

**CEGB RESEARCH
ON BOILER LEAKS AND THEIR
DETECTION IN SERVICE**

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1. INTRODUCTION

The penalty in loss of output to an electricity generation organisation as a consequence of failure to deal effectively with small LMFBR boiler leaks would be large. There is therefore a considerable incentive for these organisations to satisfy themselves that proper provisions are made to ensure that both the incidence and the severity of boiler leaks are minimised. In the UK, responsibility for the research, development and design work for this and indeed for most aspects of future nuclear power plant rests with the UKAEA and NPC; nevertheless as a consequence of its "informed operator" policy the Central Electricity Generating Board has devoted some research effort to this field in recent years.

To date, research work has been put in hand with the objective of achieving an understanding of the basic behaviour of boiler leaks. In addition, attention has been given to leak detection by monitoring the sodium for increases in oxygen and hydrogen levels. In both cases leaks into liquid sodium rather than into the gas space have been considered. In the course of the work hydrogen and oxygen meters based on the galvanic cell principle have been constructed and evaluated. The former is a new device which is comparable in performance with hydrogen meters based on the ion pump.

The present state of the work is briefly described in this paper.

2. THE BEHAVIOUR OF LEAKS

Early experiments in which small quantities of sodium were allowed to react with water and small quantities of water with liquid sodium (Halstead, 1972; Newman et al, 1973), achieved a familiarity with the system and an understanding of some of the phenomena which may be involved. More recently, attention has been concentrated on high temperature corrosion studies of ferritic steels (2 1/2 Cr 1 Mo and 9 Cr 1 Mo) and the behaviour of microleaks.

2.1 Wastage

A model for erosion by superheated water jets was developed by Pugh (1972). Erosion is ascribed to the collapse of vapour bubbles on the target surface. Support for the model was provided through experiments with superheated water jets on lead and aluminium targets. However, little effect was found with steel targets even when heated close to their melting point owing to rapid cooling at the point of impingement.

Experiments were carried out in which boiler steel materials were exposed to a flame produced by boiling sodium vapour in a water vapour atmosphere (Newman and Smith, 1974). The wastage produced was similar to that observed in boiler leak experiments. Since this type of attack was observed when velocities in the combustion region did not exceed 1 m s⁻¹, it was concluded that the wastage associated with LMFBR boiler leaks is likely to be essentially a corrosion process.

A correlation has been derived relating wastage rate to water leak rate from high-pressure boilers (Payne, 1978). It is based on published wastage data and takes account of both target spacing and sodium temperature. A feature is the incorporation of a theoretically-derived scaling law for target spacing. Figure 1 gives the correlation and figures 2 and 3 show wastage rate curves for various temperatures and spacings.

It is anticipated that refinements will be incorporated in the wastage correlation as the details of the corrosion processes involved become fully understood. Nevertheless in its present form it may be used for estimating maximum target wastage rates under most conditions of practical interest.

2.2 Microleak Behaviour

Experimental work is in progress on the behaviour of leaks which are initially smaller than the range shown in figures 2 and 3, i.e. less than 10⁻¹ gm s⁻¹. The apparatus shown in figure 4 is used to measure how the steam flow rate through leaks varies with time. A feature of the apparatus is the facility for continuous measurement of leak rate in the range 10⁻⁵ - 10⁻¹ g s⁻¹. Work so far has been with artificial defects which are nominally "round hole" filamentary leaks (Pugh et al, 1974). In practise the two leak geometries shown in figure 5 have been used. Typical test conditions are 400°C sodium and 400°C steam at 13 MPa. Some results are shown in figure 6 (Newman et al, 1978). The loss of material observed at the mouth of the leaks is illustrated in figure 7.

These studies are still at an early stage. Further data on microleak behaviour together with physical models of the hydrodynamics and the application of corrosion data are necessary for their full interpretation. Tentative conclusions are that for a given microleak size (flow rate) in ferritic steels:

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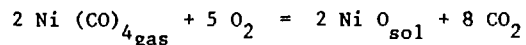
- (a) The time to escalation decreases as the sodium temperature increases.
- (b) The nearer the restriction is to the sodium side of the leak path the shorter the time to escalation.
- (c) Escalation through the 10^{-1} g s^{-1} range may occur over periods of minutes rather than seconds for typical plant operational temperatures.
- (d) Blocking may be associated with corrosion on the water side of the leak path.

2.3 Basic Corrosion Studies

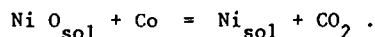
In order to understand the processes which give rise to behavioural features such as those illustrated in figures 2, 3, 6 and 7, basic corrosion studies are in progress. The available data has been reviewed by Halstead (1974). Corrosion rates are measured in static conditions by measuring the rate of hydrogen production and by weight loss measurements. The apparatus is shown in figure 8. Initial results, on the system NaOH/2½ Cr 1 Mo steel in the temperature range 750°-1000°C, have been published by Newman et al, 1977a. The essential features of the results are the formation of the ternary oxides Na Fe O₂ and Na Cr O₂ as the principle corrosion products and the parabolic kinetics caused by a rate-limiting corrosion product layer of ternary oxides (figure 9). In more recent work the addition of sodium oxide to the melt was found to result in a five-fold or more increase in the corrosion rate at 800°C, and this has been attributed to an enhancement of the solubility of sodium chromite in the oxide-containing sodium hydroxide melt (Newman et al, 1977b; Newman and Smith, 1978). Work on basic static corrosion studies is continuing, together with studies on the application of the results to flowing systems typical of the conditions occurring in target wastage and in microleak behaviour.

2.4 Microleak Blocking

Some consideration has been given to the possibility of special chemical treatments of boiler tubes in order to seal any micropores which may be present (Halstead, 1974). It has been suggested that nickel oxide could be deposited in micropores by the oxidation of the carbonyl:



followed by reduction of the oxide to the metal:



3. LEAK DETECTION BY IN-SODIUM MONITORING FOR OXYGEN AND HYDROGEN

Work is in progress on the basic physical chemistry of the method, in particular on factors affecting sensitivity and response time. An

electrochemical oxygen meter has been constructed. A new form of hydrogen meter based on similar electrochemical principles has been developed. Both of these instruments are being used for the basic studies. In addition both instruments have been shown to be capable of good performance as plant leak detection instruments provided that they are installed in specially-designed sampling sub-loops. Their evaluation is proceeding in conjunction with the UKAEA. Some studies on background control, particularly of hydrogen, in relation to leak detection performance have commenced.

3.1 Physical Chemistry Studies

The rate of solution of hydrogen in vigorously-stirred sodium has been measured (Whittingham, 1974). Figure 10 shows the absorption rate constant, which has been found to be independent of the dissolved hydrogen concentration, based upon this and other published data. Figure 11 shows solution times for hydrogen in sodium as a function of temperature for bubbles in the millimetre size range. Data are given for an absorption model and for a diffusion model (Hayes and Horn, 1972). It follows that the sensitivity and response time of in-sodium hydrogen-based leak detection is adversely affected by bubble solution at the lower temperatures.

Studies of a similar nature are in hand in relation to oxygen meter response to water leaks. Work is planned in which both oxygen and hydrogen concentrations in flowing sodium will be measured downstream of a steam microleak as a function of sodium temperature.

3.2 BNL Electrochemical Hydrogen Meter

The essential features of this instrument have been published (Smith, 1974) and some performance data was given at the BNES Nottingham Conference (Smith, 1973). A diagram of the cell is given in figure 12 and figure 13 shows a recent version of the instrument. Basic equations are given in figure 14. The cell has been shown to perform theoretically under conditions typical of LMFBR secondary circuits. Figure 15 illustrates the close agreement obtained between theory and experiment when the cell was operated at 500°C and exposed to hydrogen concentrations equivalent to 1-10 ppm in sodium. The cell may be operated in the temperature range 300°-550°C, but close control of the head temperature is desirable because its output is temperature sensitive.

