A DEVICE FOR CONTINUOUS DETECTION
OF HYDROGEN IN SODIUM

AEC Research and Development Report

ATOMICS INTERNATIONAL
A DIVISION OF NORTH AMERICAN AVIATION, INC.
LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.
A DEVICE FOR CONTINUOUS DETECTION

OF HYDROGEN IN SODIUM

By

H. STRAHL

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.
P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT: AT(11-1)-GEN-8
ISSUED: MAY 31 1962
DISTRIBUTION

This report has been distributed according to the category "Instruments" and "Reactor Technology" as given in "Standard Distribution Lists for Unclassified Scientific and Technical Reports" TID-4500 (16th Ed.), December 15, 1960. A total of 710 copies were printed.
CONTENTS

Abstract ........................................................................ iv

I. Introduction .............................................................. 1

II. Specifications ........................................................... 3

III. Apparatus and Equipment ........................................ 4

   A. Sensor Material ..................................................... 4
   B. Sensor Readout ...................................................... 4
   C. Test Loop .............................................................. 7

IV. Experimental Procedures ........................................... 9

V. Test Results and Discussions ..................................... 11

VI. Conclusions ............................................................ 19

Appendix ........................................................................ 20

References ....................................................................... 22

FIGURES

1. Bench Test Device .................................................... 6
2. Test Loop ................................................................. 7
3. Diaphragm Type Detector ........................................... 11
4. Response Time vs Temperature (3 ppm hydrogen; 2-ft/sec sodium velocity) .................................................. 12
5. Response Time vs Hydrogen Concentration (750°F bulk temperature; 2-ft/sec sodium velocity) ................................................. 13
6. Concentric Tube Detector ........................................... 14
7. Response Time vs Hydrogen Concentration (750°F bulk temperature; 2-ft/sec sodium velocity) .................................................. 15
8. Response Time vs Temperature (sensor controlled at 750°F; 3 ppm hydrogen; 2-ft/sec sodium velocity) ................................................. 15
9. Detector Output vs Sodium Velocity (3 ppm hydrogen; sodium and sensor, 750°F) ......................................................... 17
10. Sensor Output vs Sodium Temperature (3 ppm hydrogen; 750°F sensor temperature) ......................................................... 18
ABSTRACT

A device to detect the presence of hydrogen in sodium has been developed. As little as one part per million hydrogen (based on flowing sodium inventory) can be detected in a flowing sodium stream at temperatures from 500 to 1200°F with response times in the order of 5 seconds. Such a device, installed in a sodium-heated steam generator, would signal the presence of water in the sodium resulting from a leak in the sodium-water barrier.
I. INTRODUCTION

As hydrogen is a product of the sodium-water reaction, its presence in the exit sodium stream from a sodium-heated steam generator is an indication of failure in a barrier between the sodium and steam (water). Early indication of failure (hydrogen) is necessary to permit shutdown of the generator and repair or isolation of the defect because:

1) Leaks invariably start as minute flaws or cracks which may develop into a major failure of the generator if undetected.
2) Products of the sodium-water reaction (e.g., sodium hydride, sodium hydroxide, and sodium oxide) in the sodium are likely to plug small flow passages and attack other components in both the water and sodium systems; the turbine may be particularly vulnerable to damage from these impurities.
3) Impurities introduced into the system can be minimized and therefore less time will be required for cleanup and return to service.

A device, employing a nickel diaphragm, to detect hydrogen in flowing sodium had been developed at Atomics International in a previous study. One side of the diaphragm was contiguous with flowing sodium, and the opposite side formed one side of a vacuum chamber. Hydrogen diffusing through the nickel diaphragm caused an identifiable increase in the rate of pressure rise on the vacuum side of the diaphragm when the vacuum pump was isolated from the system. Spectrographic analysis of collected gas verified the presence of hydrogen.

