\sqrt{P_o} - \sqrt{P_i}\right)e^{-Q/RT} .$$

D and $\sqrt{k}$ are functions of the substance properties and the product is denoted by c, the permeation constant of the gas-metal system. Then the final equation is written in the form

$$V = \frac{cA}{X}\left(\sqrt{P_o} - \sqrt{P_i}\right)\left(e^{-Q/RT}\right)t$$

where V is the volume of gas, t is the time, and A is the area.

When t is in hours, Q is in cal/mole, R is in cal/mole-°K, T is in °K, P is in atmospheres, X and A are in cm, and C is in cm^3 (STP)-mm/hr/cm^2-$atm^{1/2}$, then V is in cm^3.

C. DESCRIPTION OF PERMEABLE DIAPHRAGM INSTRUMENTS

1. Hydrogen-Permeable Membrane

The method of using the hydrogen-permeable membrane is based upon its ability to pass the hydrogen from the liquid metal to an environment suitable for a hydrogen sensor.

The permeation rate of hydrogen through various materials is shown in Figure 48.(45,46) Nickel is the material generally used since it is compatible with the liquid metals, is a common engineering material, and has a high permeability. Palladium, which has a much higher permeability, is not compatible with liquid metals and, since it is a precious metal, is not a common engineering material. It is sometimes used with a nickel plating to protect it from the liquid metal.

The earliest instrument was developed as an alarm device to detect hydrogen generated by a water-sodium reaction in a heat exchanger leak. The requirements emphasized speed of response and sensitivity in the 0 to 30 ppm range. Other conditions relating to long trouble-free life in practical systems were imposed. One of the earliest devices was constructed as shown in Figure 49.

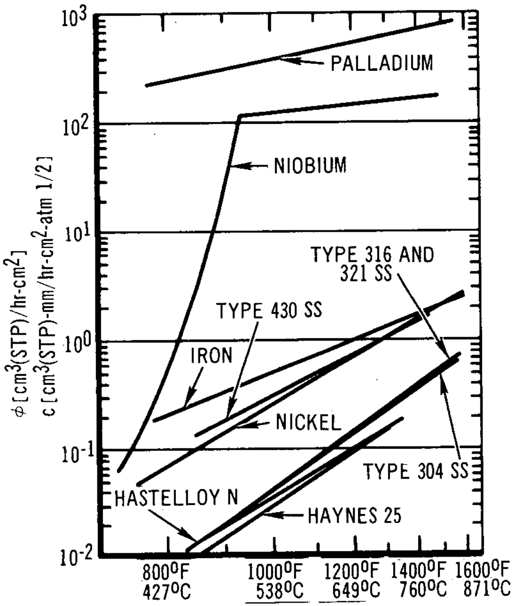

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Figure 48. Permeation Rate of Hydrogen vs Temperature for Several Materials

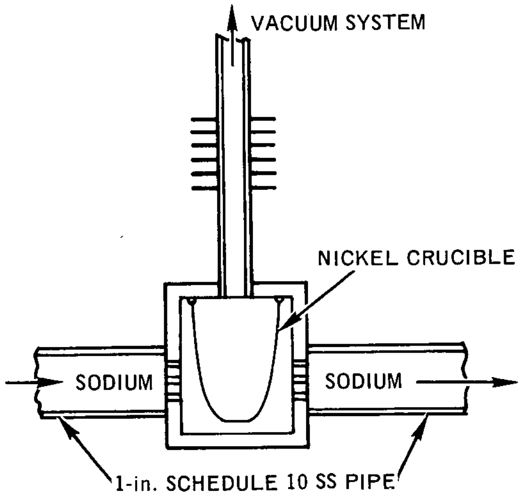

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Figure 49. Schematic of In-Line Hydrogen Extraction Device

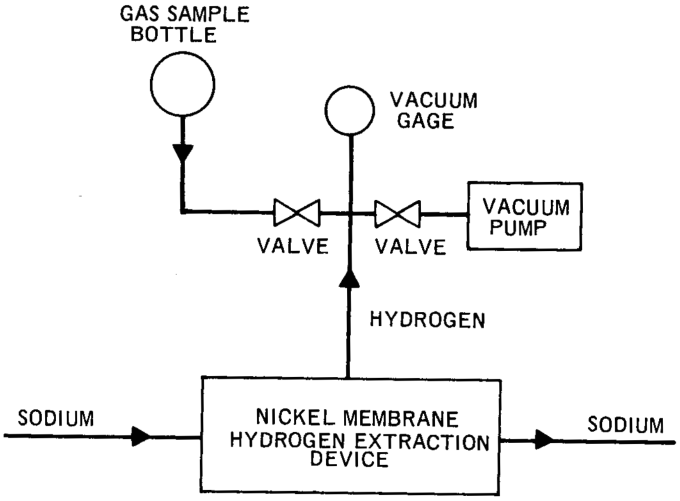

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Figure 50. Hydrogen Detector Schematic Diagram

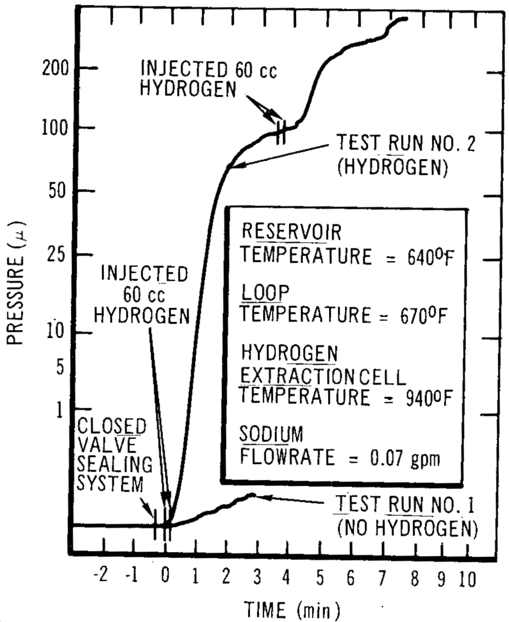

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Figure 51. Hydrogen Extraction vs Time

The device consisted of a nickel membrane in the form of a crucible (for convenience and ready availability) welded over the opening of a flanged tube. The membrane was immersed and sealed into a vessel through which sodium flowed. The tube was connected to a vacuum system and, in the absence of any permeation of the nickel, a high vacuum was attained. When hydrogen was injected upstream into the sodium, and was carried downstream past the membrane, the hydrogen adsorbed on the membrane surface permeated the membrane and appeared in the vacuum system. A conventional vacuum gage indicated the presence of the hydrogen as a gas pressure rise. The arrangement is illustrated in Figure 50. The gas sample bottle permitted collection of the gas for spectroscopic analyses. Data showing the time response are presented in Figure 51.

Another detector in the form of a concentric tube as shown in Figure 52 was made and evaluated over a range of operating conditions. The data are presented in Figures 53, 54, and 55. In these tests water was injected to produce the hydrogen. It was found that, when the tube axis was horizontal, the sensitivity was higher than when the axis was vertical. This fact, in addition to the effect of velocity as shown in Figure 53, indicates that an arrangement permitting hydrogen to accumulate on the membrane surface is beneficial.

Figure 56 shows a nickel diffusion tube hydrogen monitor constructed essentially as described in the engineering drawing presented in Reference 44. This type was tested by upstream injections of water into the upstream sodium. The resultant hydrogen readily diffused through the nickel tube and, as expected, was registered as a pressure increase.(47)

A somewhat different method of monitoring hydrogen was used in the "APDA in-line hydrogen meter"(48) shown in Figure 57. The operation as described in Reference 48 is that "...oxygen can be used to pump hydrogen through a metal wall by using it to catalytically oxidize the hydrogen to water as it emerges from the wall. Thus, sodium containing hydrogen can be passed through a tube, for example, and the hydrogen diffusing through the tube wall is oxidized to water and the water concentration can be measured. The rate of hydrogen diffusing through the tube wall is related to the hydrogen concentration in the sodium."