The sensitivity is logarithmic (figure 14). At 475°C a three per cent change in hydrogen concentration gives a 2 mV change in meter voltage. Figure 16 shows the sensitivity for 2 mV in terms of hydrogen concentration change against background concentration.

The response time is controlled by hydrogen diffusion through the iron membrane which contains the electrolyte, and is therefore a function of operating temperature and membrane thickness. Figure 17 (Smith, 1973) shows theoretical and experimental response curves at 500°C for a cell having an 0.44 mm thick iron membrane. Seventy per cent response is obtained in five seconds for these conditions.

3.3 Electrochemical Oxygen Meter

A freeze-seal air reference oxygen meter has been constructed using a commercially-available thoria 7½ wt % yttria electrolyte thimble (figures 18 and 19). Basic cell equations are given in figure 20. The meter has been calibrated by admission of aliquots of oxygen gas into oxygen-free sodium. Typical results are shown in figure 21, (Simm, 1978). Operating the meter at 435°C, it is found that after an initial 30-day period during which output is a few per cent down, good agreement between theory and calibration measurements is obtained. Lifetimes in excess of two years have been achieved with this meter in a laboratory sodium rig. The sensitivity of the oxygen meter on an atom percentage basis is half that of the electrochemical hydrogen meter but effective sensitivities may be similar for this design when temperature coefficients are taken into account (figure 16).

3.4 Electrochemical Oxygen and Hydrogen Meters as In-Sodium Leak Detectors

Some consideration has been given to the leak detection performance which might be achieved if oxygen and hydrogen galvanic cells were used together in secondary circuits as an alternative to the in-sodium katharometer hydrogen detectors chosen for PFR.

As shown in figure 16, the sensitivity of the electrochemical instruments increases with decreasing background levels whereas the katharometer (Davies et al, 1971) has the opposite characteristics. It has been concluded that with low background levels improved leak detection performance can be achieved with the electrochemical meters. Figure 22 shows the calculated sensitivity to water leaks of these meters mounted in a 200 Te secondary circuit as a function of time from leak initiation. Detection performance corresponds to about 20 g water ingress. The initial sensitivity is a function of the system flow rate and is independent of the sodium inventory; in figure 22 complete mixing in a 2 Te s⁻¹ sodium flow and 100% detector response have been assumed.

In practice hydrogen background levels may vary as a consequence of ingress of corrosion hydrogen through the walls of the boiler tubes. Figure 22 also shows how the electrochemical hydrogen meter detection performance would be degraded if the background level were allowed by cycle between 0.1 and 0.2 ppm within a period of a few days. This type of background variation could occur if an intermittent hydrogen-trapping system were adopted.

Some consideration has been given to the design of suitable sampling sub-loops for the installation of meters of this type in reactor circuits (Simm and Hayes, 1977).

4. CONCLUSIONS

To date CEBG Research Division work on LMFBR boiler leaks and associated problems has concentrated mainly on the behaviour of small

leaks, with particular emphasis on basic studies related to wastage and self-enlargement, and to leak detection by oxygen and hydrogen monitoring.

These studies, which are continuing, have led to a better understanding of leak behaviour and effects. A correlation for predicting maximum wastage rates for ferritic steels under most conditions of practical interest has been derived.

Advances have been made in understanding the self-enlargement of leaks too small to cause rapid wastage on adjacent material.

Advances have been made in in-sodium instrumentation which have application for leak detection and for other purposes.

Whilst it is premature to draw conclusions in relation to boiler leak detection requirements from these studies, it appears that there may be advantages in using techniques which increase sensitivity at the expense of response time, such as in-sodium monitoring for oxygen and hydrogen over several circuit turn-overs. However there is no evidence at this stage to obviate the requirement for fast detection and passivation to protect against the larger leaks.

ACKNOWLEDGEMENT

This paper is published with the permission of the Central Electricity Generating Board.

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THE PREDICTION OF WASTAGE CAUSED BY SMALL LEAKS IN SODIUM-HEATED BOILERS

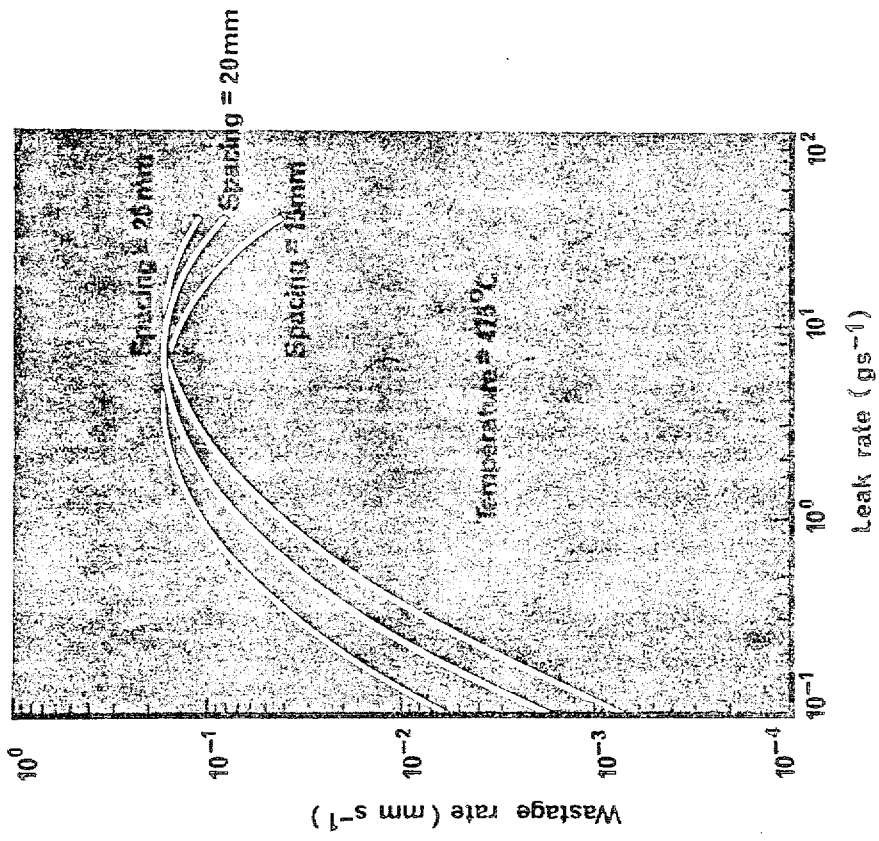
$$W = 252 \exp - \left\{ 0.255 \left[\ln \left(\frac{59.8m}{x^2} \right) \right]^2 + \frac{5460}{T} \right\}$$

Where W = Wastage rate (mm s^{-1})

m = Leak rate (g s^{-1})

x = Leak to target spacing (mm)

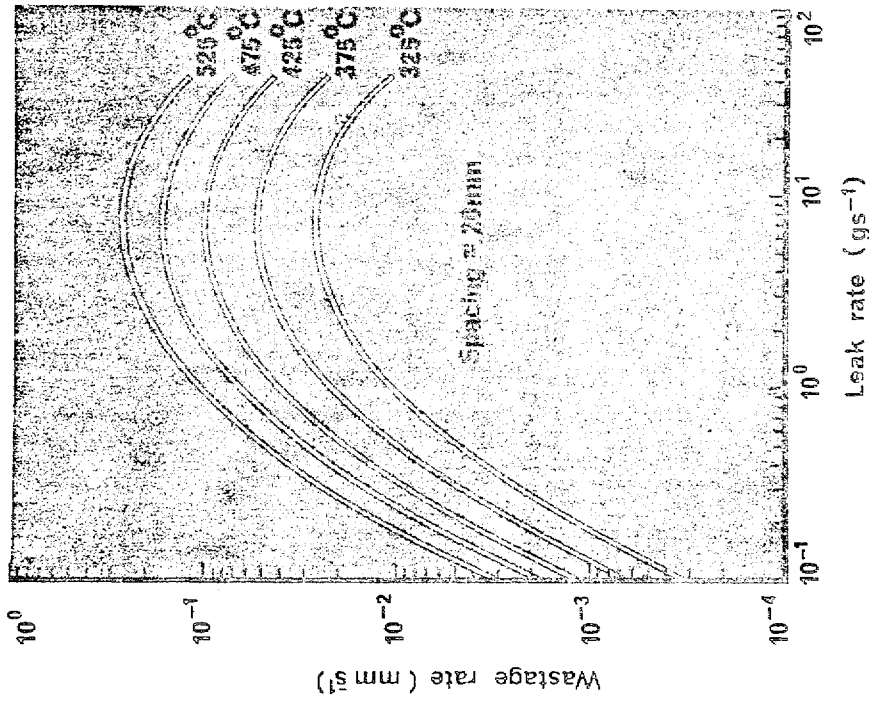
T = Sodium temperature ($^{\circ}\text{K}$)



