375

NAA-SR-3638

COPY

MASTER

CONTROL OF OXYGEN CONCENTRATION IN A LARGE SODIUM SYSTEM

AEC Research and Development Report

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.

DISCLAIMER

NAA-SR-3638
REACTORS-POWER
46 PAGES

CONTROL OF OXYGEN CONCENTRATION
IN A
LARGE SODIUM SYSTEM

By

R. B. HINZE

This document is
PUBLICLY RELEASABLE
Hugh Kinsey
Authorizing Official
Date: 8-23-2013

ATOMICS INTERNATIONAL

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

CONTRACT: AT(11-1)-GEN-8
ISSUED: DECEMBER 1, 1959

DISTRIBUTION

This report has been distributed according to the category "Reactors-Power" as given in "Standard Distribution Lists for Unclassified Scientific and Technical Reports" TID-4500 (15th Ed.), August 1, 1959. A total of 620 copies was printed.

ACKNOWLEDGMENT

The author wishes to acknowledge the contributions and guidance of G. E. Deegan, L. E. Glasgow, and D. H. Johnson and the suggestions of members of the Sodium Graphite Reactors group.

CONTENTS

IV. Appendices

TABLES

FIGURES

ABSTRACT

The performance of two types of cold trap in the 50,000-lb radioactive sodium system at the SRE has been determined:

Type	Oxygen Trapping Rate (lb/hr)	Na_2O Capacity (lb)
Boiling-Coolant	0.009	2.6
Forced-Convection-Cooled	0.02	10.8

These rates were determined when trap inlet oxygen concentrations were in the range 8-10 parts per million. Oxygen concentration can be readily controlled down to 8 ppm using a cold trap.

Extraction of oxygen from sodium by zirconium at 1200°F (hot trapping) reduces the concentration below the limit of detection, i.e., oxide solubility saturation temperature below 225°F; the theoretical limit for the equilibrium oxygen concentration has been calculated to be less than 7×10^{-6} ppm. The observed extraction rate of 0.009 lb oxygen/hr, was one-half of the rate predicted from material behavior studies.

I. INTRODUCTION

The objective of this work was the determination of operating characteristics of cold traps and a hot trap, components used to control oxygen concentration in sodium systems. Trapping rates, trap capacity, and attainable system oxygen concentration were determined in a large (50,000-lb) sodium system. The relation between the predicted hot trapping rate and the actual rate was established. The control of oxygen concentration in sodium permits taking advantage of the natural inactivity between pure sodium and structural materials in the reactor system. Also, oxide plugging of small piping is prevented, radioactive mass transfer is minimized, and an increase in the fatigue life of zirconium is realized when oxygen concentration is controlled. This investigation was a part of the initial operation of the Sodium Reactor Experiment, which is being conducted for the United States Atomic Energy Commission by Atomics International, a division of North American Aviation, Inc.

In the experimental program a plugging meter was used to determine sodium saturation temperature. Oxygen concentration was then obtained from a temperature-solubility curve.[1] Trapping rates have been calculated from the change in the amount of dissolved oxygen in the system. The capacity of the cold trap has been calculated from the observed volume and density of the sodium oxide collected. Ultimate hot trap capacity was computed from the chemical reaction equation. Extraction during the pedictable rate period was calculated from the experimentally determined behavior of zirconium in the sodium-oxygen system.[2] Estimation of the oxygen concentration attainable in a hot trapped sodium system was based on thermodynamic considerations.

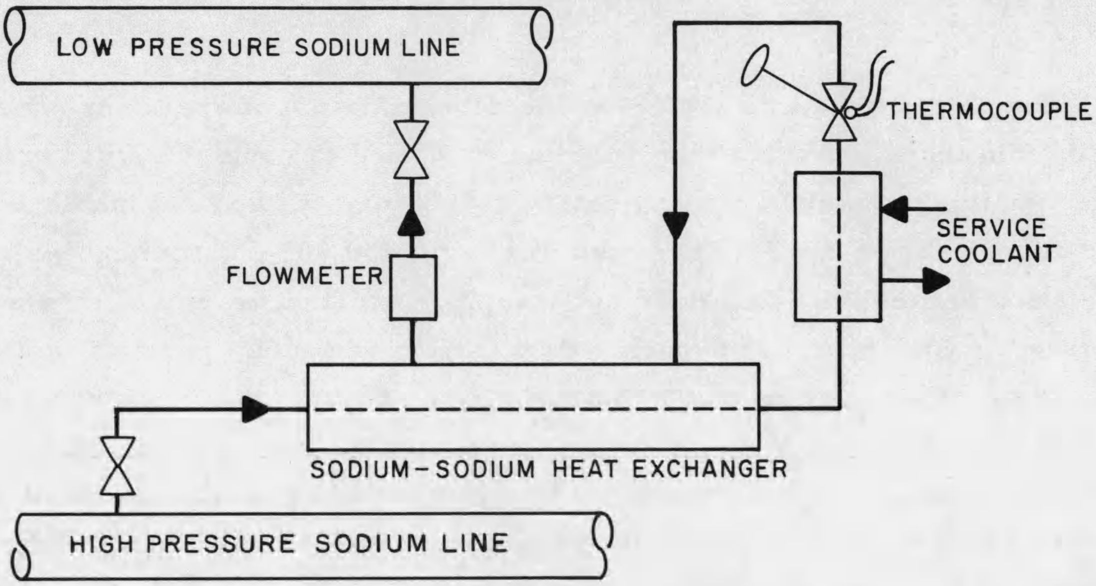


Figure 1. Plugging Meter

Figure 2. Drilled Plugging Valve Disk

II. COLD TRAP

A. DESCRIPTION OF EQUIPMENT

At the SRE a plugging meter is used to determine saturation temperature. In the plugging meter a portion of the main sodium stream is cooled and passed through orifices. When the saturation temperature of this sodium-sodium oxide solution is reached, a flow decrease caused by solid sodium oxide particles plugging the orifices is observed. The saturation temperature is often called the plugging temperature. Oxide concentration is then estimated from Gray's temperature-solubility curve.[1]