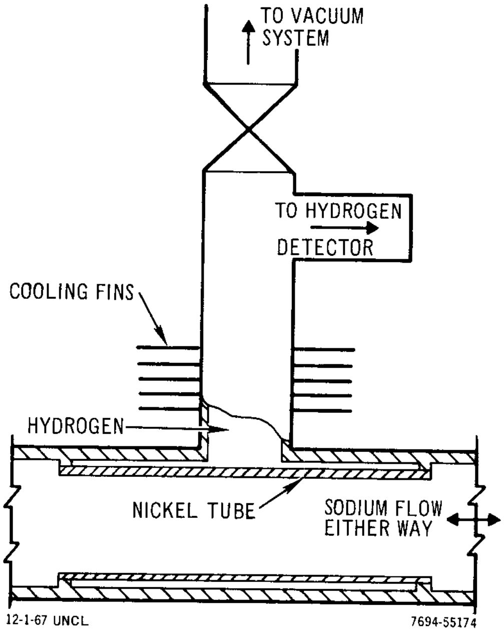

Figure 52. Concentric Tube Detector

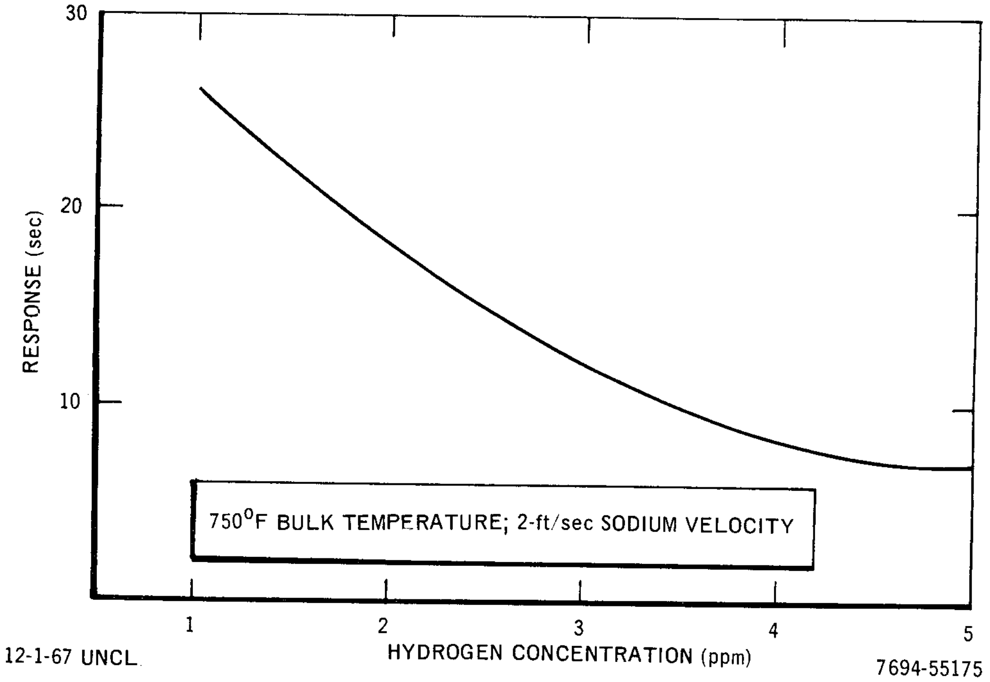

Figure 53. Response Time vs Hydrogen Concentration

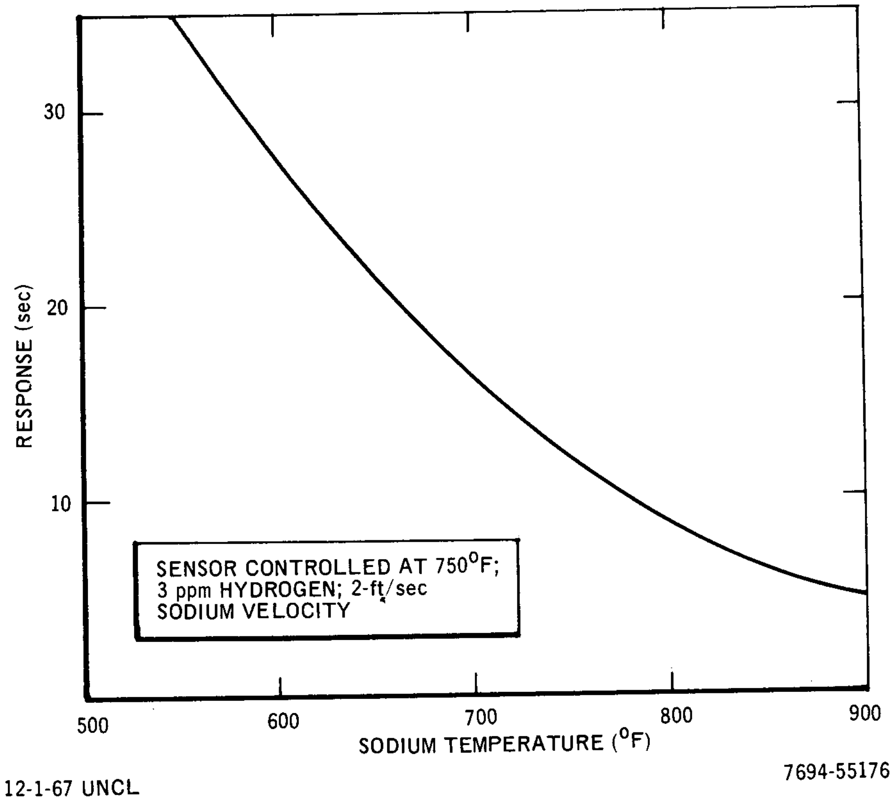

Figure 54. Response Time vs Temperature

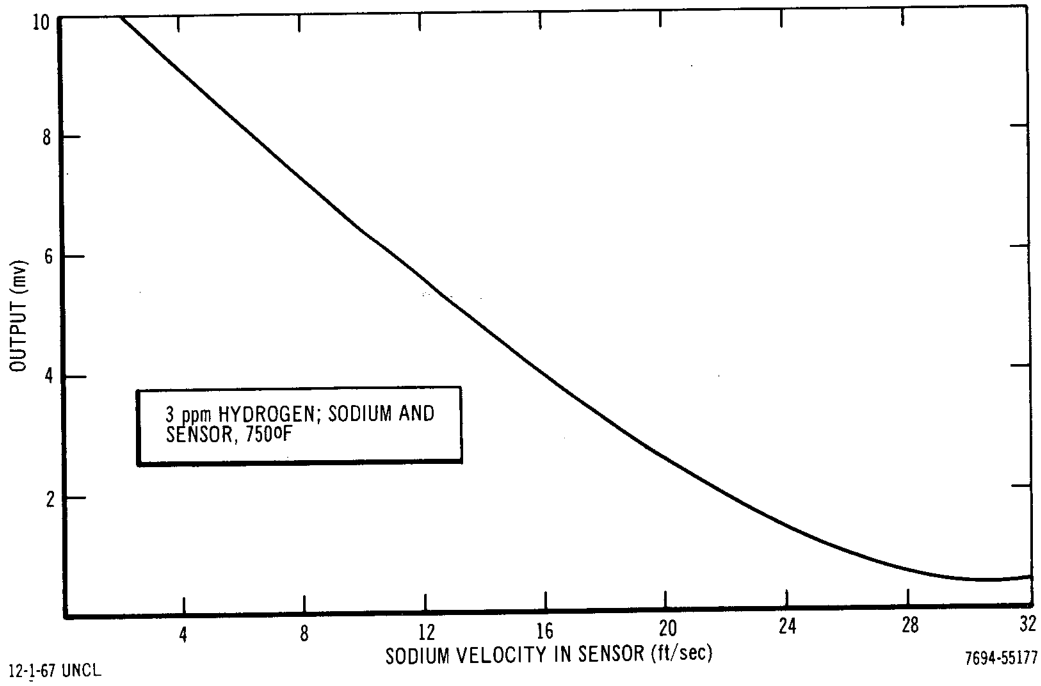

Figure 55. Detector Output vs Sodium Velocity

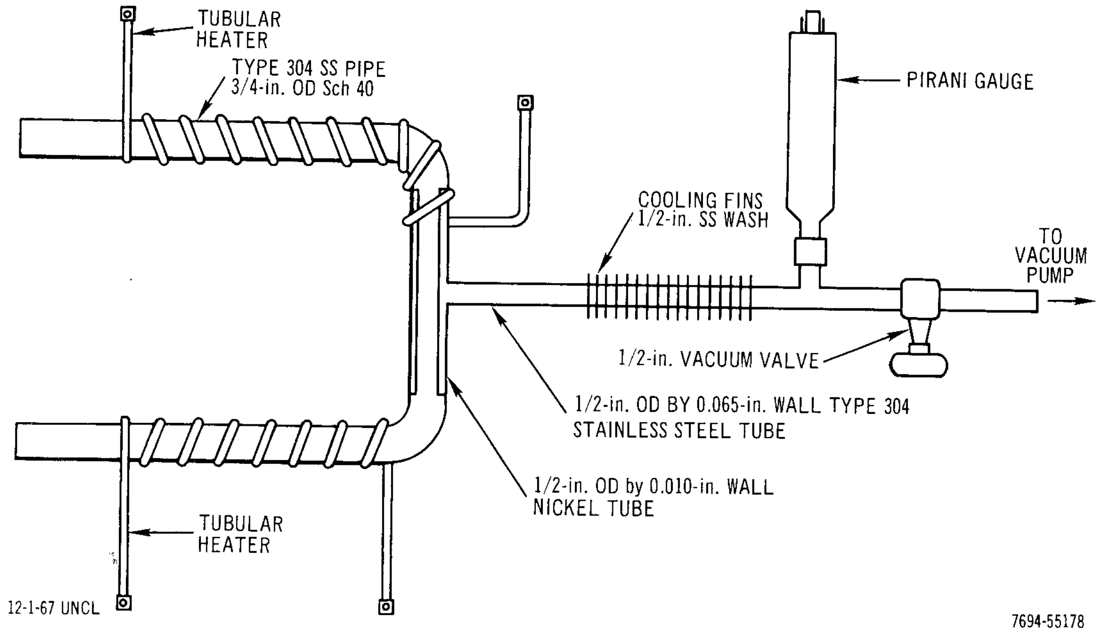

Figure 56. Nickel Diffusion-Tube Hydrogen Monitor Schematic

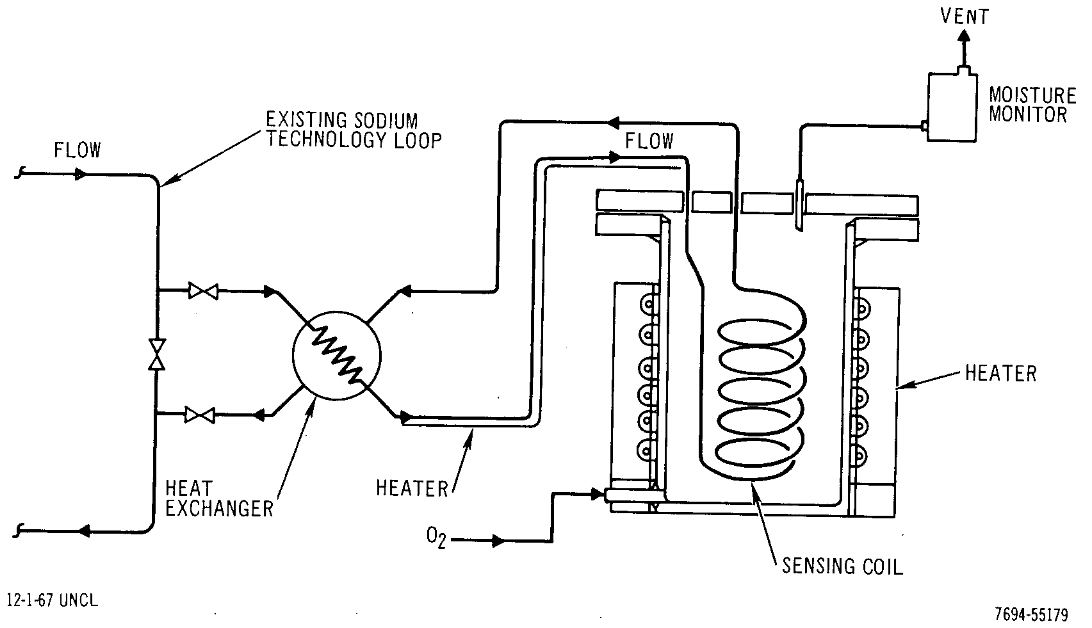

Figure 57. In-Line Hydrogen Meter

Three types of sensor coils which have been evaluated are described(42) below.

1) Nickel plated palladium, 0.002-in. nickel plate on 0.010-in. palladium
2) Palladium-plated nickel, 0.0002-in. palladium on the inside of 0.010-in. nickel.
3) Nickel-clad palladium, bimetallic tubing drawn together to 0.003-in. nickel on 0.012-in. palladium.

Each of the coils was made of 1/4-in. OD tubing, ~100-in. long, and wound in the form of a helix 4-in. in diameter and 4-in. high.

Coil Type 1 appeared to be less responsive than the other types. This was attributed to a high phosphorous content in the nickel plating, hindering the hydrogen diffusion. Also, brittle blisters had formed on the nickel plate after about one month of operation at 700 to 950°F.

2. Carbon Permeable Membrane

Carbon permeability of compatible membrane materials is relatively low (compared to hydrogen). To be useful in passing a sufficient amount of carbon to satisfy detection instrument requirements, a relatively high membrane temperature must be used. This factor – plus others such as liquid metal compatibility, carbon solubility, and carbon stability – limits the choice of membrane materials to iron, cobalt, and nickel. Cobalt is not readily available in a form suitable for this application, so for immediate use the choice is limited to iron and nickel.

The permeability is related to the solubility and diffusivity of carbon in the membrane. Figures 58 and 59 show the solubility of carbon in iron and nickel, respectively, and Figure 60 shows the diffusivity.(49)

While the scientific and engineering investigations of solubility and diffusivity of carbon in iron and nickel have been active for many years, the application to the development of a instrument for monitoring carbon in liquid metals is very recent and is apparently limited to one development program. The development by United Nuclear Corporation is expected to result in a commercially available off-the-shelf instrument.