THE EFFECT OF LEAK TO TARGET SPACING ON WASTAGE

FIGURE 3

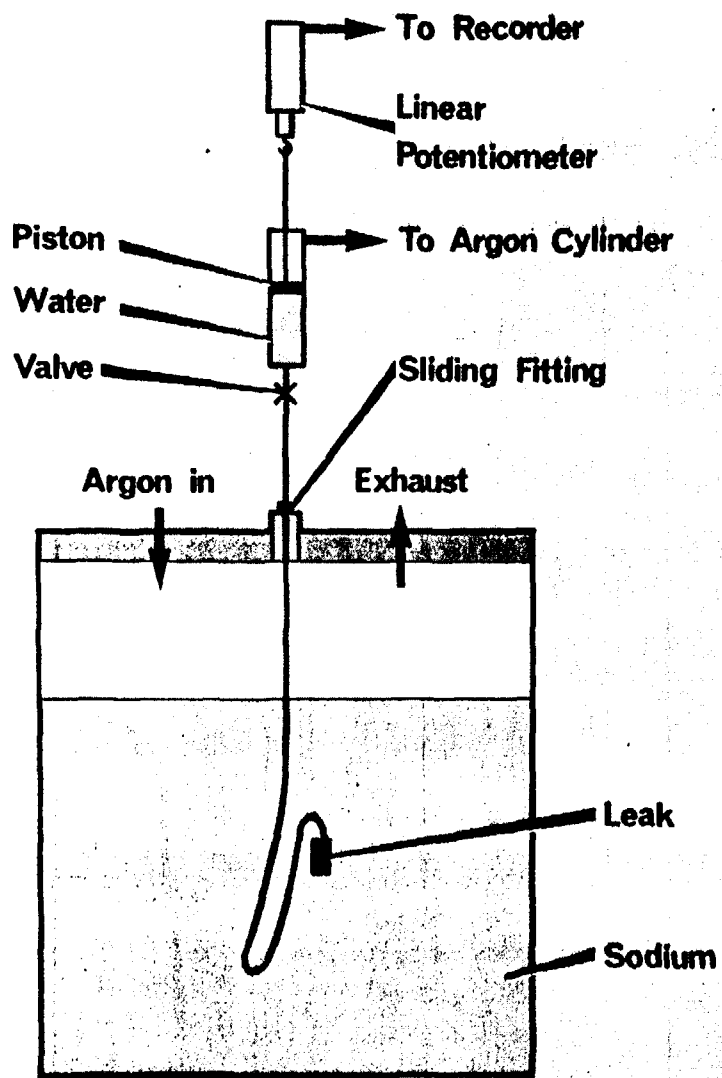
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THE EFFECT OF TEMPERATURE ON WASTAGE

FIGURE 2

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APPARATUS FOR TESTING SODIUM-WATER MICROLEAKS

FIGURE. 4

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ARTIFICIAL MICROLEAK DEFECT GEOMETRIES

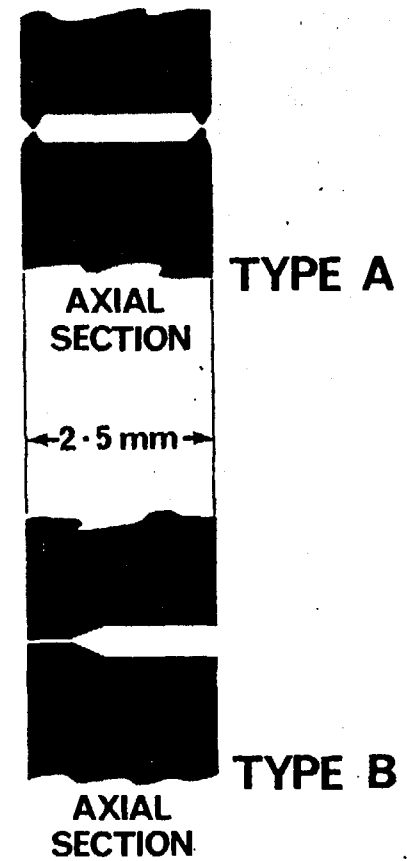
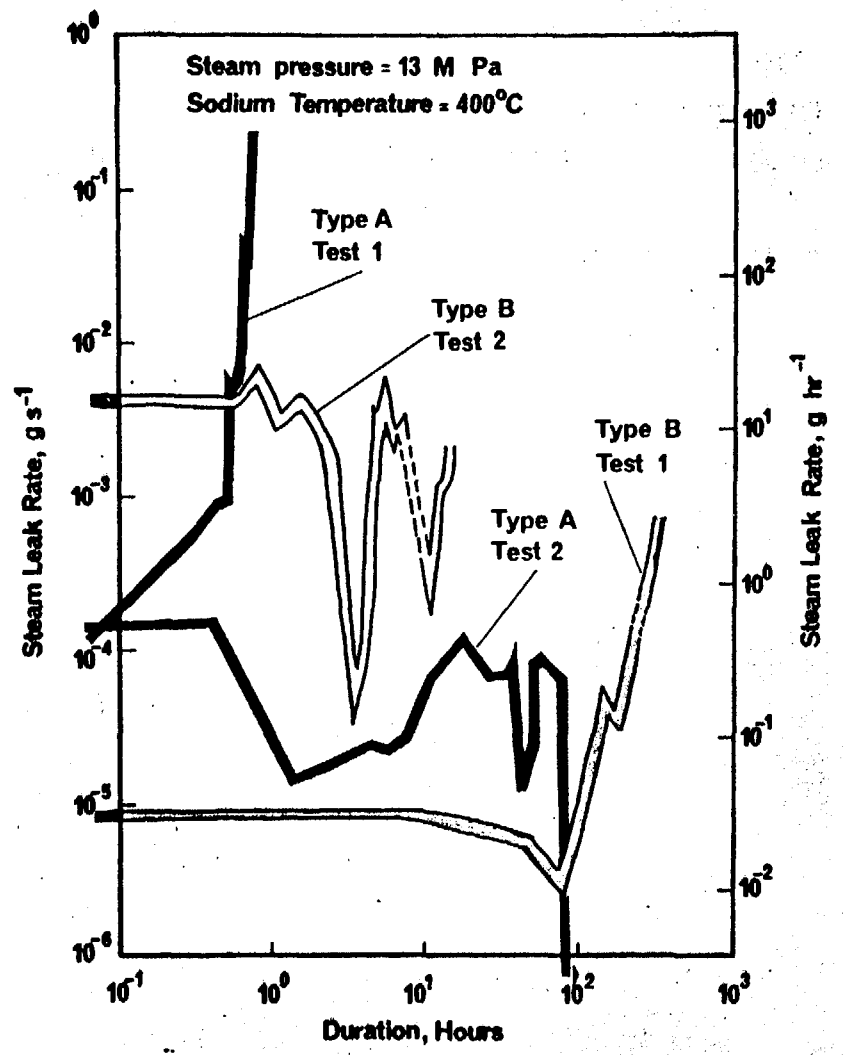