Although the laboratory study had demonstrated the feasibility of utilizing a metal diaphragm for detecting trace amounts of hydrogen gas in sodium, important questions remained to be resolved and improvements made before such a detector could be used with confidence in a sodium-heated steam generator. The laboratory study had utilized a batch sampling technique, and a method of continuous monitoring, necessary for early detection of a leak, was yet to be developed; the batch sampling technique was somewhat unwieldy in operation and was not readily amenable to unattended operation. Because the initial laboratory study was performed with hydrogen injected into sodium as a gas, it also

NAA-SR-6986
remained to be determined if the method would be satisfactory for detection of hydrogen evolved from leakage of water into sodium. In addition, there remained numerous questions as to what effect the parameters of temperature, fluid velocity, detector location, and detector configuration had on both the time and magnitude of the response (pressure change). Therefore, the objective of this program was to develop a continuously monitoring hydrogen-detection device capable of detecting a water leak into a sodium system stream and to evaluate the effect of the important operating parameters.

The detector developed evolved from the laboratory device described above. The principle on which it is based is the separation of the hydrogen from sodium by the diffusion of the hydrogen through a thin nickel tube (the sensor) into an evacuated region. The pumping rate of the vacuum system is adjusted to just maintain a preset pressure of ~5 microns. When hydrogen diffuses through the nickel tube, the resultant gaseous mixture has a higher thermal conductivity, causing a sharp rise in the pressure indication given by a Pirani vacuum gage. By recording the output of the vacuum gage as a function of time, it is possible to determine when hydrogen was introduced and also to obtain a measure of the amount of hydrogen (or water) involved. The commercial instrumentation incorporated with the sensing device can be equipped with an alarm to indicate the presence of hydrogen in the sodium.

Before testing of sensing devices in sodium, a study was done to select the best sensor material and to select commercial instruments suitable for indicating hydrogen on a continuous basis. A preliminary test of the instruments selected was made, and the most suitable one was chosen for further development. Tests to determine the effect of temperature, fluid velocity, sensor configuration, and sensor location were performed following the selection of diaphragm material and instrumentation.
II. SPECIFICATIONS

The original specifications for the detection device are listed in the appendix. Early in this development program it became apparent that detection at low temperatures would be more difficult than at the specified maximum of 1200°F. Also it appeared that the 1200°F maximum sodium temperature was unwarranted since the device would be utilized in the sodium outlet stream of heat-transfer equipment where temperatures do not exceed 900°F for the advanced plants proposed. Therefore, effort was focused on the 500 to 900°F range. At temperatures above 900°F the only potential problem may involve the mechanical strength of the sensing element as the sensitivity would actually improve. The specifications pertaining to total sodium in loop and sodium system flow rate were not considered mandatory since the same information could be obtained using a smaller scale system, and hence cost of a larger system and time for cleaning up a system of the size specified did not appear to be warranted.
III. APPARATUS AND EQUIPMENT

A. SENSOR MATERIAL

For the sensing-device, it was necessary to select a material with a low resistance to hydrogen diffusion, compatible with sodium, and capable of withstanding the specified pressure and temperature conditions. Materials with low resistance to hydrogen diffusion (in order of increasing resistance) are palladium, nickel, and iron. Palladium is not compatible with sodium and was eliminated from further consideration. Nickel has a lower resistance to hydrogen diffusion than iron at the temperatures under consideration (500 to 900°F) and hence was chosen as the diaphragm material.

B. SENSOR READOUT

There are a number of physical properties which vary considerably from one gas to another and may, therefore, be used as a means of identifying a particular gas in a mixture. Hydrogen, for example, is widely different from oxygen in thermal conductivity, density, refractive index, viscosity, and specific heat. Numerous methods are available for determining each of these properties, any one of which might be used for the purpose of analysis. The hot-wire method of measuring the thermal conductivity has outstanding advantages of accuracy, simplicity, and speed of response. Therefore, three types of commercial hot-wire instruments (described below) were chosen for test, namely, thermocouple gage, conductivity cell, and Pirani gage.