The plugging meter consists of a sodium-sodium economizer, a sodium-tetralin heat exchanger in which the sodium is cooled, a plugging valve containing an orifice plate and a thermocouple, and a permanent magnet flowmeter. The arrangement of these components is shown in Figure 1. Tetralin (tetrahydronapthalene) is used as the service coolant at the SRE. The plugging orifice is mounted in a 1-in. "Y"-pattern valve body. The standard valve disk is replaced by a Type 304 stainless steel disk shown on Figure 2. The face of this disk is perforated with a number of size 60 holes, the number dependent on the pressure drop available across the plugging meter. The sides of the disk downstream from the seat are also drilled, permitting a small flow through the orifices when the valve is in the closed position. The advantage of this disk arrangement is the ease of cleaning compared with a fixed orifice plate. After a plugging determination, the valve is partially opened and the disk is held in the flowing sodium stream for rapid cleaning. A grooved disk, shown on Figure 3, has been substituted for the drilled plug; both are satisfactory.

The plugging meter used at the SRE is a simple, yet reliable instrument. Operating experience has demonstrated that it gives results which are reproducible within 5°F. This corresponds to a concentration range of 1-1/2 ppm at 370°F, or to 5 ppm at 450°F. The plot of a typical determination of saturation temperature is shown in Figure 4. The original record was made with a two-pen recorder. The cooling rate during this determination was 6-1/3°F/min. The standard rate is 5°F/min, but a deviation of this magnitude does not affect the result. The formation of solid sodium oxide particles is indicated by the

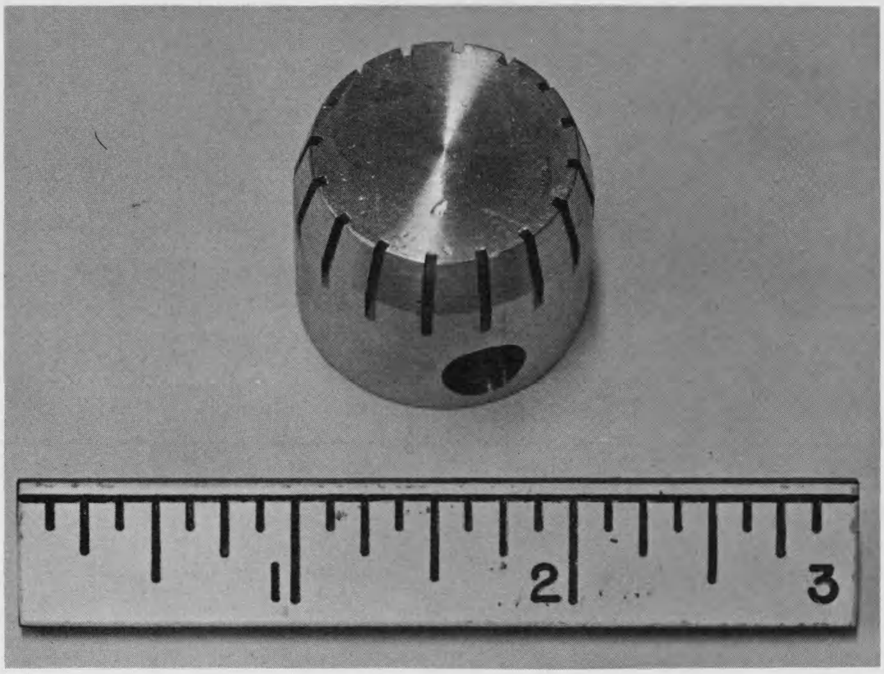


Figure 3. Grooved Plugging Valve Disk

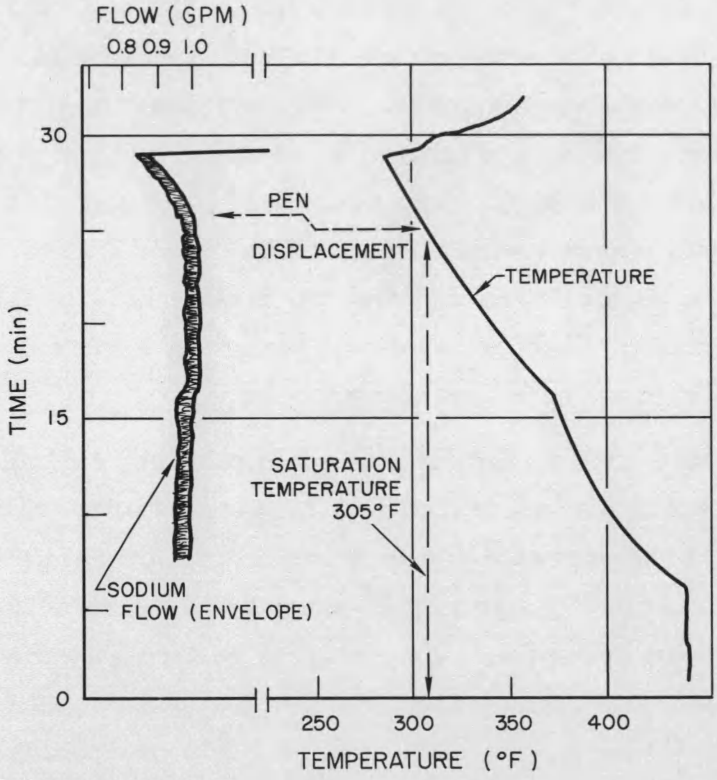


Figure 4. Typical Two-Pen Recording of Plugging Determination

decrease in sodium flow rate, the point marked with an arrow. The temperature, at the time the flow starts to decrease, is used as the saturation temperature.

In a cold trap, sodium temperature is lowered below the saturation temperature causing precipitation of sodium oxide. The process can occur in a cool stub, off the main sodium piping. This pipe stub arrangement, called a diffusion cold trap, has been used extensively in small experimental sodium loops (less than 500 lb). In large sodium systems oxygen concentration is controlled by circulating cold traps. In these traps, the sodium is pumped through the vessel in which it is cooled, and the precipitated oxide is collected on the coils of wire mesh. The wire mesh serves as a surface on which the oxide crystals can grow, and as a filter for the collection of suspended oxide particles. Two types of circulating cold traps have been used at the SRE: a boiling-coolant trap and a forced-convection trap.