FIGURE. 5

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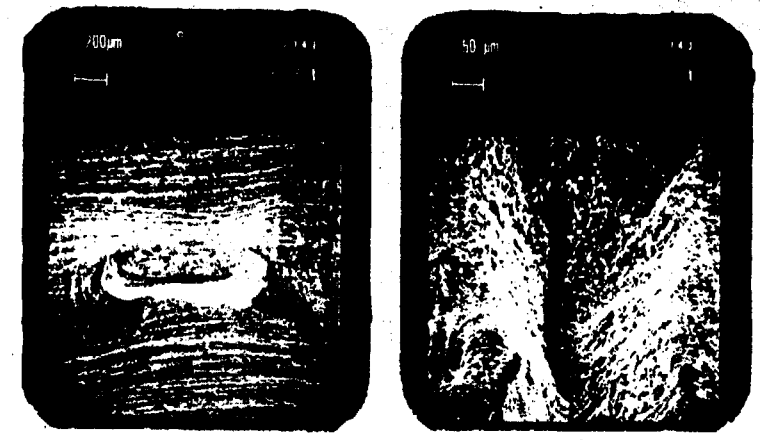
EXAMPLES OF "WASTAGE" IN MICROLEAKS



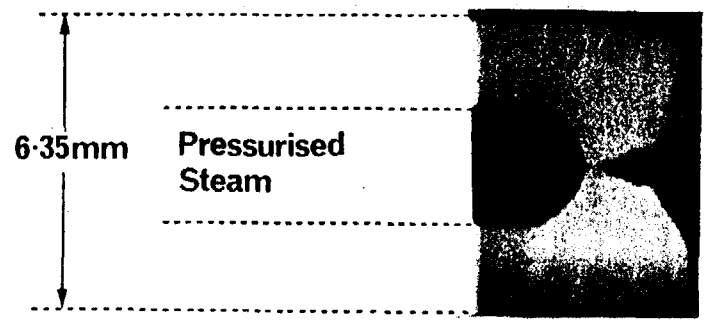
EXAMPLES OF BEHAVIOUR OF FERRITE STEEL MICROLEAKS

FIGURE. 6

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A: Electron Micrograph of Specimen Type A Test 2: Sodium Side.



B: Microradiograph of Specimen Type B Test 1: After Test.

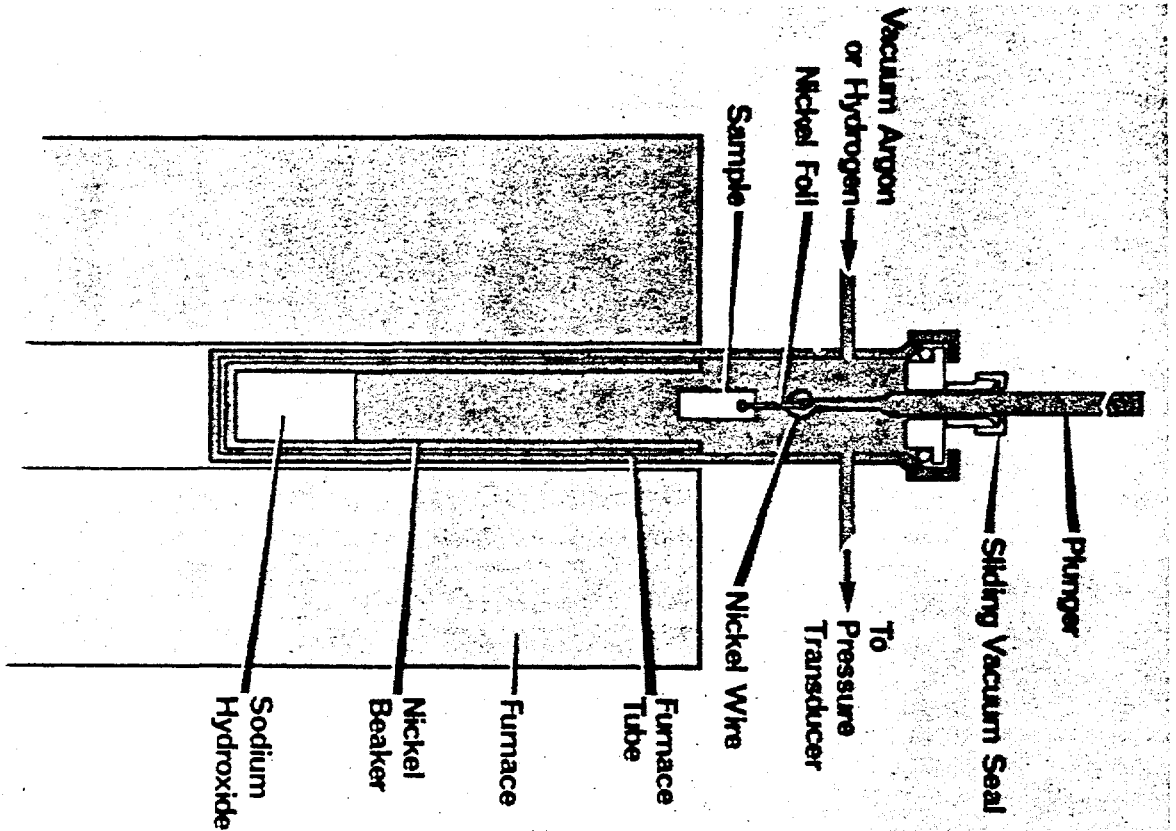
FIGURE. 7

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FIGURE.8

APPARATUS

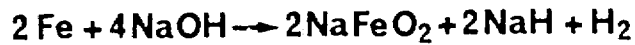
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Results of Basic Corrosion Experiments

Material: 2¼ Cr 1Mo ferritic steel
 Corroding agent: Pure Sodium Hydroxide
 Temperature Range: 750°–1000° C

Corrosion Equation:-



Rate Law:- Parabolic

Rate Constant:-

$$k = 0.604 e^{-\frac{37000}{T}} \text{ (moles H}_2 \text{ mm}^{-2}\text{)}^2 \text{ s}^{-1}$$

FIGURE.9

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**RATE CONSTANT FOR HYDROGEN ABSORPTION
BY LIQUID SODIUM AS A FUNCTION OF
ABSOLUTE TEMPERATURE**