The thermocouple gage, one of the simplest types of vacuum gages, consists of a thermoelectric junction (thermocouple) which is heated by electric current, supplied by a constant voltage source, flowing through a resistance heater. These gages have the advantage of being simple, rugged, and inexpensive. The temperature of the heated junction will vary inversely with the amount of heat energy conducted away from the junction by the gas molecules (pressure) within the system. Thus, the temperature of the junction (the output of the thermocouple) is a measure of the system pressure. The EMF developed across the terminals of the thermoelectric junction is of such a magnitude that it can be measured directly with a calibrating potentiometer and galvanometer.
The operation of the Pirani gage, a thermal-conductivity vacuum gage, is based upon the change in resistance with temperature of a heated filament; the temperature change is a function of the pressure of the surrounding gas. Resistance is measured in a conventional Wheatstone bridge circuit which is made insensitive to ambient temperature changes by use of a compensating tube in one arm of the bridge. A sensitive micro-ammeter, scaled in pressure units, is used to measure the unbalance of the bridge. The power supply for the bridge consists of a step-down transformer, a full-wave selenium rectifier, and an automatic current-regulator tube which develops a constant voltage drop across the bridge voltage potentiometer.

Four-filament hot-wire thermal-conductivity cells are similar to the Pirani gage in principle of operation. The four filaments, made from wire with a high coefficient of resistivity, are located in four identical cavities in a common steel block (heat sink) and form the legs of a bridge. Two cavities communicate with a reference gas and the remaining two with a mixture of the reference gas and the gas being monitored. When the atmosphere in the reference and test cavities is the same, the output of the bridge circuit, with a constant current impressed, is zero. When a gas with a higher conductivity than the reference stream is introduced into the sample stream, filaments in the test cavities (now surrounded by a better heat transfer medium) cool and decrease in resistance with a resultant unbalance of the bridge.

A simple detection apparatus (Figure 1) was constructed for use in tests to discriminate between the various commercial instruments capable of indicating hydrogen. With the sensing element of the instrument undergoing test connected to the vacuum side of the diaphragm, the apparatus was heated in air to a predetermined temperature, hydrogen was injected into the 1-in. pipe, and the instrument output was noted.

Tests with the three types of instruments demonstrated that the thermal conductivity cell was too insensitive for the desired application, and that the thermocouple gage and the Pirani gage were both capable of monitoring for and detecting minute quantities of hydrogen gas on a continuous basis at diaphragm temperatures as low as 550°F. Of the latter two, the Pirani gage was the more sensitive. At 550°F the Pirani gage started to indicate the presence of hydrogen within 15
sec after small quantities of hydrogen were injected on the outside of the dia-
phragm, and within 30 sec indicated a pressure rise of 10 microns. Under the
same conditions, the respective times with the thermocouple gage were 25 and
40 sec. The response time for both the Pirani and thermocouple gage decreased
(an improvement) as the diaphragm temperature was increased.

The Pirani gage, with a Consolidated Vacuum Corporation type GP-105
power supply was selected for all subsequent tests. The power supply incor-
porates an automatic control relay adjustable to operate throughout the entire
pressure range and has recorder taps on a circuit board for connection of a
10-millivolt recorder. This instrument (which may also be used for leak detection using hydrogen gas) can be switched to the leak detector scale to verify that hydrogen is diffusing through the diaphragm when a leak is indicated and that a failure of the sensor or vacuum system has not occurred.

C. TEST LOOP

The test loop (Figure 2) was comprised of 2-in. schedule-40 stainless-steel pipe, a 40-gpm electromagnetic pump, hydrogen and water injector, hydrogen

Figure 2. Test Loop
detection apparatus, flow meter, surge tank, and a diffusion cold trap. A drain tank was attached to the loop to allow the sodium to be drained when modifying or changing the hydrogen device. The total amount of sodium in the loop was \( \sim 180 \text{ lb} \) of which 60 lb were in the flowing stream. The injector tube for either hydrogen or water, a 1/2-in. stainless-steel pipe, was located 14 ft upstream from the hydrogen detector. The flow meter was used to indicate the sodium flow rate in the loop. The surge tank was incorporated to allow free volume for expansion and contraction of the sodium while changing temperatures in the loop. The cold trap was used to remove impurities from the sodium. Helium at 5 psig was used as the cover gas.
IV. EXPERIMENTAL PROCEDURES