Boiling-coolant traps were installed when the reactor was constructed. In this type of trap, a uniform jacket temperature is maintained at 233°F by boiling toluene at atmospheric pressure. Figure 5 is a diagram of the complete

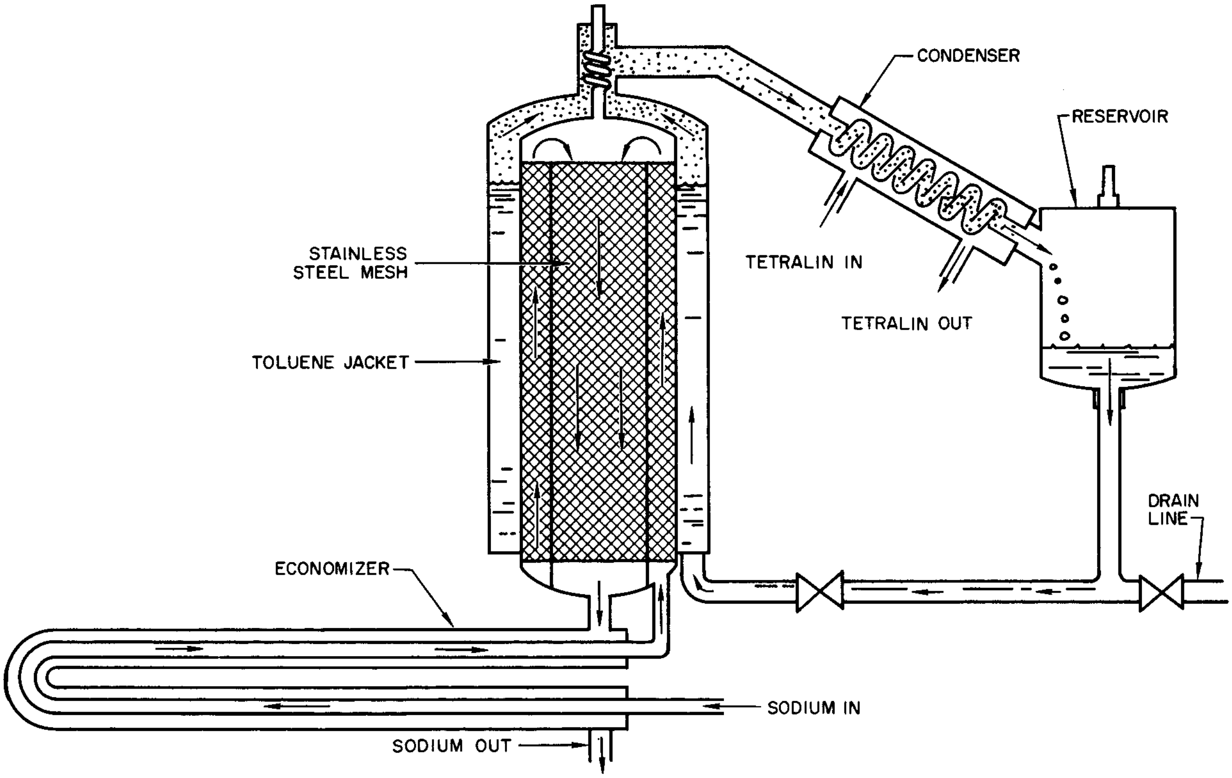


Figure 5. Boiling Coolant Cold Trap

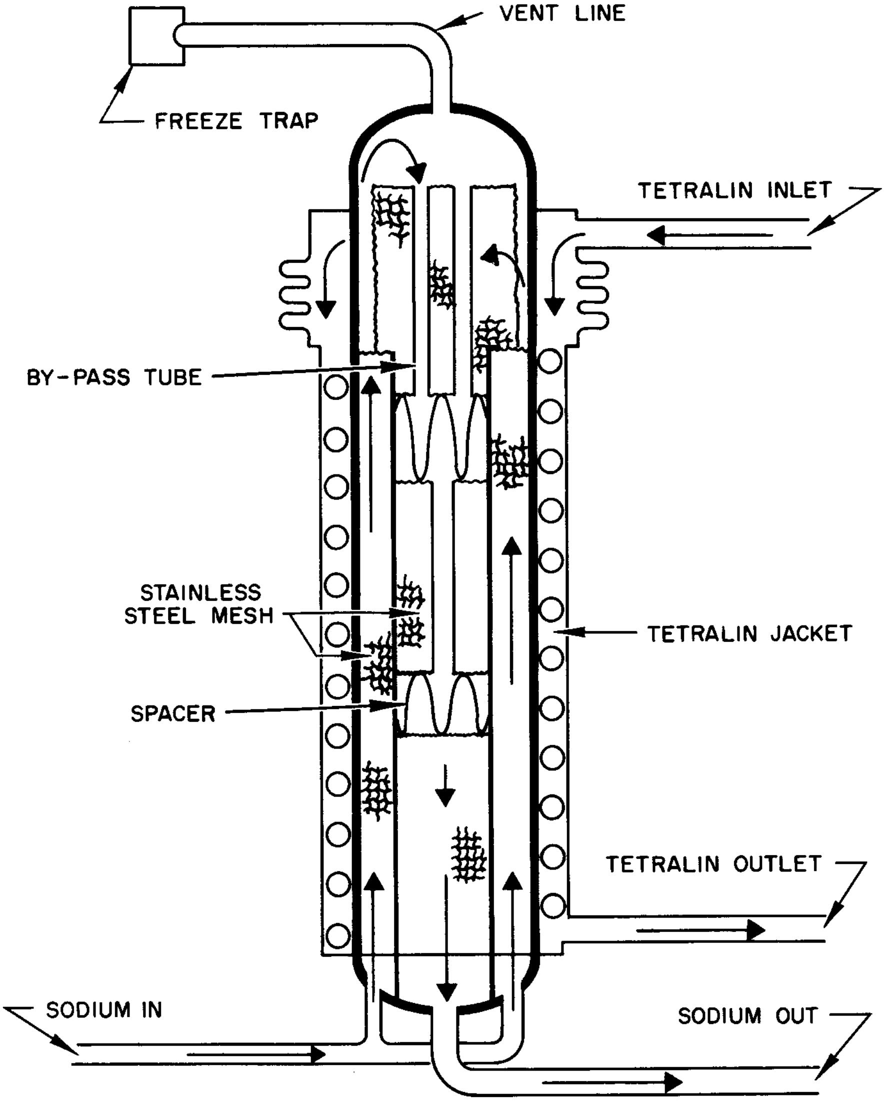


Figure 6. Forced-Convection Cooled Cold Trap

trap assembly showing the toluene cycle and including the sodium economizer. The feed sodium stream is cooled in the economizer; it then enters and flows into the trap. Here the incoming sodium loses heat primarily to the toluene; some heat transfers to the sodium circulating down the central tube. The toluene boils in the outer jacket; its vapor is condensed by the service coolant, tetralin; and the condensate returns to the reservoir. Liquid toluene returns to the jacket by gravity. The sodium vessel is 12-in. schedule-40 pipe; the outer diameter of the inner tube is 8 in., and the mesh section is 3 ft in length. All sodium piping and equipment is fabricated from Type 304 stainless steel.