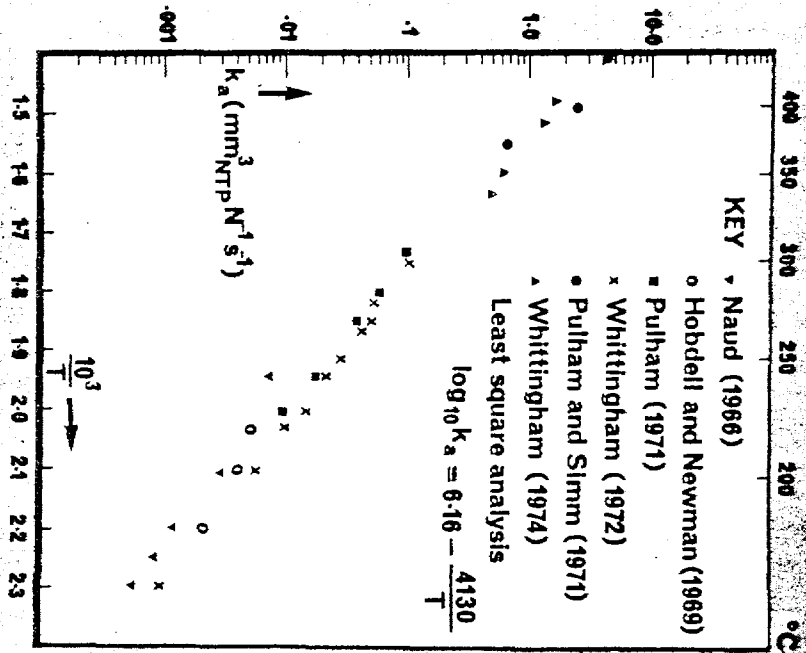
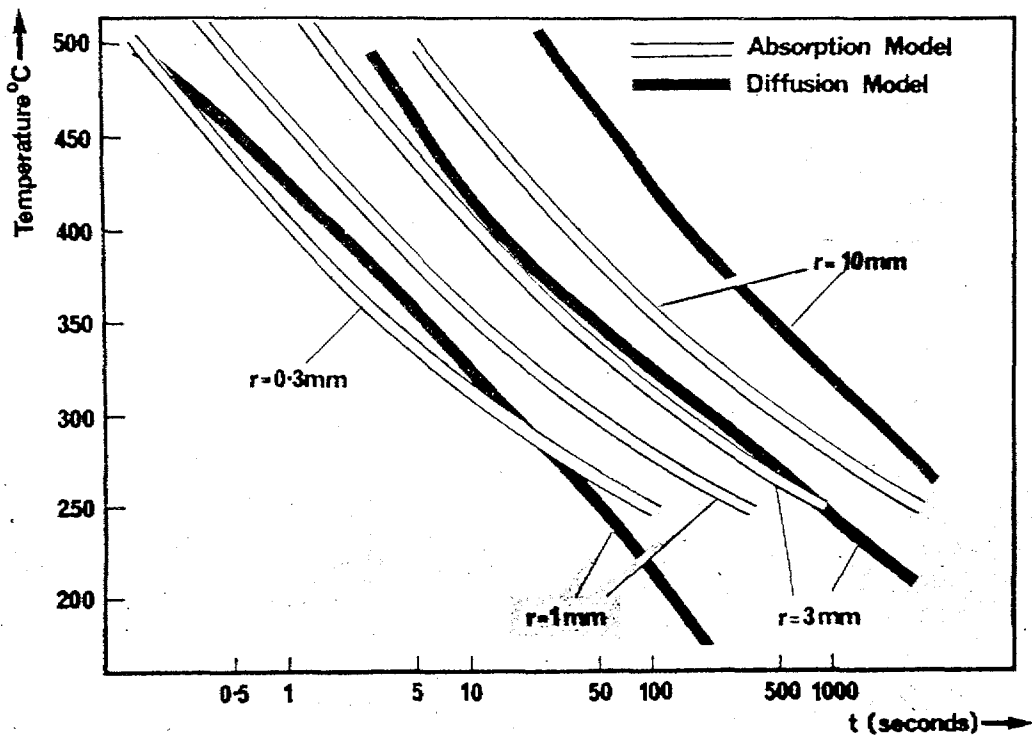


FIGURE 10

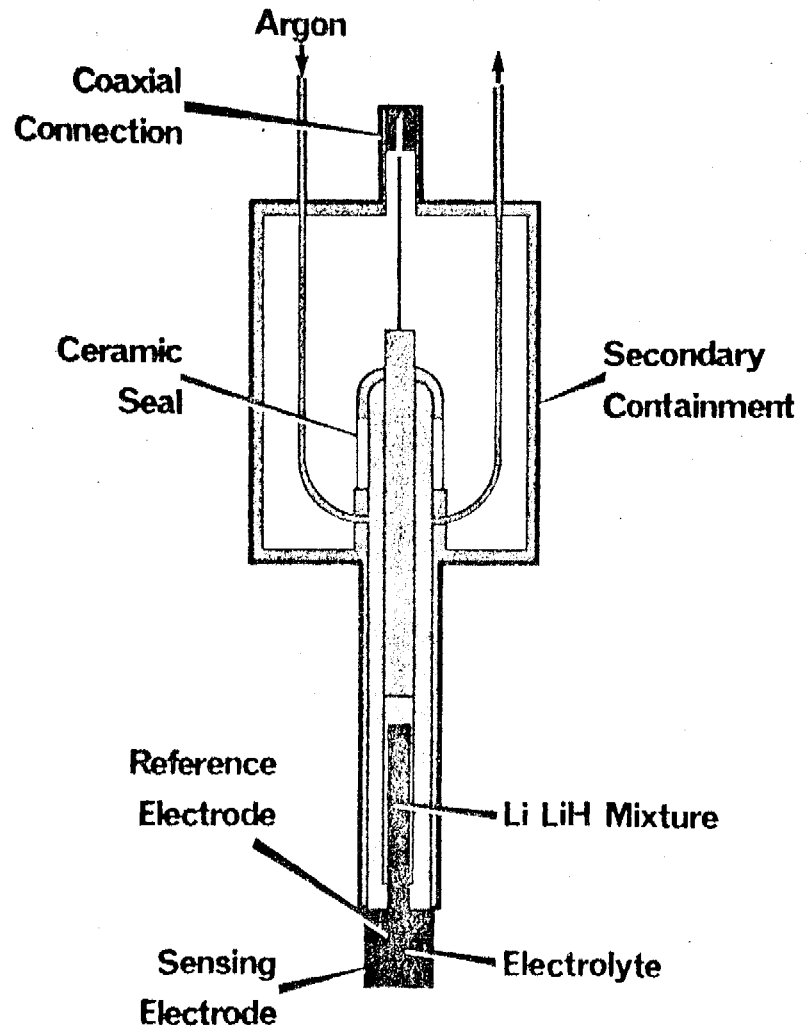
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SOLUTION OF HYDROGEN BUBBLES IN SODIUM

FIGURE 11

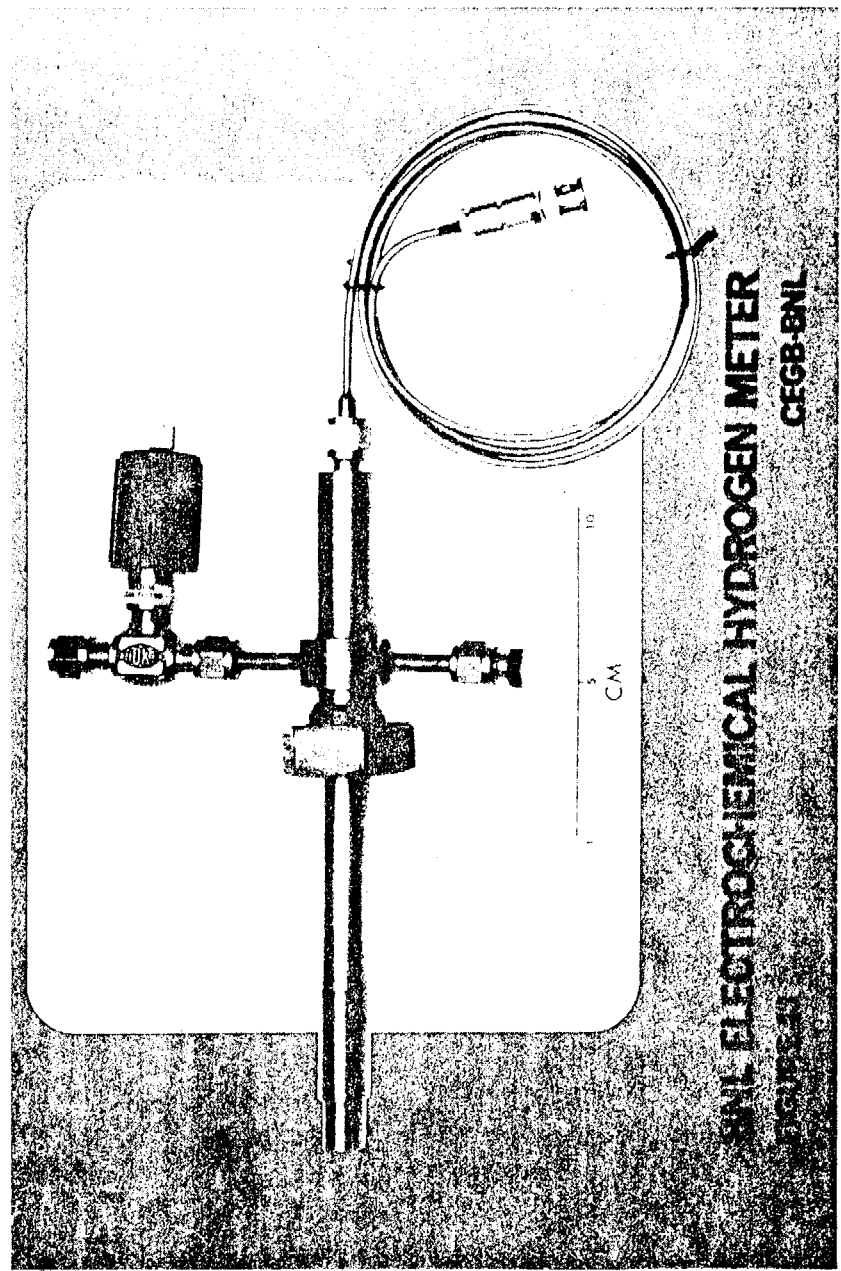
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GALVANIC CELL HYDROGEN METER