Tests were conducted in the flowing sodium stream using injections of both hydrogen gas and water. The hydrogen was charged into a small container from which it passed through the injection tube and expanded into the volume of the loop to give the required concentrations. Subsequent tests measured hydrogen evolved from the sodium-water reaction; the water was measured in a 1-gram hypodermic syringe and injected into the flowing sodium stream. Both the hydrogen gas and water were injected at a point 14 ft upstream from the sensing device. During the tests the hydrogen concentration, the sodium flow rate, and the temperature were varied to determine effect of each variable on the response time of the detection system. Two different sensor configurations were used during the water test program. The temperature was varied from 500 to 900°F, the flow was varied from 10 to 40 gpm, and hydrogen concentration from 1 to 5 ppm. (It should be noted that the hydrogen concentrations quoted in this report are based on the assumption that the hydrogen was uniformly distributed in the total flowing sodium inventory of 60 lb. Concentrations could be higher before complete mixing takes place, and lower after mixing because of loss of hydrogen to the top of the surge tank.)

The hydrogen sensors used in the tests were leak tested with a mass-spectrometer helium leak detector, prior to installations in the sodium loop; this test was repeated with the detectors mounted in the system and heated to 900°F. These results proved not only that the sensors were leak tight but also that the helium cover gas did not diffuse through the nickel diaphragm at elevated temperatures. (This latter result was as expected in that helium is not soluble in nickel and there is no known case of diffusion through a metal in which the gas is not soluble.\(^2\)) One of the sensors was also heated to 1200°F and pressurized to 200 psi to ensure that the unit would comply with the specifications.

The loop was heated to 450°F and the sodium was forced from the drain tank into the loop by pressurizing the tank with helium. Following the loop filling operation the electromagnetic pump was energized and the vacuum valve opened to the hydrogen sensor. The loop was heated to the test temperature by resistance heaters mounted on the exterior surface of the loop piping. After the desired temperature was attained, the electromagnetic pump was adjusted to the
desired flow rate. Subsequently, the valve to the vacuum pump was partially closed until the pressure started to increase and then reopened until the pump was just able to keep the system pressure constant at about 5 microns above the previous equilibrium pressure. This procedure assured that a continuous sample of the atmosphere inside the sensor was being obtained and that a maximum effect would be exhibited by any diffusion of hydrogen. Flow of hydrogen through the valve to the vacuum pump was substantiated by the fact that the indicated pressure in the sensor, after pressure rise resulting from injection of hydrogen into the loop, would decrease with time without additional opening of the vacuum valve. Readings of sensor pressure vs time were recorded on a Sanborn Company model 150 recorder. It was possible to read indicated pressure changes as low as 1 micron on the Sanborn recorder. Prior to the start of a subsequent run, the pressure, as indicated on the Sanborn recorder, was allowed to return to the original reading. This demonstrated that the sodium in the loop was free of hydrogen.

After each water or hydrogen injection, the hydrogen was removed from the sodium stream by diffusion through the nickel diaphragm and by venting it off the top of the surge tank. Following each low temperature run (temperatures below 700°F) it was necessary to heat the loop above 700°F to dissociate sodium hydride formed below this temperature. Cold trapping was continuously conducted to minimize the oxide content of the loop. The sodium was periodically drained into the drain tank at 750°F and returned to the loop at 450°F in order to remove the oxide and sodium hydride from the sodium in the loop.
V. TEST RESULTS AND DISCUSSIONS

Two different sensor types, a diaphragm type and a concentric-tube type, were used during the tests with flowing sodium. The diaphragm type (Figure 3), designed to be installed in the main sodium stream, used 2-in.-diameter nickel diaphragms, 0.010 in. thick. The diaphragms were supported by 1/8-in.-thick perforated plates fabricated from Type 304 stainless steel. Two diaphragms, one positioned vertically in the center of the sodium stream and one positioned horizontally above the stream, were used independently of each other to determine if the physical location would significantly affect sensitivity. The tests demonstrated that the horizontal sensor located above the stream had a 10-sec
faster response and approximately twice the sensitivity of the vertical sensor located in the center of the stream.