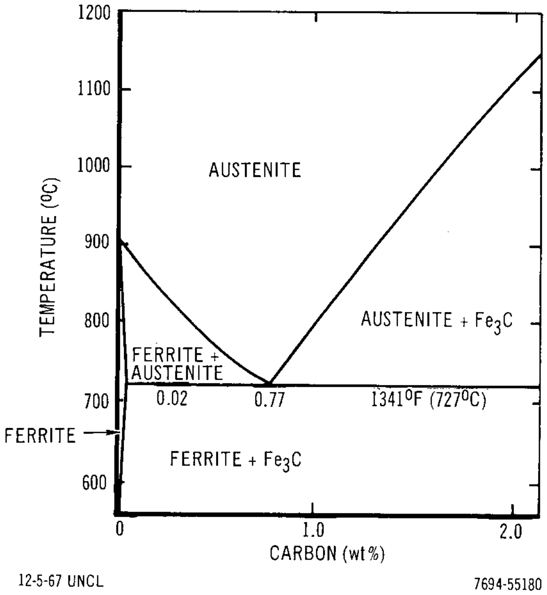

Figure 58. Fe-Fe_3C System

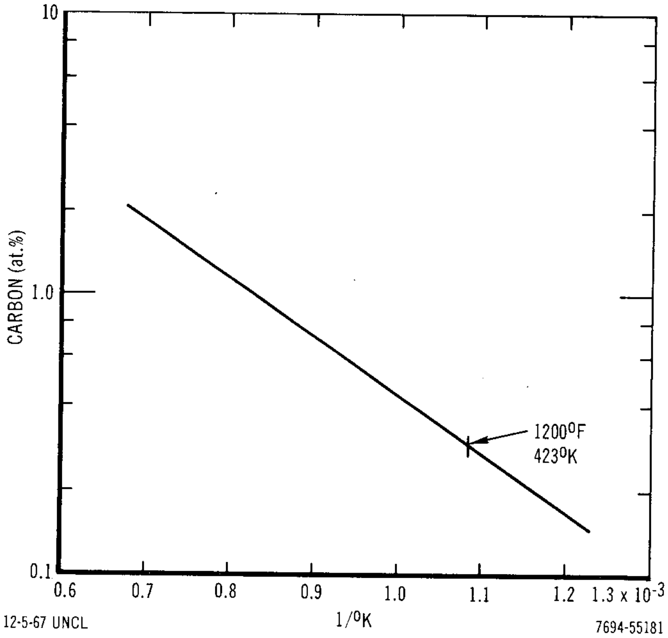

Figure 59. Solubility of Carbon in Nickel

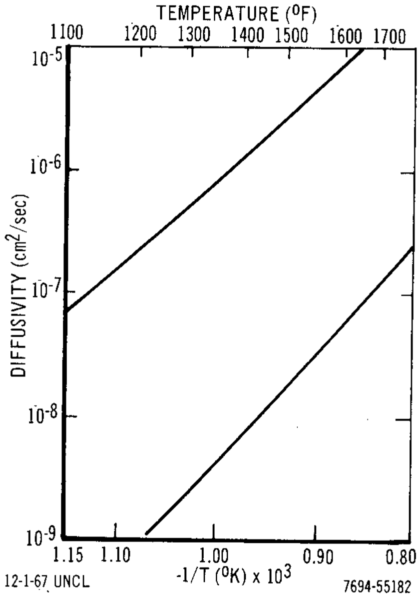

Figure 60. Diffusivity vs 1/T for Carbon in Iron (α), Iron (γ), and Nickel

The initial design is illustrated in Figure 61.(49) The sodium flowing through the Tee flows in contact with the carbon-permeable membrane in the form of a closed-end tube immersed in the sodium. Carbon permeates through the membrane to the interior surface of the tube. A decarburizing gas flowing through the tube interior removes the carbon from the interior surface. The resulting gas is passed into a gas analyzer which indicates the amount of carbon present.

The choice of decarburizing gas is based upon consideration of its compatibility with the membrane, its stability, the formation of a product amenable to detection by conventional analyzers, and freedom from objectionable permeation through the membrane into the liquid metal. Consideration has been given to the use of hydrogen. It has the advantage of reacting with carbon to produce methane, CH_4, a readily detectable gas. Water vapor, however, is more attractive in several ways. The products of its reaction with carbon are carbon monoxide, CO, and hydrogen, H_2.

Tests have demonstrated feasibility of this instrument and current effort is directed toward further development.

D. DISCUSSION AND EVALUATION

The instruments based upon the use of a permeable membrane to separate the impurities from the liquid metal are still in the development stage. Accordingly the performance data available are limited to those from development tests.

Present results are promising. Feasibility has been demonstrated, and no formidable technical obstacles are evident.

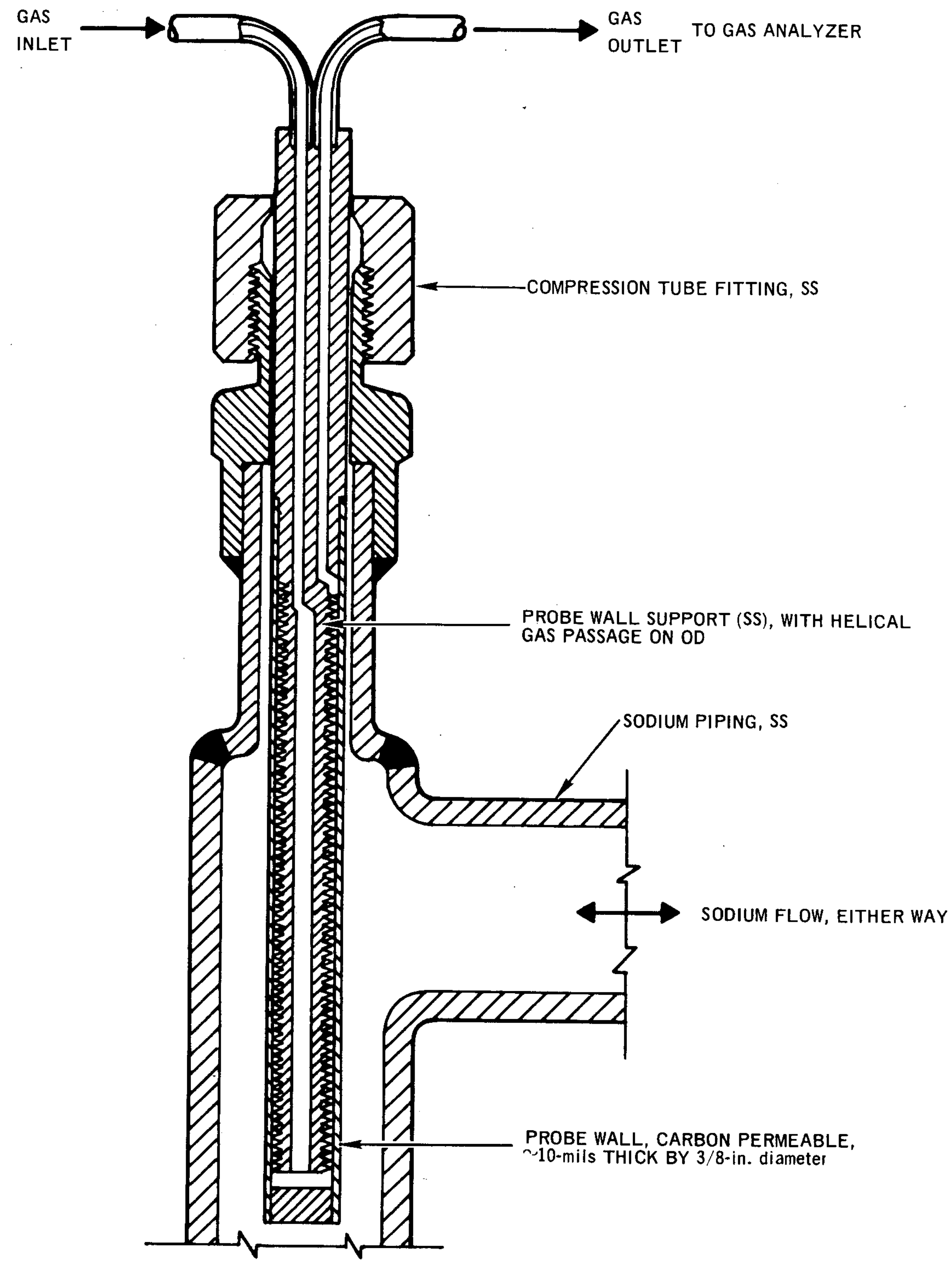

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Figure 61. Carbon Meter Probe Schematic Diagram

VI. RESISTANCE METER

A. BACKGROUND

The effect of impurities and of alloying on the resistivity of metals has been investigated for many years. Accordingly a substantial body of scientific and engineering literature on the matter has been produced. In recent years a considerable amount of literature (References 50 through 55) treating resistivity in liquid metals has appeared.

Early in the development of liquid metal technology, when interest in an in-line, continuous monitor of impurities was developing, the possibility of using the resistance method was considered. Active pursuit of this approach was impeded by a consideration of several discouraging factors. The main deterrent was the need for a well-developed temperature control or compensator, since the effect of typical temperature variations was known to have an effect on resistivity of the same order of magnitude as the impurities. Other factors involved shunt resistance effects of the liquid metal container and the series resistance effects in the contacts.

In various other scientific studies, these series and shunt resistance effects were eliminated by use of the transformer principle in which the electric current was induced into a glass loop containing the liquid. The method described in Reference 56 is an example.

The main problem of measuring very small changes in resistivity due to impurities in the presence of temperature effects was viewed by L. R. Blake(57,58) as manageable if the ratio of resistivity change-to-impurity change is high enough. The enhanced sensitivity had been demonstrated for some materials, notably copper and iron. Counting on a sufficiently high sensitivity, Blake began the development of the Rhometer using the transformer method to avoid electrode problems and a special compensating circuit to minimize the temperature problems. The development was continued through production and the instrument, called the "Liquid Metal Rhometer" has become commercially available off-the-shelf. The instrument is known also as the "Blake Resistivity Meter."