FIGURE. 12

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BNL ELECTROCHEMICAL HYDROGEN METER
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BNL GALVANIC CELL HYDROGEN METER

Nernst Equation: $E = \frac{RT}{nF} \ln \frac{a}{a_{ref}}$

Cell: H in Na/Fe/CaH₂ in CaCl₂/Fe/LiH in Li

Lithium Hydride Dissociation:

$$\log a_{ref} = \frac{-9600}{T} + 11.227$$

(torr)

Meter Equation:

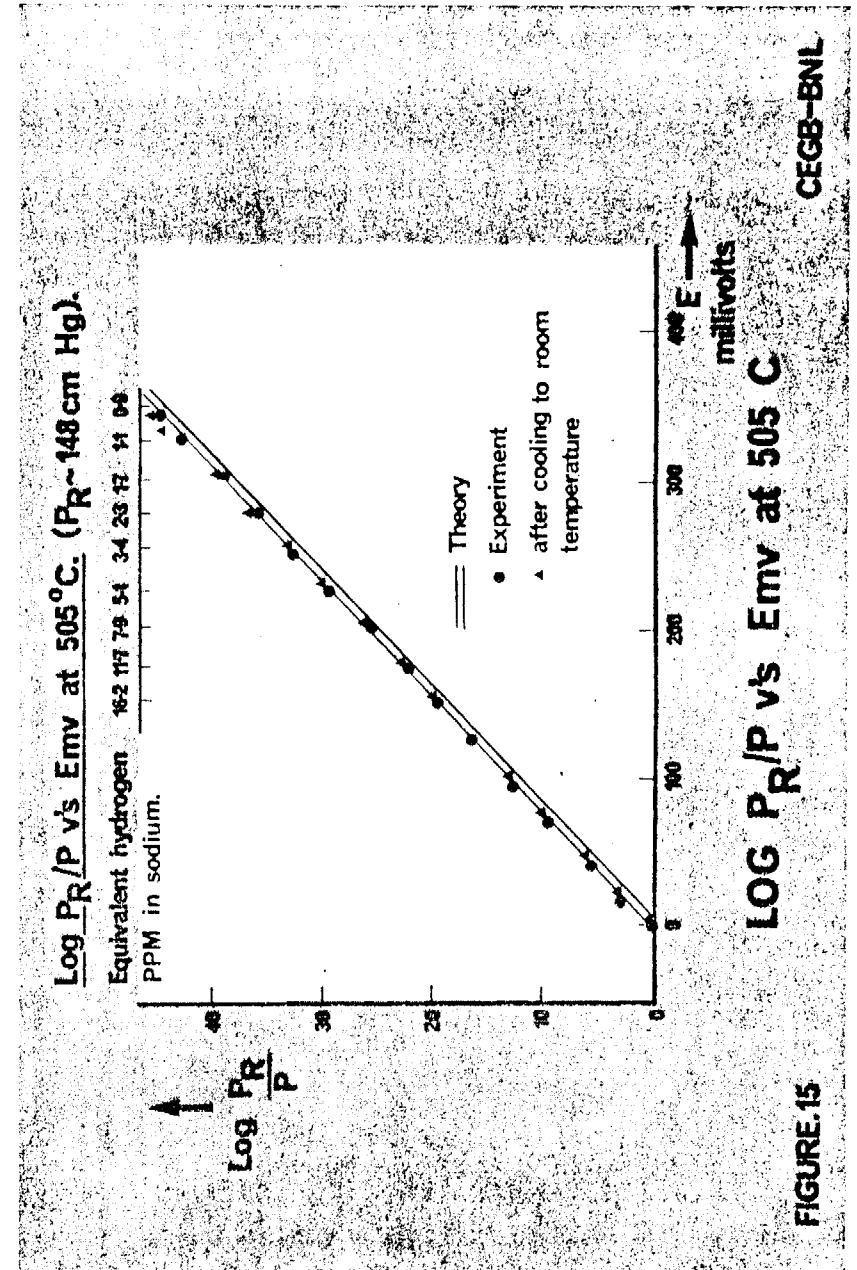
$$E_{mV} = 1.2409K - 952 - 0.1983K \log C_H \quad (C_H: \text{ppm wt.})$$

Meter Equation at 750 K, 477°C:

$$E_{mV} = -(21 + 148.7 \log C_H)$$

FIGURE 14

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SENSITIVITIES OF HYDROGEN AND OXYGEN METERS vs. BACKGROUND LEVELS

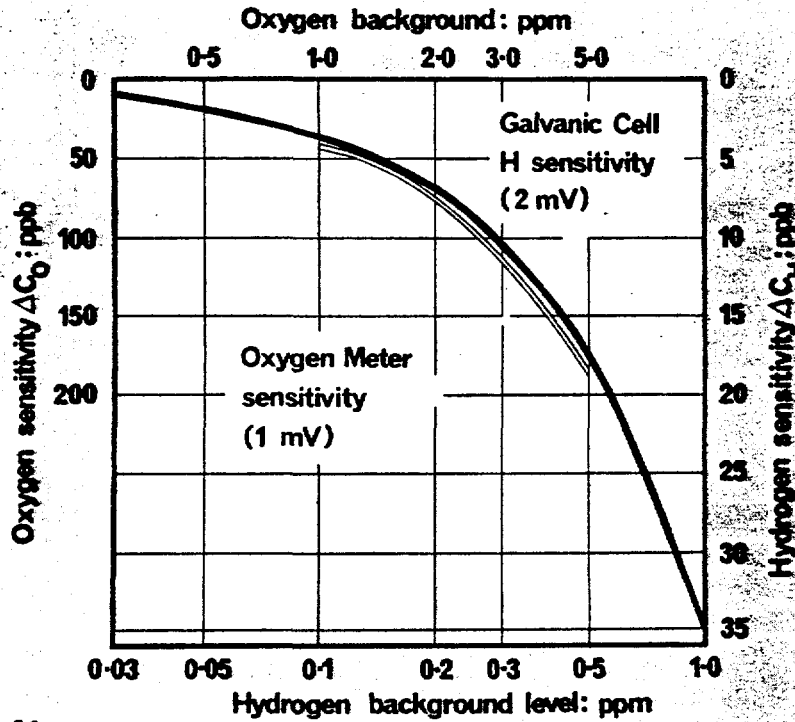
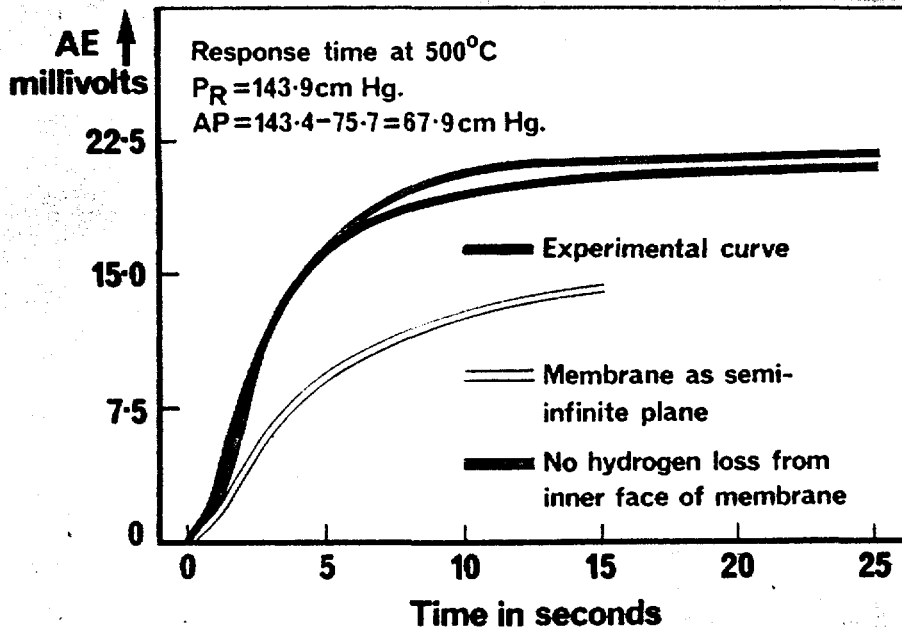