The recorded data, Figure 4, using the horizontally positioned diaphragm-type sensor and the Pirani gage, indicated that 630°F was the lowest temperature at which 3 ppm of hydrogen (evolved from the sodium water reaction) could be detected. A test, reported at the end of this section, performed with a detector located above the sodium in the surge tank demonstrates that this temperature limitation is principally due to the fact that sodium hydride, to which the detector is insensitive, is formed at the lower temperatures and is not completely dissociated below 700°F; apparently sufficient dissociation occurs about 630°F for the presence of hydrogen to be indicated. A second factor, of course, is the lower diffusion rate of hydrogen through the nickel diaphragm at the lower temperatures.

Response time (time elapsed between injection and the first indication on recorder including transport time from the point of injection, 14 ft away) of this

Figure 4. Response Time vs Temperature
(3 ppm hydrogen; 2 ft/sec sodium velocity)
sensor improved with increase in bulk sodium temperature (Figure 4). The response times also become smaller as indicated by Figure 5, with increasing concentrations of hydrogen.

![Graph showing response time vs hydrogen concentration](image)

Figure 5. Response Time vs Hydrogen Concentration (750°F bulk temperature; 2-ft/sec sodium velocity)

Since some of the proposed sodium-heated steam generators have a sodium outlet temperature below 630°F, the detector should be capable of detecting a failure below this temperature. For this reason a concentric-tube sensor (Figure 6), the second type tested, was designed for use in a bypass stream where the sensor could easily be heated to 750°F or above while the bulk sodium temperature was 500°F or below. The concentric-tube sensor was constructed using a 0.10-in.-thick nickel tube welded inside a 1/8-in.-thick stainless steel tube. A 0.020-in. annulus was maintained between the two tubes; sodium flows within the inner (nickel) tube. This by-pass configuration was tested while mounted horizontally above a horizontal section of the loop and also in a vertical position off a vertical leg of the loop.
The horizontally mounted concentric-tube sensor was capable of detecting 1 ppm hydrogen (evolved from the sodium water reaction) at a sodium velocity of 2 ft/sec when the sensor was maintained at 750°F with a bulk sodium temperature of 500°F. The time response improved as the hydrogen concentration was increased as shown in Figure 7 for the horizontally mounted case. Time response also became smaller, Figure 8, as the bulk sodium temperature increased.

With a blocking valve installed in the main sodium line to force all the sodium through the sensing tube, flow rates as high as 32 ft/sec through the sensor were obtained during the tests with the concentric-tube sensor. With the heat density available it was impossible to maintain the sensor at 750°F and the bulk sodium at 500°F during this series of tests. For this reason the high-
Figure 7. Response Time vs Hydrogen Concentration (750°F bulk temperature; 2-ft/sec sodium velocity)

Figure 8. Response Time vs Temperature (sensor controlled at 750°F; 3 ppm hydrogen; 2-ft/sec sodium velocity)
flow-rate tests were run with a bulk temperature of 750°F. At the larger flow rates the sodium tended to sweep the hydrogen gas through the sensor and not allow the hydrogen to collect. The sensor did indicate the presence of hydrogen during the high flow tests but did not give signals large enough to actuate an alarm (a 10-micron rise is needed to actuate the alarm). A plot of sodium velocity vs detector output is shown in Figure 9.

The concentric-tube sensor mounted vertically off a vertical run of pipe was less sensitive than the horizontally mounted sensor. It did indicate the presence of hydrogen with the bulk sodium and sensor at 750°F and 3 ppm of hydrogen but did not give a large enough signal to actuate the alarm.

The fact that either type of horizontally mounted sensor is more sensitive than the vertically mounted sensor and that the sensitivity is rather sharply dependent upon velocity tends to indicate that the hydrogen concentrates along the top of the pipe; the horizontal sensor would therefore "see" more of the hydrogen.