The various evaluations of the resistivity method of measuring impurities have used the commercial models. The instrument used in the work described in References 18 and 59 was not of the same commercial source, but was of similar design.

B. PRINCIPLE OF OPERATION

The electric current, I, through a conductor is equal to the driving force, voltage V, divided by the retarding factor, resistance R. This relationship is known as Ohm's law.

The resistance is the product of two factors – (1) the conductor material resistivity ρ, and (2) the geometry – as expressed in the relationship,

$$R = \rho \frac{L}{A}$$

where L is the conductor length and A is the area through which the current passes. (The current is assumed to be distributed uniformly over the area).

1. Geometry Effects

The presence of an impurity in the conductor can affect the resistance by altering either of the two factors, resistivity or geometry. Consequently, a measure of the voltage across a conductor, and the current through it, may provide an indication of an impurity.

In a liquid metal system, material of relatively low conductivity suspended in the measuring region alters the geometry so far as the current distribution is concerned. For example, gas bubbles or particulate matter such as precipitated sodium oxide, increase the effective value of L/A, and hence increase the resistance.

The impurity distribution has a profound effect on the effective value of L/A. In one extreme case the impurity could extend over the entire area in cross section, thereby greatly reducing or blocking the flow of current and permitting a false indication of the impurity quantity. At the other extreme, the impurity could be distributed along a line parallel to the direction of current flow and thereby have minimum effect on the current flow. This would also give a false indication. Neither of these two extremes is typical in practice, but rather the impurities are nearly uniformly distributed throughout the volume.

The resistance can be expressed in terms of a unit volume V as,

$$R = \frac{\rho}{V^{1/3}} .$$

To simplify the discussion the impurity is assumed to have a very low conductivity compared to the liquid metal, so that the volume it occupies is equivalent to a void. Moreover, it is assumed to be distributed nearly uniformly. Then,

$$V_e = V_t(1 - C)$$

where V_e is the effective volume of the conductor, V_t is the volume of the conductor and impurity, and C is concentration by volume.

$$R = \frac{\rho}{V_t^{1/3}(1 - C)^{1/3}} = \frac{\rho}{V_t^{1/3}}\left(1 + \frac{C}{3} + \frac{2C^2}{9} \ldots\ldots\right) .$$

Since concentration generally is expressed in terms of weight, this becomes,

$$R = \frac{\rho D}{V_t^{1/3}}\left(1 + \frac{C_w}{3d} + \frac{2C_w^2}{9d} \ldots\ldots\right)$$

where d is the impurity density, D is the liquid metal density, and C_w is concentration by weight.

The resistance change for a concentration of 100 ppm of a uniformly distributed gas is of the order of a few percent. This magnitude is acceptable for measurement. A concentration of 10 ppm reduces the change in resistance to the order of a fraction of a percent, and this measurement may be obscured by interferences such as those caused by temperature changes.

2. Resistivity Effects

Electric conduction is the movement of free electrons through a material. The mechanisms and factors involved are most easily visualized by considering the material as a crystalline solid. A crystalline solid is a structure consisting of atoms in a particular pattern or array; the average position of each atom in relation to the array or lattice "structure" is fixed. When viewed in terms of conduction, the atom is considered as having two parts: (1) an atom core consisting of the nuclei with the surrounding closed shells of electrons and (2) the valence electron. The atom core is relatively massive and is the "atom" in terms of the lattice structure. The atom core is charged, hence the array is characterized by a periodic electric field distribution. The valence electrons are loosely bound to the respective atom cores and are thus distributed through the volume, and their charge neutralizes the field of the cores so that the crystal as a whole is neutral. An external field impairs the neutrality at the boundary and, since the valence electrons are relatively free, their average position changes under the influence of the external field. This transport constitutes the electric current.

Several conditions contribute to impeding the progress of free electrons through the array of atom cores. These conditions are generally termed "scattering." Free electrons pass through a perfect crystal lattice for an infinite distance without being scattered. Any disturbance to the periodicity of the lattice results in scattering and imposes a finite mean free-path for the electron. The disturbances which impair the periodicity include thermal vibrations, crystal boundaries, and foreign atoms or impurities.

The resistivity ρ is readily derived (see various textbooks, for example, Reference 60) and is given by the relationship

$$\rho = \frac{m}{ne^2\tau}$$

where n is the number of free electrons per unit volume, e is the charge on the electron, m is the mass of the electron, and τ is the relaxation time (time between encounters). The quantity of concern here is the value of τ, since it is a function of impurities. It has been the subject of numerous theoretical treatments, but none of these lead to an expression for conductivity as a function of a specific impurity in terms of quantities having established numerical values.

For the purpose of treating the utilization of conductivity measurement as a means of measuring impurities, it is sufficient to know the ratio of resistivity change to impurity concentration. It can be shown (Example, Reference 61) that the total scattering (resistance) is proportional to

$$C(1 - C)$$

where the ratio C to $1 - C$ expresses the relative number of atoms in two components of a solution. Since $C << 1$ in the impurity ranges considered here, this equation can be reduced to the statement that the scattering resistance is proportional to the impurity concentration. Then the resistivity ρ is expressed by the relationship

$$\rho = \rho_o(1 + C)$$

where ρ_o is the resistivity of the pure metal and C is the concentration.

The discussion has been based upon behavior of free electrons in a crystalline solid. As temperature is increased, the thermal vibrations increase, with the consequent impairment of periodicity and increased resistivity. At the melting point there is a "step" increase in resistivity. In the liquid state, the order, characteristic of the crystalline lattice, certainly does not exist; however there are limits in the extent of disorder. The exact nature of certain aspects of conduction in liquid metals remains uncertain but, in general, the mechanisms of conduction in liquid metals follow that in solid metals. Thus, in terms of the quantities of interest here, the relationship for resistivity as given above is applicable to liquid metals.

The resistivity of liquid metal is affected by factors other than impurities but only the temperature effect is of concern here. The temperature coefficient of resistivity is significant, and it must be taken into account when measuring impurity in terms of resistivity.

At this point, attention is called to the fact that a plot of resistivity as a function of temperature is a smooth curve in the temperature range in which the impurity is in solution but that a distinct break occurs when the temperature becomes low enough to cause precipitation. Data(54) showing the results with various metals dissolved in sodium are cited as an example. The curves are presented in Figure 62. These curves show that the solubility limit may be determined by a resistivity measurement when the liquid metal is cooled. The determination of solubility limit is the operating principle of the plugging meter. Hence, rather than use plugging as the criterion of solubility limit, these data suggest that resistivity might be used. This method appears to be more attractive than the plugging method. Compared to the conventional method of rhometer operation, it has the distinct advantage of not requiring elaborate temperature-compensating devices like those of the conventional rhometer. The effect of precipitation in rhometer operation has been observed and its use as a precipitation indicator has been recommended.(57,58)

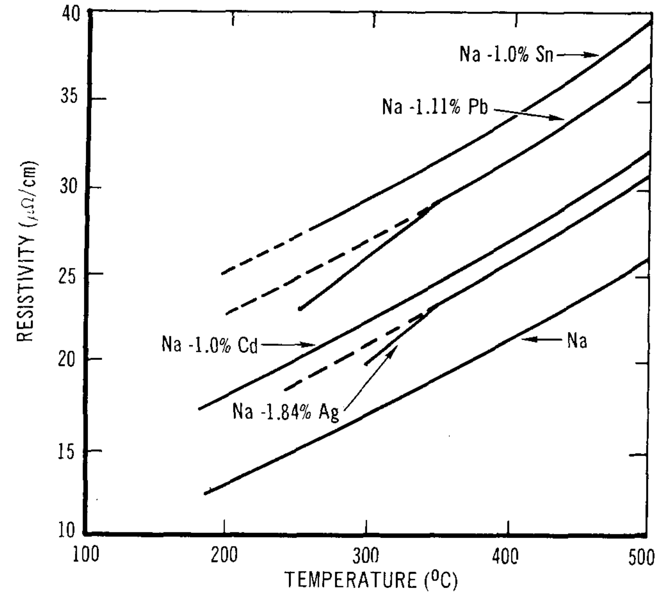

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Figure 62. Resistivity of Dilute Alloys Showing Deviations as the Result of Precipitation

3. Measurement Methods

The measurement of resistivity of liquid metals involves several special considerations, the main ones being design of a suitable containment vessel, and a means of contacting the liquid metal.