The forced-convection-cooled cold trap shown in Figure 6 uses tetralin, the reactor service coolant which passes down the coolant jacket. Sodium flow is as shown in Figure 5, i.e., up the annulus and down the 6-in.-OD tube. The mesh in the central tube has been separated and bypass tubes installed to provide additional filtering area. The upper coil of mesh is of slightly smaller diameter than the vessel, to permit the oxide slurry to pass over the top of the coil to the bypass tubes and to enter the side of the upper coil. Knitted wire mesh is used. It is made of 0.011-in.-diameter, Type 304 stainless steel wire; the apparent density of the mesh is 24 lb/ft^3. During fabrication the central tube is welded to the bottom cap, and then the mesh is installed. Figure 7 shows this insert ready for assembly in the 12-in. pipe vessel. The mesh is retained on the tube with stainless steel wire. The leads of three sheathed thermocouples protrude out of the mesh and through a fixture in the top cap. The assembled component is shown in Figure 8. Ring-joint flanges are used in the sodium and vent lines. These lines are preheated with tubular heaters (approximately 15 watts/in. of

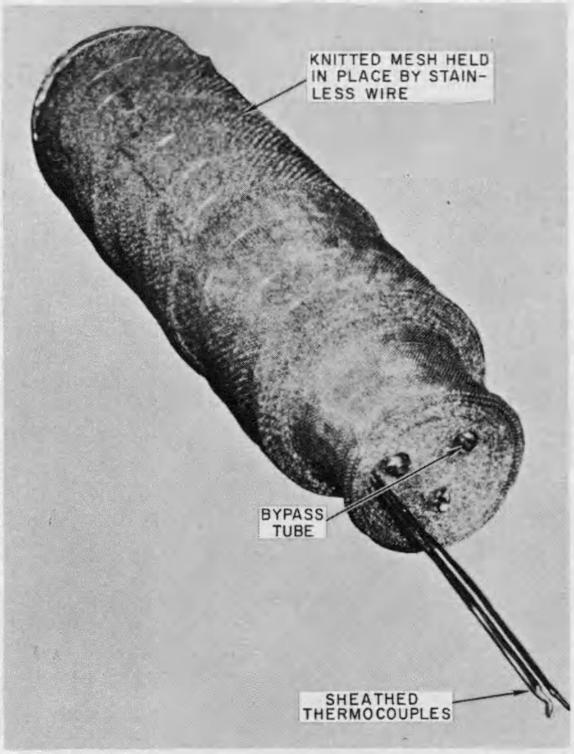


Figure 7. Cold Trap Insert

pipe). The vessel is preheated with 230-volt, 750-watt strip heaters. Twelve heaters are installed, of which four are spares.