FIGURE 16

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Response time of Hydrogen Meter at 500°C

FIGURE 17

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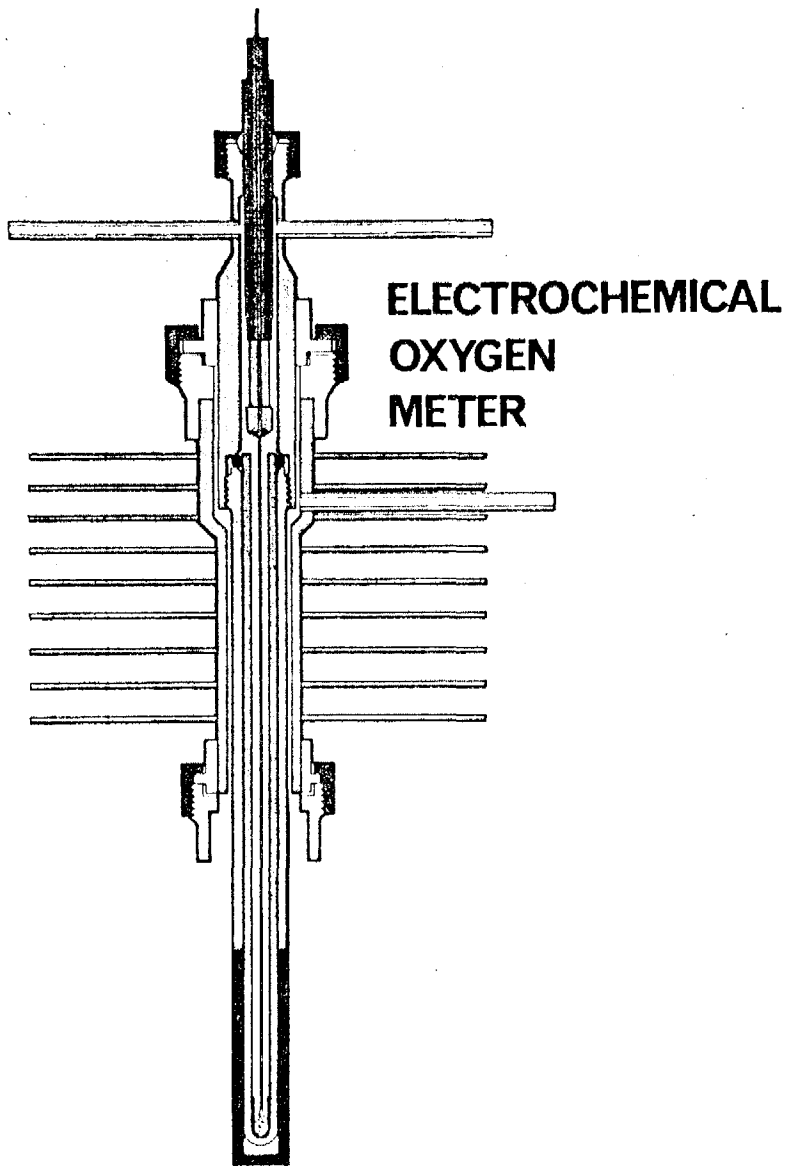
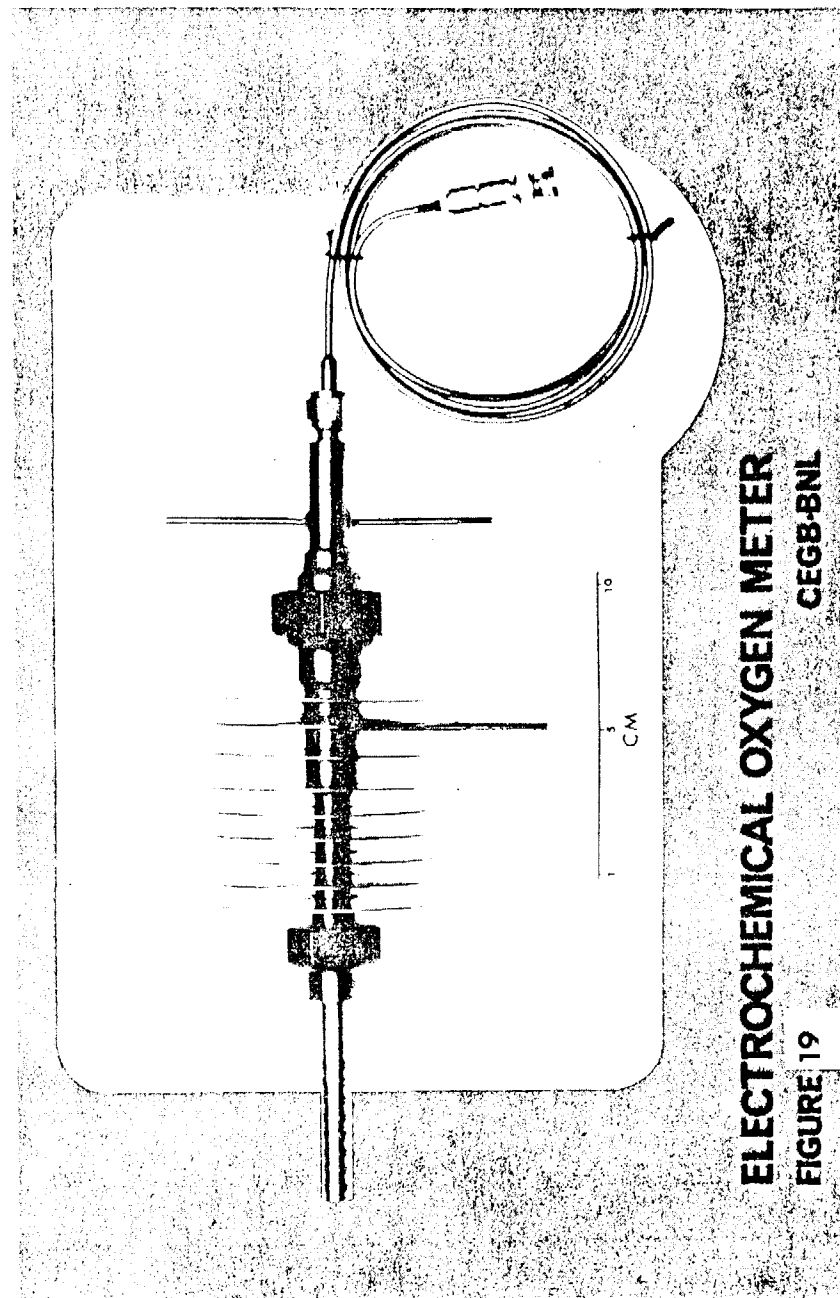