The containment vessel material generally is a metal, usually stainless steel. For the alkali metals, and particularly sodium, stainless steel is chosen since it is compatible with the alkali metals, can be used at high temperature, is sufficiently rugged, and has a relatively high electrical resistivity. The high resistivity is significant since the containment vessel wall constitutes a circuit in parallel with the liquid metal, contributing to the indicated value of circuit resistance.

The means of contacting the liquid metal is a problem since most liquid metals do not readily wet the contacting surfaces uniformly without special surface treatment. Poor wetting results in erratic electrical contact and high contact resistance. Since liquid metals have low resistivity, a high contact resistance significantly contributes to the measurement difficulties. Generally, at temperatures up to about 425°C (797°F), wetting is greatly dependent upon the surface condition of the metal. At this temperature, and higher, wetting is satisfactory without special surface treatment, and after the wetting temperature has been attained, wetting is retained at lower temperatures.

Several methods of measuring resistivity of liquid metals have been used. These include: (1) sealing the liquid metal in a tube fitted with electrodes and measuring with a dc bridge; (2) inserting the tube into a liquid metal loop and measuring with a dc bridge; (3) placing a coil energized with an alternating current near the liquid metal and measuring the load created by the eddy currents; and (4) forming a tube filled with liquid metal into a loop so that an electrical current may be induced in the loop of liquid metal by an induction circuit, and the current may be measured by an inductive coupling.

The method using a dc bridge to measure the resistance of a length of liquid metal enclosed in a tube is illustrated in Figure 63. Upon satisfying the contacting requirements, the measurement is made according to well-established methods using a bridge. The bridge indicates the resistance R consisting of

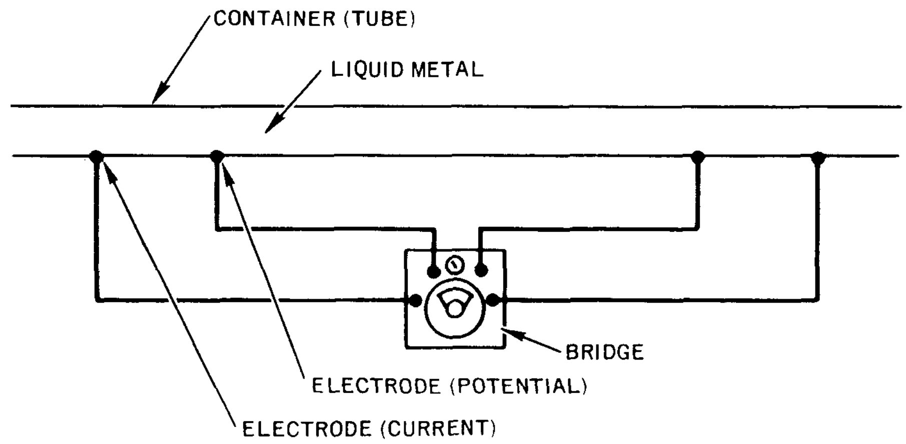

Figure 63. Schematic Diagram of a Method of Measuring Liquid Metal Resistance Using a Bridge

the parallel resistances R_L of the liquid metal and R_C of the container or tube. Then,

$$R_L = \frac{R}{1 - \frac{R}{R_C}} .$$

The tube resistance R_C may be calculated or measured with the tube empty (at the temperature at which liquid metal measurements are to be made). In terms of impurity concentration, the indicated resistance is

$$R = \frac{1}{\frac{1}{\frac{L}{A}\left[\rho_o(1 + C)\right]} + \frac{1}{R_C}}$$

where L is the distance between the potential electrodes and A is the cross-sectional area of the tube in that region.

This method, making direct electrical contact with the liquid metal, has not been in common usage in liquid metal systems although it was used in the work reported in Reference 62. Experimentation with this method has been increasing within the past year. It is popular, although somewhat misleading, to refer to this as the "absolute resistivity measuring" method.

Measurement based upon the induction of a current into the liquid metal and thereby determine the resistivity, is used where it is desirable to avoid direct contact. The method is illustrated in Figure 64. The electromagnetic field created by the alternating current in the coil induces a current in any conductor in the field. The flow of the induced current in eddies in the conductor results in Joule heat losses (I^2R losses) which are supplied from the power delivered to the coil. A change in the conductor resistance is sensed in terms of a change in input power; hence the power measurement indicates the impurity content. This type of sensor responds to the resistance of the container and the liquid metal, so a correction for the container must be made. Moreover, the frequency of the alternating current must be low enough that the electromagnetic field penetrates the container and results in the generation of eddy currents within the liquid metal. The extent of penetration follows an exponential decrease, and the amplitude has the value of 1/e of the surface value at a distance δ given by the relationship,

$$\delta = \frac{1}{2\pi}\sqrt{\frac{\rho \times 10^9}{\mu f}}$$

where f is the frequency in cycles per second, ρ is the resistivity in ohm cm, and μ is the permeability in cgs units.

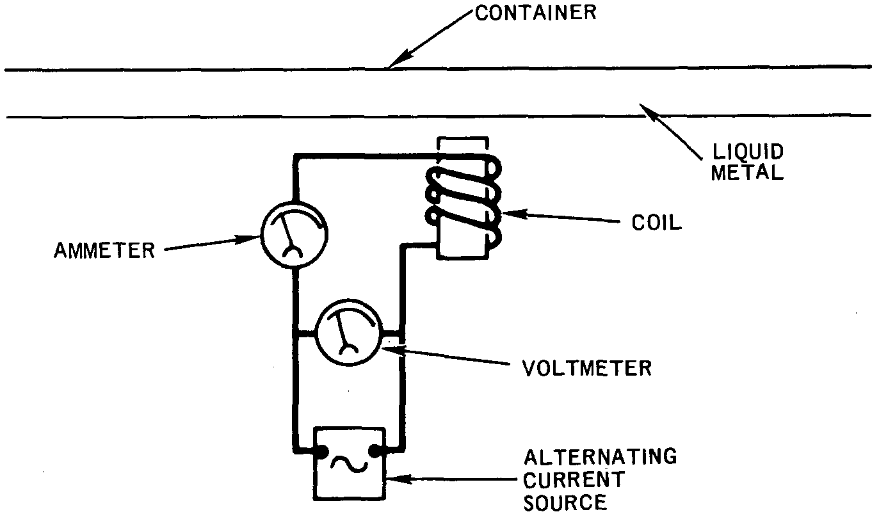

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Figure 64. Eddy Current Method of Measuring Resistance of Liquid Metal