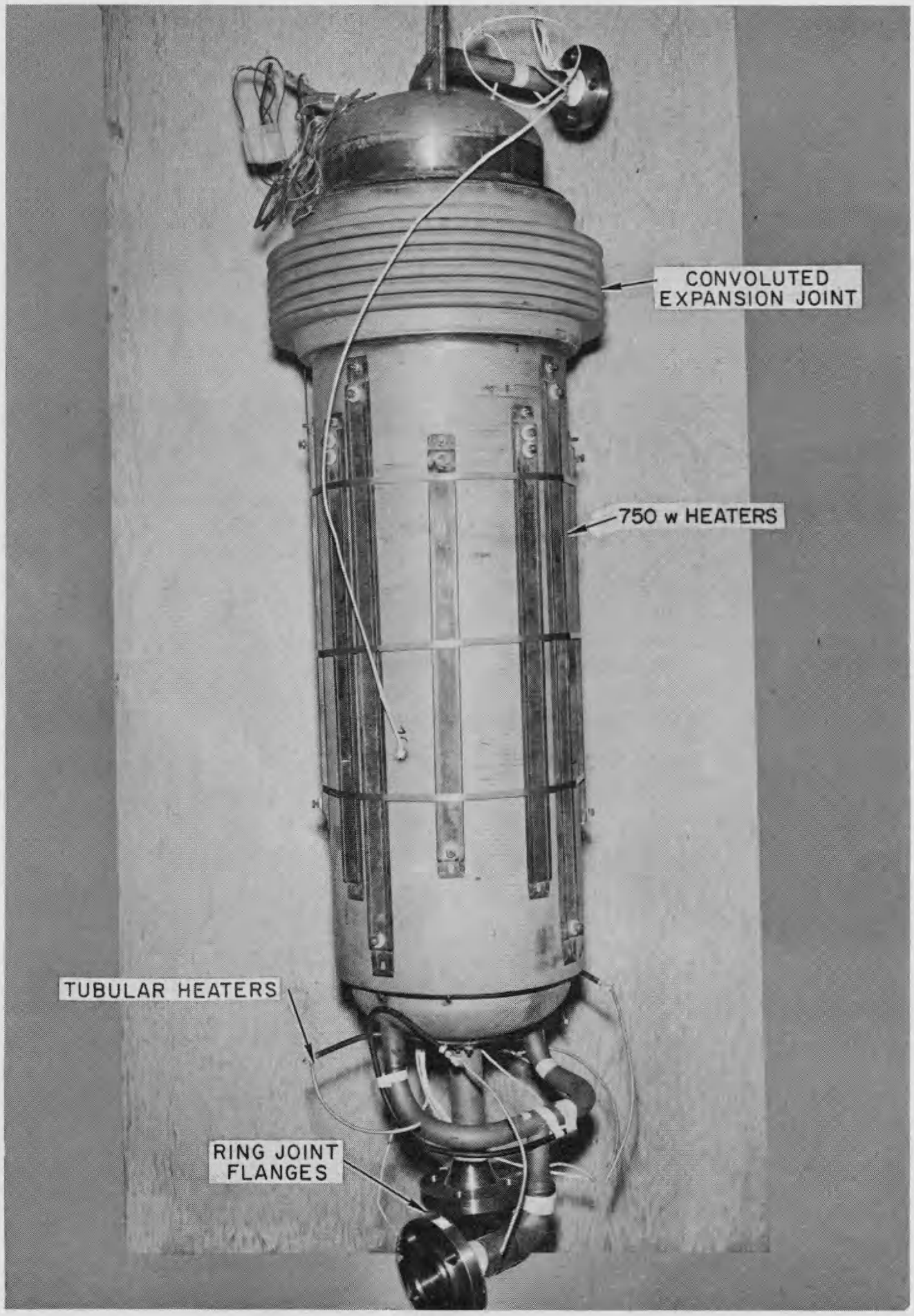


Figure 8. Assembled Cold Trap

B. PROCEDURE

Trapping rates are based on the change in dissolved oxygen in the system. Sodium saturation temperature is monitored during reactor operation by use of the plugging meter. The saturation temperature and the system temperature are plotted against time as shown in Figure 9. A portion of this graph has been expanded and reproduced as the upper curve in Figure 10. The slope of any chord of this curve can be converted to a trapping rate as calculated in Appendix A.

The calculation of the quantity of sodium oxide collected in a cold trap is based on the apparent density of oxide in the wire mesh and the effective trapping volume. In one experiment a sodium-sodium oxide slurry was passed through a wire mesh filter under essentially isothermal conditions until the filter was plugged. Plugging was indicated by a flow stoppage. All of the oxide collected was found in the first 2 in. of the filter; the remainder of the cartridge had drained clean. In this experiment the first 2 in. of the filter, shown in Figure 11, filled to its maximum capacity with sodium oxide. From a determination of the total amount of sodium and sodium oxide retained in the mesh, and the concentration of oxide in this mixture of sodium and sodium oxide, the apparent density of sodium oxide in the mesh has been calculated to be 0.0208 lb/in.^{3} (Appendix B).

The effective trapping volume was determined by inspection, where possible, as the volume of mesh containing sodium oxide with a density of deposition equal to that observed on the mesh in the slurry filtering experiment. Mesh containing slight oxide deposition was not included. Where the depth of deposition could not be visually observed, a 2-in. deposit was assumed. This assumption was based on results of the slurry filtering experiment. Trap capacity was calculated (Appendix B) as the product of apparent density and effective volume.

Cold trap parameters (temperature and sodium flow) were observed during trap operation; typical steady state values have been reported in Section II-C. Heat transfer rates were calculated on the sodium side of the traps. Organic coolant flow rates were calculated from the heat transfer rate and enthalpy changes, since there were no flow rate observations. Overall heat transfer