A concentric-tube sensor was mounted above the surge tank to demonstrate that the hydrogen evolved from the sodium-water reaction readily formed sodium hydride at the lower temperatures and thus did not travel with the sodium stream as hydrogen gas. If hydrogen gas, it would rapidly appear above the free surface in the surge tank independently of the bulk sodium temperature. During these tests the sensor was maintained at 750°F and the bulk sodium temperature was varied. Water (equivalent to 3 ppm hydrogen) was injected into the sodium stream. The data recorded during these tests (Figure 10) indicate that sodium hydride is formed, because if gaseous hydrogen, rather than sodium hydride, had formed, then detector output would not have so rapidly increased with temperatures. These data also indicate the hydride dissociation increases rapidly above 600°F.

It should be noted that for either sensor design failure of a nickel tube or diaphragm would cause an immediate increase in the pressure actuating an alarm. The sodium leaking through the diaphragm would freeze at the finned section above the sensing unit and thus be contained.
Figure 9. Detector Output vs Sodium Velocity
(3 ppm hydrogen; sodium and sensor, 750°F)
Figure 10. Sensor Output vs Sodium Temperature (3 ppm hydrogen; 750°F sensor temperature)
VI. CONCLUSIONS

A practical device has been developed to detect the presence of hydrogen in sodium. The device will detect the admission of water to a sodium system such as would occur during a leak of high-pressure steam into liquid sodium in a sodium-heated steam generator. Commercially available instrumentation incorporated with the sensing device can be equipped with an alarm to indicate the presence of hydrogen in sodium. The detector is suitable for systems operating at temperatures up to 900°F as determined by actual test and would be expected to improve in sensitivity at higher temperatures. The response time has been shown to be as low as 5 sec with the system at 900°F; i.e., 5 sec after injection of water (equivalent to 3 ppm H₂) into the sodium flowing at 2 ft/sec the detector, located 14 ft from the point of water injection, gave a discernable signal.

Nickel was shown to be a suitable material for the hydrogen diffusion barrier. It meets the requirement of compatibility with sodium and has a satisfactorily low resistance to hydrogen diffusion. Of the sensors tested, the horizontally mounted nickel tube located in a bypass line was shown to be the most sensitive.

A Pirani vacuum gage used with a Consolidated Vacuum Corporation Type GO-105 power supply and equipped with an alarm circuit proved to be suitable for use with the nickel sensor as a means of indicating the presence of hydrogen.

The intent of the specifications for a device for detecting hydrogen in a sodium system has been satisfactorily met.

An engineering drawing of the detector is included at the back of this report.

NAA-SR-6986
19
JUSTIFICATION

A considerable number of the nuclear power plants under construction include in the primary heat cycle a Na-H\textsubscript{2}O steam generator. A mixture of sodium and water will react violently resulting in the generation of heat, Na\textsubscript{2}O, NaOH, NaH, and hydrogen gas. The early detection of a leak from the high pressure H\textsubscript{2}O to the sodium is vital to the life of this component and possibly to the operation of the entire plant.

PURPOSE

To develop a rugged and sensitive device that can detect hydrogen, in minute quantity, from a Na-H\textsubscript{2}O reaction in a flowing stream of high temperature sodium.

NATURE AND SCOPE OF WORK

The various existing devices for measuring the individual products of a non-radioactive NaH\textsubscript{2}O reaction, or allied devices, should be surveyed. A device that appears most promising shall be fabricated and tested in a facility provided by the AEC. The device shall be designed for nuclear power plant use.

FUNCTIONAL SPECIFICATIONS

The instrument for detecting the presence of hydrogen in sodium shall be capable of the following:

1. Measure hydrogen from a H\textsubscript{2}O-sodium reaction in the range of 0-30 ppm
2. Accuracy <1% of range
3. Response time 5 sec
4. Pressure -14.7 to 175 psig
5. Sodium temperature 1200 °F maximum
6. Sodium velocity 30 ft/sec
7. Total sodium in loop 10,000 gal
8. Sodium system flow rate  5,000,000 lb/hr
9. Design life  10 years
10. No plugging permissible
11. Easily maintained or replaceable as a unit
12. Remote reading and recording of generated signal
13. Must comply with Section VIII of ASME boiler and pressure vessel code including methods of attachment to or sampling from code vessels.
REFERENCES