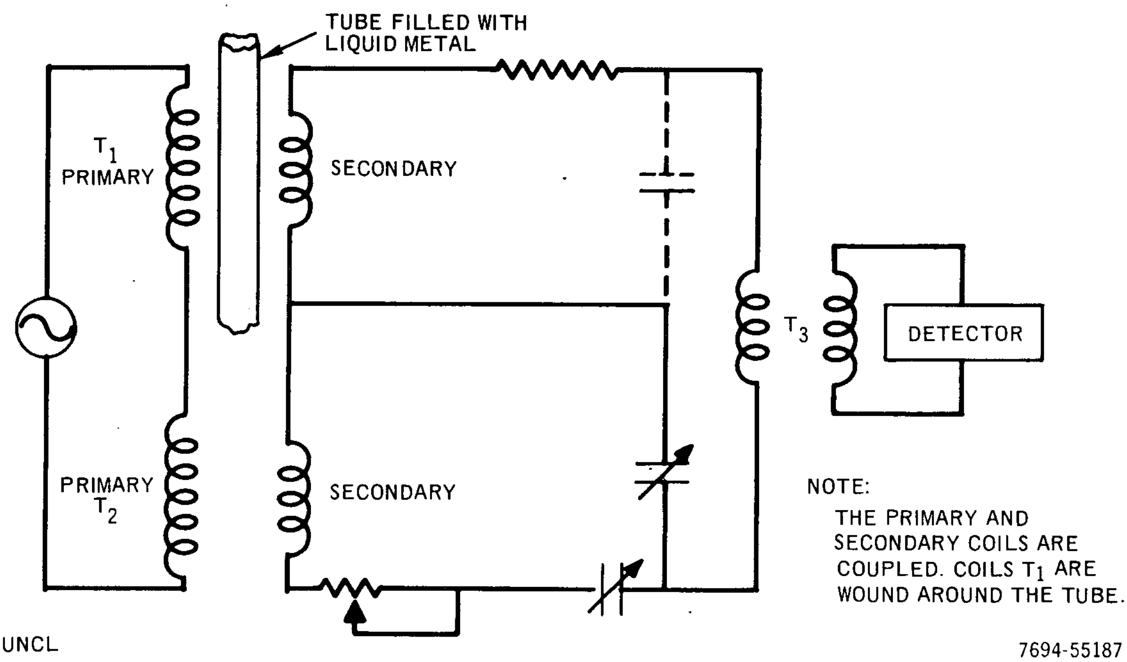

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Figure 65. Circuit for Measuring Electrical Conductivities by Electrodeless Method

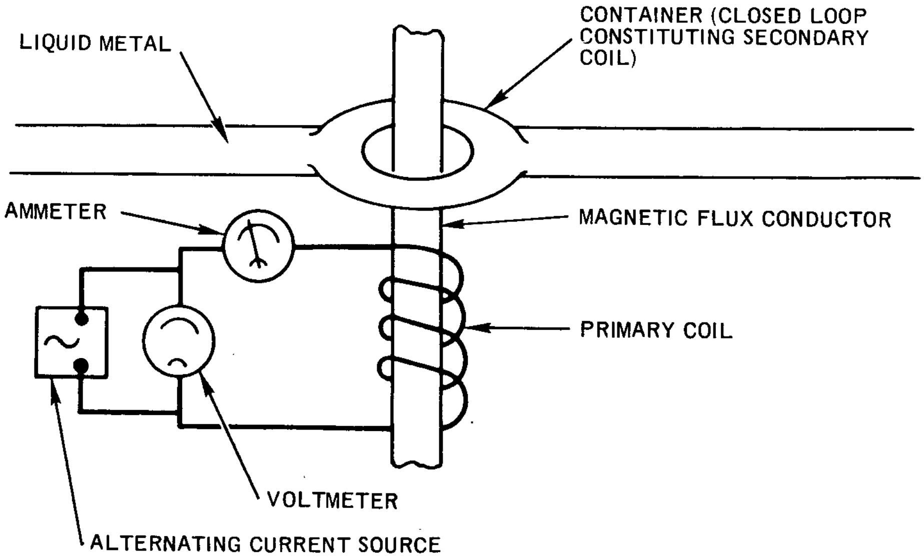

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Figure 66. Schematic Diagram of the Induction or "Transformer" Method of Measuring Liquid Metal Resistance

An analytical expression relating the coil current to the liquid metal resistivity in terms of all the parameters is unnecessary since, in any practical use of this method, only a change in resistivity is measured. Thus the sensor coil is placed near the liquid metal (pure) and the coil current is calibrated in terms of the liquid metal resistivity. The resistivity can be changed by changing the temperature so measurement of the temperature and reference to the resistivity vs temperature relationship provides an indication of resistivity. The relationship between impurity and resistivity has been given on Page 95. A variation, described in some detail in Reference 63, is illustrated in Figure 65.

Measurement based upon induction of a current in a loop or toroid and using the "transformer principle" is illustrated in Figure 66. The alternating current flowing through the primary coil induces a current in the secondary coil, which is a closed loop of the liquid metal. The coupling between these coils is enhanced by a magnetic flux conductor. The resistance R_S of the secondary circuit is given by

$$R_S = \frac{R_C R_L}{R_C + R_L}$$

where R_C is the container (toroidal loop) resistance and R_L is the liquid metal resistance. Assuming "ideal transformer concepts" this resistance, when viewed from the primary side, is

$$R_P = R_S \left(\frac{N_P}{N_S}\right)^2$$

where the N's refer to the number of turns. Since the secondary is a single turn, this reduces to

$$R_P = R_S N_P^2 .$$

Since the ratio of the voltage to current, as indicated by the voltmeter and ammeter in the primary circuit, is a measure of the primary circuit resistance,

$$\frac{V}{I} = R_S N_P^2 .$$

Since R_S is expressible in terms of the liquid metal resistance, which in turn is expressible in terms of impurity concentration, the ratio V/I is a function of liquid metal impurity.

The method as described facilitates illustration of the basic principles involved. Other arrangements and more elaborate design are used in practice to deal with the factors ignored here. Since the temperature of the liquid metal has a significant effect upon the resistivity, it must be taken into account. Accordingly, temperature control or compensating circuits are needed.

The problems of achieving suitable electrical contact may be avoided in the use of the inductive coupling methods. The method based upon inducing a current in a loop has been used for some time in measurements of this nature,(56) and more recently in the development of the rhometer for monitoring impurities in liquid metals.(57,58)

C. DESCRIPTION OF THE RESISTIVITY METER

The commercial Liquid Metal Rhometer* is the only resistivity impurity monitor in substantial usage and the only monitor on which descriptive data are available.

The operating principle is illustrated by Figure 67. The magnetic flux created by the primary coil is linked with the two secondary circuits, (1) the liquid metal toroidal loop and (2) the sensor coil. The toroidal loop imposes an electrical load on the primary circuit, and the magnitude of the load is a function of the resistance of the toroidal loop. The load is sensed by the sensor coil since the voltage induced in it is a function of the load imposed by the toroidal loop. The toroidal loop is approximately 3 in. in diameter and is formed of 1/2-in. stainless steel tubing. Since the resistance is a function of the resistivity, geometry, and temperature, a change in any or all of these affects the induced voltage. Impurities in solution affect the resistivity and impurities, as bubbles or particulate matter affect the resistance, hence any of these factors is registered. To minimize the effects of temperature, a temperature-compensation circuit is added. This circuit and the basic resistivity meter

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*Manufactured by Bruce Peebles Co., (Edinburgh, U.K.), according to original designs of L. R. Blake. The prefix rho indicates the symbol of resistivity.

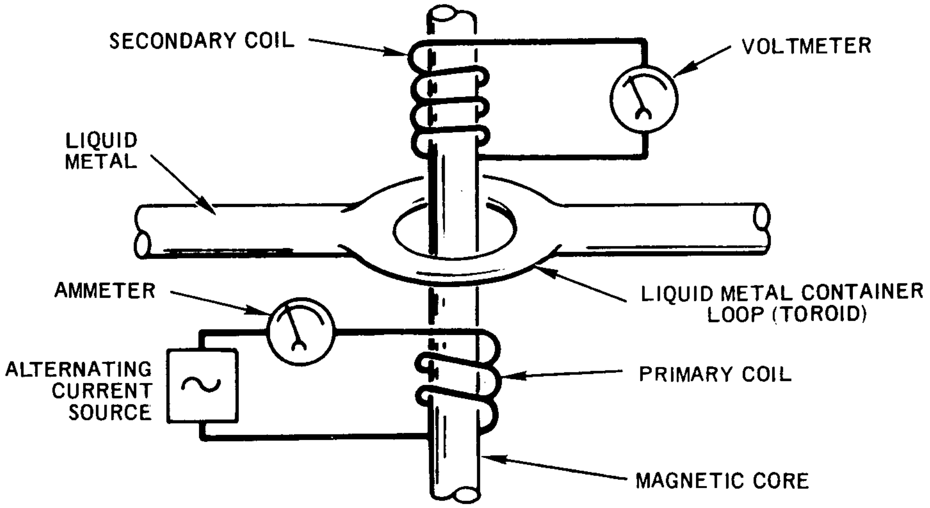

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Figure 67. Induction Method of Measuring Resistance Using a Secondary Sensing Coil

circuit are incorporated in a bridge circuit. By using a bridge circuit, the instrument is responsive to changes only, and therefore is more sensitive than a simpler circuit. The complete circuit is shown in Figure 68.