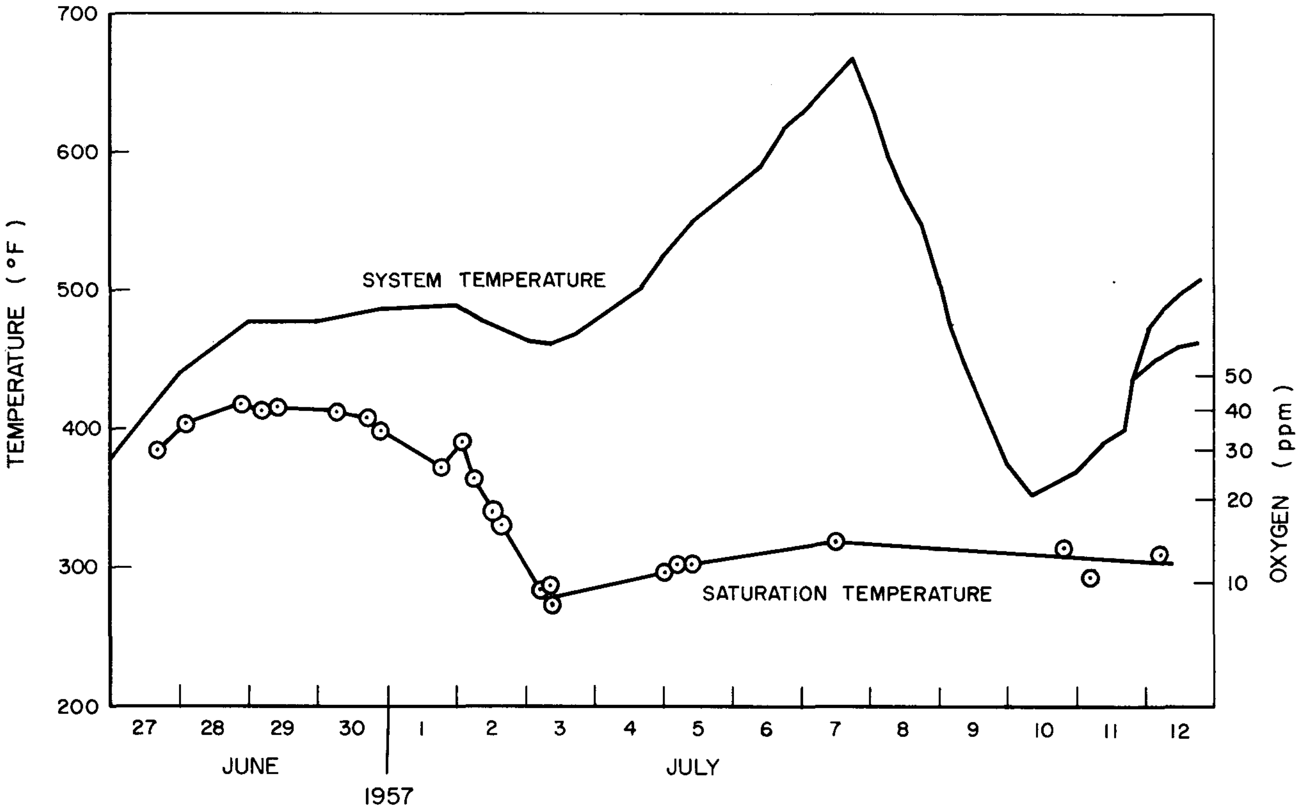


Figure 9. Primary Sodium Cleanup

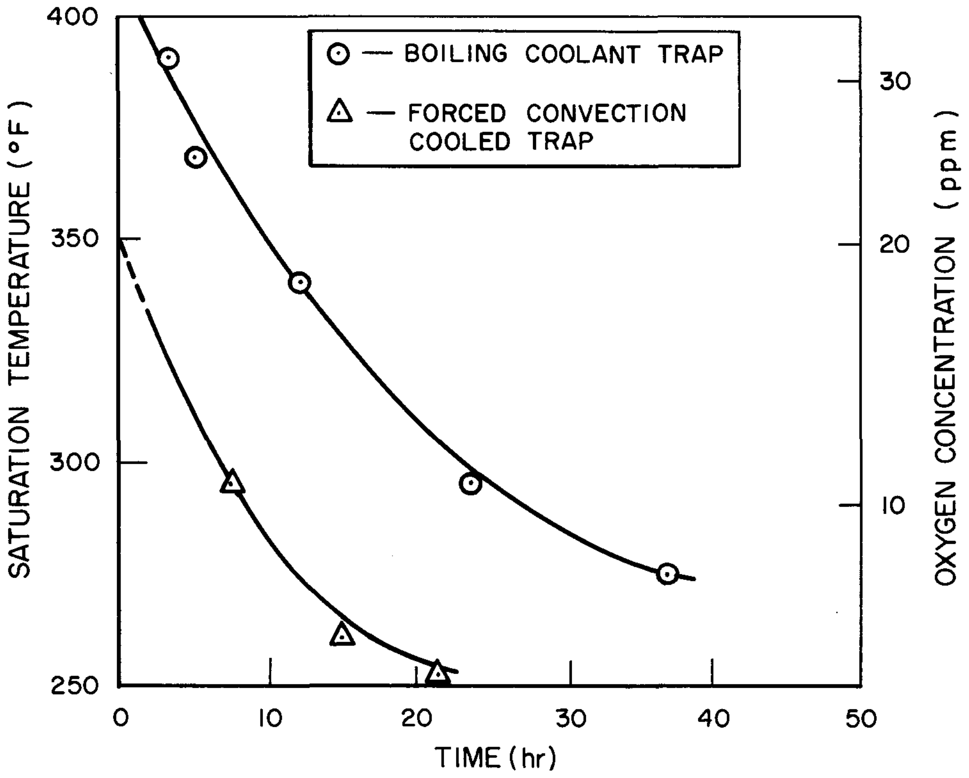


Figure 10. Cold Trap Performance

coefficients were based on the inside surface area of the 12-in. pipe and the log mean temperature difference.