FIGURE. 18

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BNL GALVANIC CELL OXYGEN METER

Nernst Equation: $E = \frac{RT}{nF} \ln \frac{a}{a_{ref}}$

Cell: O in Na/Y₂O in ThO₂ / (Pt) O (Air)

Oxygen Solubility:

$$\text{Log } O_s \text{ (ppm)} = 6.2571 - \frac{2444.5}{K} \quad (\text{Noden})$$

Sodium Oxide Enthalpy of Formation: ΔG

$$\Delta G = 139K - 419856 \text{ J}$$

Meter Equation:

$$E_{mV} = 1938.6 - 0.1767K - 0.09916K \log C_O \quad (C_O \text{ in ppm wt})$$

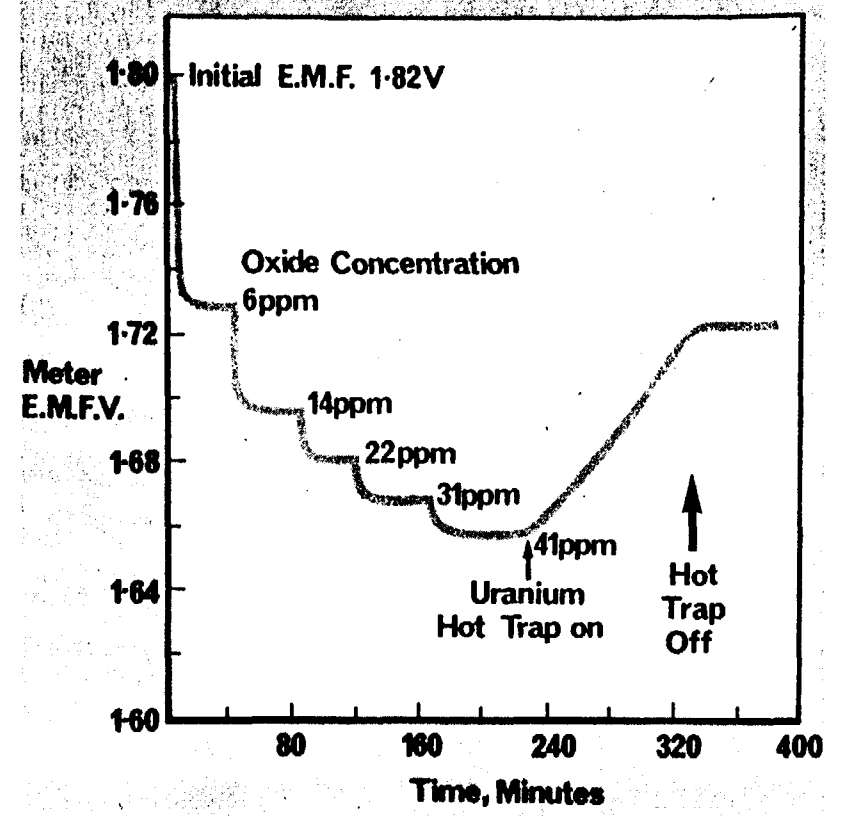
Meter Equation at 750K, 477°C

$$E_{mV} = 1806.1 - 74.37 \log C_O$$

Assumptions:
Ionic Transport No = 1
Henry's Law obeyed

FIGURE 20

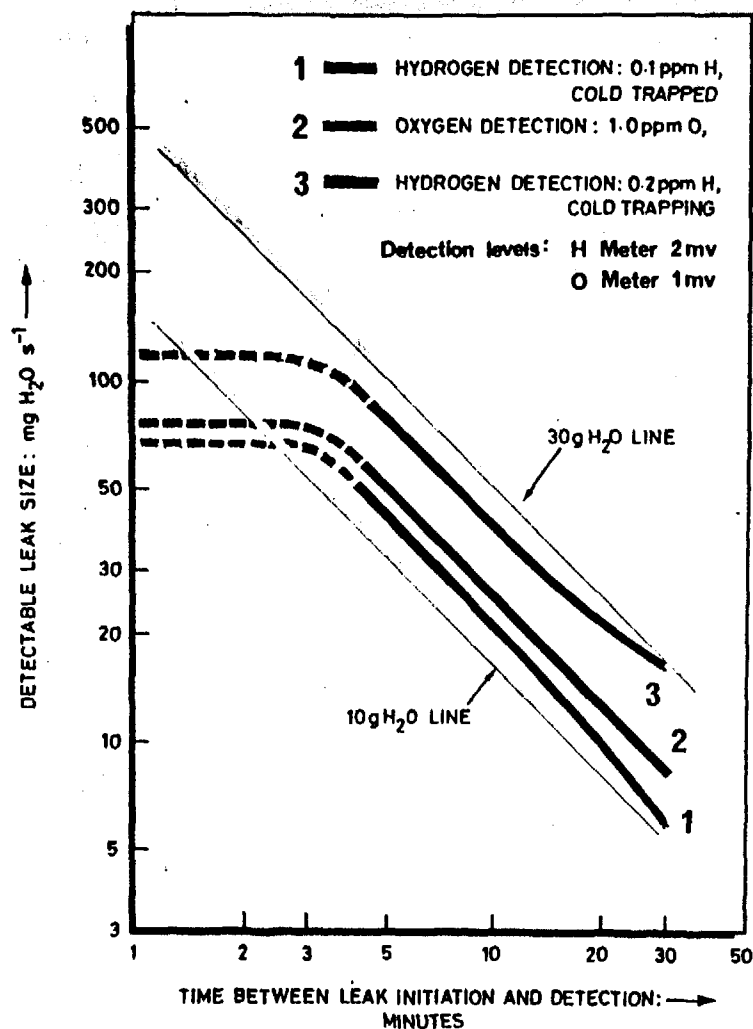
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RESPONSE OF OXYGEN METER TO OXYGEN ADDITIONS AT 435°C

FIGURE 21

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POSSIBLE SENSITIVITIES FOR WATER LEAK DETECTION IN 200 Te CIRCUIT

FIGURE 22

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LMFBR STEAM GENERATOR LEAK DETECTION DEVELOPMENT IN THE UNITED STATES

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ABSTRACT

Leak detection for Liquid Metal Fast Breeder Reactor steam generators is an important economic factor in the shutdown, repair and restart of a plant. Development of leak detection systems in the U.S. has concentrated on four areas: (1) chemical (H_2 and O_2) leak detection meters; (2) acoustic leak detection/location techniques; (3) investigation of leak behavior (enlargement, damage effects, plugging and unplugging); and (4) data management for plant operations. This paper discusses the status, design aspects, and applications of leak detection technology for LMFBR plants.

1.0 INTRODUCTION

Common Liquid Metal Fast Breeder Reactor (LMFBR) steam generator design practice in the U.S. and in Europe utilizes single wall tubes as a barrier between the secondary sodium circuit and the high pressure water/steam circuit. Although thorough material specification, weld development, state-of-the-art inspection techniques and quality control will render the probability of a large failure of a tube extremely low, the possibility of small defects cannot be completely eliminated. Experimental work with very small orifices, through which water/steam is injected, indicates that even if such defects are initially plugged, they will eventually enlarge and remain open. When water is injected into sodium continuously, a sodium/water reaction zone is formed. Should other heat transfer tubes lie in this zone, impingement wastage can cause secondary failures to occur leading to the possibility of a major sodium/water reaction, and the potential for major damage to the unit. To minimize the possibility of such an occurrence, a rapid response leak detection system is provided.

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