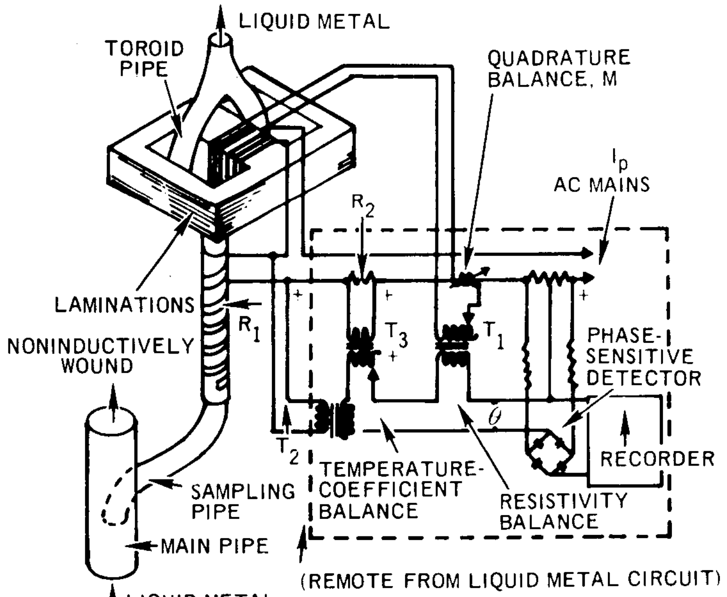

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Figure 68. Rhometer Circuit Diagram

The resistance R_1 is a noninductive resistance in close thermal contact with the pipe. The resistance material is chosen to satisfy the temperature-compensating requirements of the circuit. To enable compensation for variations in the alternating current source, the resistance R_2 is connected in series. The voltages across R_1 and R_2 are appropriately added to the sensor coil voltage.

Assuming ideal transformer conditions,

$$I_P N_P = I_S N_S$$

where I is the current and N is the number of turns, with the subscripts P and S denoting the primary and secondary, respectively. Since the toroid is a 1-turn coil, $N_S = 1$. The current I_S is expressed by

$$I_S = \frac{V_S}{R_S}$$

where V_S is the voltage and R_S is the resistance. The voltage V induced in the sensor coil of n turns is

$$V = nV_S \ .$$

Then

$$R_S = \frac{V}{nN_P I_P} \ .$$

To attain a null in the bridge circuit, the voltage V must equal RI_P, where R is the sum of the compensating resistors R_1 and R_2. Then

$$R = nNR_S \ .$$

As R_S varies with impurity content, R is adjusted to maintain the null condition. Since R is not readily amenable to adjustment, the equivalent change is achieved by taps on the transformers. The resistance of the liquid metal R_L is related to R_S by the relationship

$$R_S = \frac{R_t}{\frac{R_t}{R_L} + 1}$$

and the value of R_L is expressed by the toroid inside dimensions and the liquid metal resistivity.

D. DISCUSSION AND EVALUATION

The resistivity of liquid metals is a function of temperature as well as of impurity concentration. Moreover, the effect is sufficiently large that, unless special corrective measures are taken, the temperature effects may mask the impurity measurements.

An additional difficulty exists in the methods based upon the direct contact of electrodes to the liquid metal. The uncertainty in wetting is the major factor involved and, consequently, this method is seldom used. It has not been used in in-line applications.

The eddy current method has not been widely used and has not been used in any in-line applications. No specific major shortcomings are evident.

A number of the transformer type impurity instruments have been produced. Some of these have been placed in operation in typical applications and others have been subjected to performance evaluation in various laboratories. Substantially all the instruments are produced by the Bruce Peebles Co. Ltd., Edinburgh, U. K., according to designs formulated originally by L. R. Blake. The instrument is known as the Liquid Metal Rhometer, the prefix rho indicating the symbol of resistivity.

The object in developing the rhometer was to provide a simple, reliable, in-line instrument to continuously monitor the impurity content of liquid metal systems. Oxygen was the impurity of greatest interest and seemingly the most prominent, hence the instrument became known as an oxygen-indicator. This label was unfortunate since the instrument can respond only to resistance changes.

The instrument performs well in monitoring impurities or voids which alter the resistance of the liquid metal circuit in the toroid.

1. Operating Characteristics and Limitations

a. Temperature

The upper temperature limit is 315°C (600°F), a value established by the compensator.(64) The coil windings deteriorate as the liquid metal temperature is raised to 400°C (750°F).(64) The transformer core, made of supermumetal must be operated below its Curie temperature, 432°C (800°F). The upper limit can be extended by compensator modification, and by providing better thermal insulation between the toroïd and the core and coils.

b. Accuracy

A figure of accuracy has not been given. Factors to consider in relation to accuracy are as follows:

(1) Stability

The stability was originally(57) stated to be one part in 10^4. In one subsequent performance evaluation(64) the drift was considered to be "...not of significant magnitude...," however in a later evaluation changes in sensitivity were found.(3) According to another evaluation(40) it was concluded that drift was significant and that the "...rhometer is of limited value in applications as an oxygen monitoring device in typical sodium systems."

(2) Temperature Sensitivity

An uncompensated rhometer is unpractical due to the very high temperature sensitivity. Compensation reduces the inherent temperature sensitivity to an acceptable value. The error is negligible over a ±5.5°C (±10°F) range about the set point, and a range of ±27.8°C (50°F) results in a change in indication corresponding to a 10 ppm change in oxygen content.

(3) Calibration

The rhometer is calibrated by relating the resistivity change to a concentration change. In an early performance evaluation,(64) the "...calibration of the rhometer for oxygen contamination was successful within the 10 to 80 ppm range."

However, in view of the fact that the resistivity change-to-concentration change ratio has later been found to be different in different tests,(3) the success of the calibration is in doubt. (See the paragraph on sensitivity below.) Calibration is affected by a change in flowrate. At very low flowrates, such as below 63.3 cm^3/sec (1 gpm), the heat generated by the current in the toroid is not readily dissipated and raises the temperature, resulting in an increased resistance. At high flowrates, such as over 1266 cm^3/sec (20 gpm) some cavitation occurs in the toroid and this results in an erratic signal.(64) A flowrate of 475 cm^3/sec (7.5 gpm) is recommended since, at about this value, the resistance change-to-flow change relationship is linear. An 8% flowrate change produces a resistance change corresponding to a 1 ppm change in oxygen.

(4) Selectivity

The rhometer is a very sensitive device for measuring changes in resistance. Resistance is composed of two factors, (1) resistivity, a material property and (2) geometry. Impurities which affect the geometry, (entrained gas or suspended matter) are clearly indicated. The rhometer has been tested for response to a number of impurities; however, the results of the various tests are in question. The responses as a function of impurity level for H_2O, NaH, NaOH, O_2, and Na_2CO_3 were presented in Reference 47. Carbon was said to be detectable.(64) However, the same group later expressed doubts of the validity of the testing method (use of cold trap heating to release impurities),(42) and further stated that "...when sodium monoxide is directly injected into the loop, the rhometers shows poor sensitivity. High meter sensitivity has been reported for only those cases where the cold trap is used as the injection device."(42) This finding is essentially in agreement with the results reported in References 62 and 65. These two reports show that resistivity is not significantly affected by oxygen (in the concentration range of interest) but is greatly affected by hydrogen.

(5) Response Time

The inherent characteristics of the rhometer indicate that the response time is established by the frequency used and the time constant of the circuits. For commercial power frequencies, the response time may be taken to be about one second. To this figure must be added any time required for adjustment or zeroing.

c. Environment

Preliminary tests in an x-ray radiation field have indicated that the rhometer response is not affected by the radiation.(42) This does not imply that the materials of construction are radiation-resistant.

Since the rhometer is very responsive to entrained gas, the meter should be vertically mounted to prevent the formation of gas pockets. Also the connection to the system loop should be on a vertical section.

The sensor components (toroid and transformer) are relatively rugged and easily withstand ordinary handling. Other components may be less rugged.

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