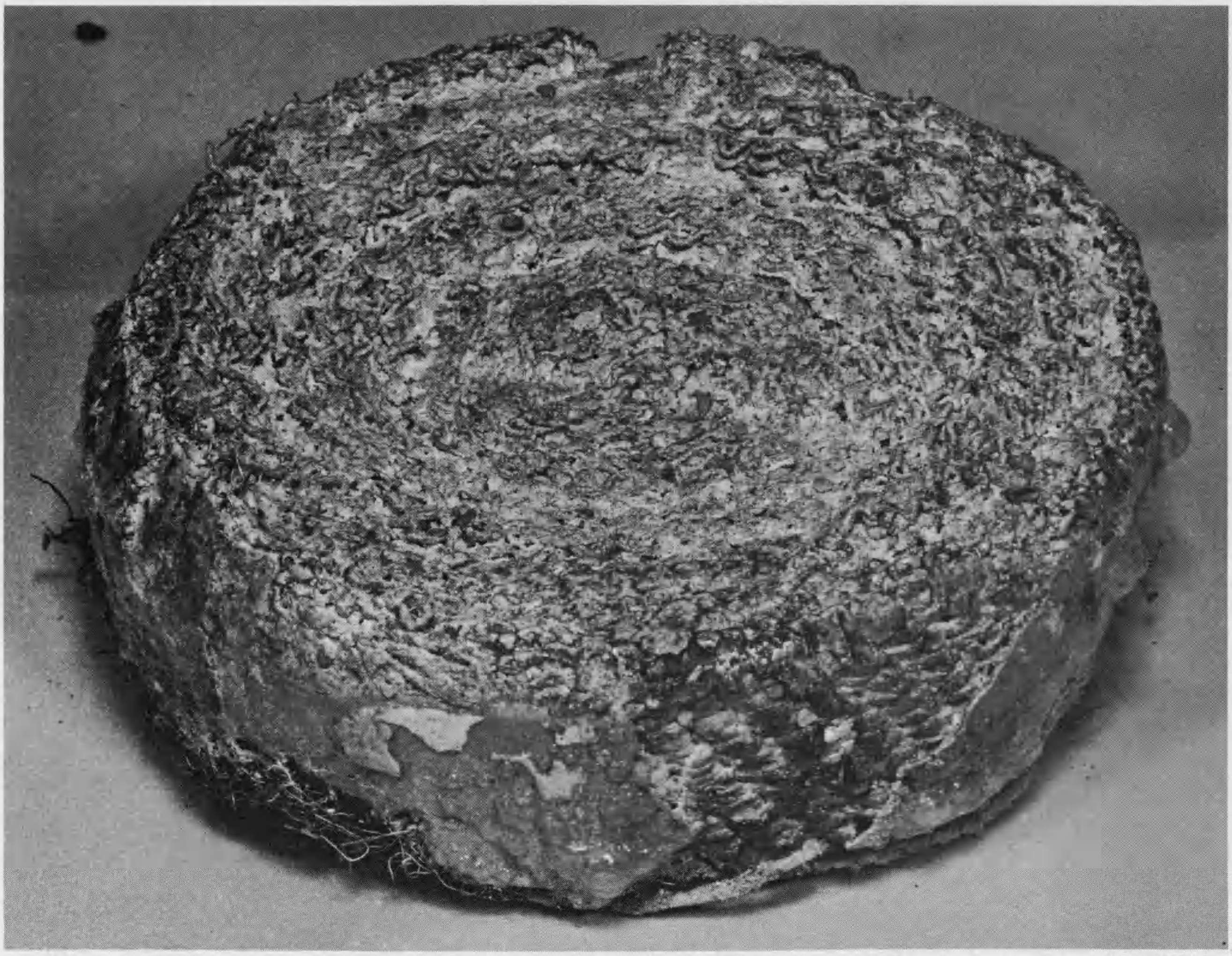


Figure 11. Filter Mesh Filled With Oxide

C. RESULTS

Cold trap performance is summarized in Table I.

An oxygen concentration of 8 ppm in the 50,000-lb primary system can be expeditiously obtained by use of a cold trap.

TABLE I

COLD TRAP PERFORMANCE

Trapping Rates

Trap	Oxygen Trapping Rate (lb/hr)
Boiling-coolant	0.009
Forced-convection-cooled	0.02

Trap Capacity

Trap	Oxygen (lb)	Sodium Oxide (lb)
Boiling-coolant trap at SRE	0.67	2.6
Prototype trap	1.35	5.25
Forced-convection-cooled trap	2.8	10.8

Cold Trap Operating Parameters

Parameter	Sodium	Organic
Boiling-Coolant Trap		Toluene
Flow rate (gpm)	5	0.8
Temperatures (°F)		
Inlet	484	193
Outlet	400	234
Minimum	358	-
Heat Transfer Rate (Btu/hr)	62,000	
Overall Heat Transfer Coefficient (Btu/hr-ft^2-°F)	35	
Forced-Convection-Cooled Trap		Tetralin
Flow rate (gpm)	32	24
Temperature (°F)		
Inlet	345	100
Outlet	305	141
Minimum	257	-
Heat Transfer Rate (Btu/hr)	190,000	
Overall Heat Transfer Coefficient (Btu/hr-ft^2-°F)	94	

D. DISCUSSION

The normal inertness of pure sodium with respect to reactor structural materials may be diminished by sodium-transported oxygen. Stainless steel, at temperatures less than 1200°F, is unaffected[2] when the oxygen content of sodium is less than 50 ppm (0.005 wt %). In the SRE it has been demonstrated that cold traps can readily maintain an oxygen concentration of 10 ppm. Consequently, there is no reaction between the sodium coolant and the stainless steel components.

It has been mentioned that oxygen will precipitate in a cool stub off the main sodium piping. In a large system, branch lines containing stagnant sodium will act as diffusion cold traps, if the lines' minimum temperature is less than the saturation temperature of the sodium in the system. If sufficient oxide is collected, the branch line can become completely plugged. When oxygen concentration is held at 10 ppm, the oxide plugging of small branch piping has been non-existent.

Cold trap operating experience has been obtained in the 15,000-lb main secondary system as well as the 50,000 lb primary system. The boiling-coolant trap in the SRE main secondary (non-radioactive) system gave 18-months' satisfactory service. Two of the cold trap units with economizers, described in Section II-B, were located in the primary heat transfer system. A third boiling-coolant trap that did not have an economizer was installed in the primary service vault. The performance of these units in removing oxide from the 50,000-lb primary system is shown in Figure 9. Both the system and saturation temperatures have been plotted during the period of initial sodium purification.

For complete knowledge of the oxygen content of a sodium system, one must consider both saturation and system temperature, since the saturation temperature alone indicates only the amount of oxygen dissolved in the system. If the saturation temperature equals the system temperature, the sodium is saturated with oxygen, and there may be a second phase of solid oxide in the piping system. If the observed plugging temperature is within 50°F of the system temperature, the system is considered to be saturated for the purpose of planning cold trap operations.

In the SRE primary system, one of the cold traps with an economizer, was started on June 27, 1957, and the second on June 28. Their operation was intermittent, undoubtedly due to flow restrictions in the economizer. Subsequent operating experience with cold traps with an economizer, when the oxygen concentration was somewhat higher than it was during June 27-30, demonstrated that cold traps with this type of economizer are not suitable for use when the saturation temperature approaches the bulk sodium temperature (the condition that often exists during prepower cleanup). The difficulty of avoiding precipitation of oxide in the economizer tube with consequent loss of sodium flow makes them unsuitable. When the sodium entering the economizer tube is saturated, any decrease in temperature will cause supersaturation. Nucleation takes place, probably due to wall and weld roughness. Now the sodium in the cold trap must be cooled below the saturation temperature to remove oxide. The sodium leaving the cold trap is somewhat below saturation temperature; this cool sodium enters the economizer shell. Resultant heat transfer across the economizer tube wall cools the feed stream, and crystallization of sodium oxide starts. The crystal formation grows and blocks sodium flow. The two cold traps with economizers were later removed from the galleries because they were ineffectual in the large sodium system.

Operation of the trap without an economizer was started early July 2, and the saturation temperature decreased rapidly as shown in Figure 9. The data taken July 2 and 3 are also presented in the upper curve of Figure 10. When these data were obtained, the bulk temperature was at least 100°F above the plugging temperature; the plugging temperature did not significantly increase after the trap was taken out of service July 4. These facts mean that this curve represents the total amount of oxygen in the system, and that calculations based on this curve will give a true trapping rate. The chord of the upper curve on Figure 10 between 8 and 10 ppm has a slope which can be converted to a rate of 0.009 lb oxygen/hr (Appendix A).

Since the sodium-oxygen solubility temperature curve is exponential, rate calculations based on any given slope on a saturation temperature-time curve will be dependent on the saturation temperature (or oxide concentration) of the feed stream. Any one trap operating with a constant temperature gradient and sodium flow will have a higher trapping rate when the feed stream is rich in oxygen. It is for this reason that the concentration range must be specified for a trapping rate.

As a matter of general interest, the system temperature peak in Figure 9 shows the temperatures during the isothermal prepower sodium system circulation tests. This was immediately followed by the first generation of electrical energy from the nuclear reactor on July 12; the graph shows establishment of the reactor temperature gradient.

After initial power operations, a 40-in.-diameter plug was withdrawn from the reactor loading shield to permit removal of a damaged fuel cluster.[3] Although argon was used as a cover gas during this operation, an appreciable amount of oxygen entered the reactor. Shortly after this core element removal, sodium flow through the cold trap stopped, indicating that the trap had plugged. When the trap was removed from the system and disassembled, examination showed that most of the oxide had collected in the first 2 in. of the mesh. This demonstrated the general tendency of a boiling-coolant trap to precipitate oxide at the trap entrance due to the sharp temperature gradient existing at the inlet. Similar findings of the prototype testing program[4] were confirmed. Examination of mesh removed from the prototype trap, Figure 12, showed that practically all the oxide was collected in the lower 12-in. coil with the heavy precipitation occurring in the first 4 in. at trap inlet. This localized oxide deposition limits the effective trapping volume and trap capacity.

A new design was prepared to improve trap capacity and heat transfer capability. Overall trap size was fixed by existing space in the sodium service vault. The forced-convection-cooled trap described in Section II-B was developed using the method of Bruggeman.[5] In this trap, a temperature gradient is established along the 12-in. pipe wall which prevents localized precipitation of the oxide.

The lower curve of Figure 10 shows performance of the forced-circulation trap (on April 19, 1958) starting from a saturated condition at 350°F. At approximately 25 hr the trap was shut down; the saturation temperature then increased. The interpretation of these facts is that there was solid oxide in the system which was going into solution during the trapping operation. The rate calculated from the chord of this curve between 8 and 10 ppm is 0.02 lb/hr; the

Figure 12. Mesh From Prototype Cold Trap Annulus

actual rate is somewhat greater since oxygen was going into solution during the period of observation.

An expended insert from a forced-convection-cooled trap is shown in Figures 13 and 14. There was practically no oxide in the lower mesh shown at the right-hand side of Figure 13. The white material clinging to the coil was the small quantity of sodium that did not drain out of the trap. Oxide collection started at the grey area to the left of center of Figure 13. The top portion of the insert was filled with oxide (Figure 14).

Since most SRE trapping was done from saturated solutions, it was not possible to calculate the total oxide collected in these traps from the change in the amount of dissolved oxygen in the system sodium. It must be remembered that when the traps were operating, the reactor was being prepared for power generation runs, and it was not feasible to adjust sodium system temperatures to get all the desirable cold trap performance data. It was therefore necessary to calculate the amount of oxide collected using the method described in Section II-B and illustrated in Appendix B. The chief limitation of this method was the assumption of 2-in.-deep oxide deposition in the central tube mesh of the forced-convection-cooled trap. This assumption was made since the depth could not be measured (Appendix B). Also, visual estimation of effective trapping volume (as a volume of

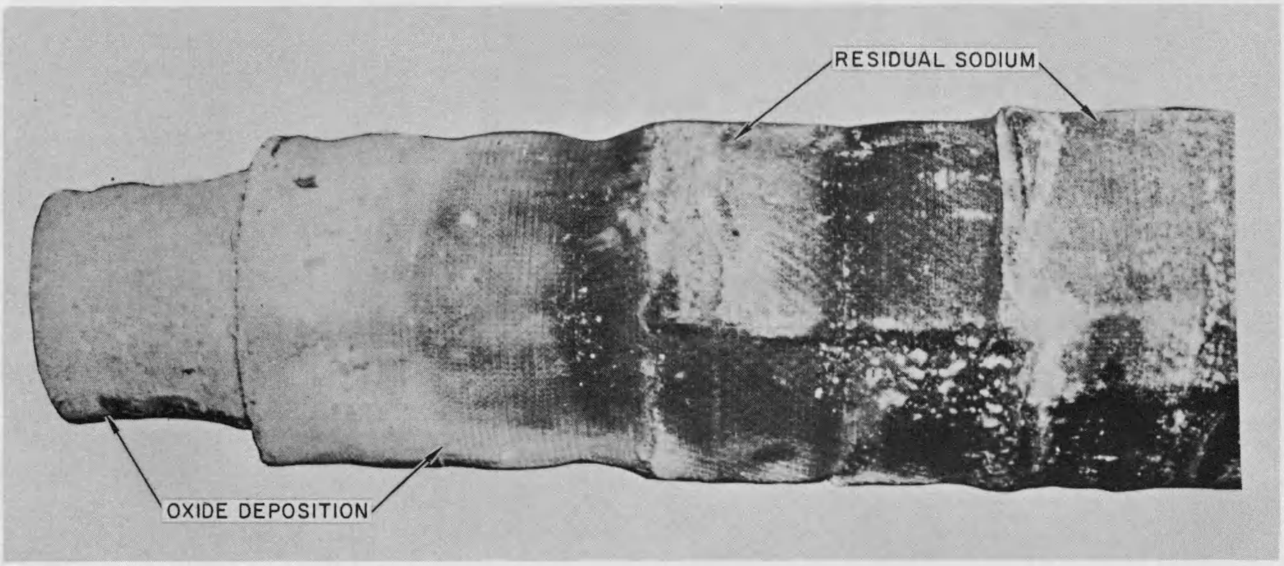


Figure 13. Side View of Expended Cold Trap Insert

Figure 14. End View of Expended Cold Trap Insert

mesh containing sodium oxide with a density of deposition equal to that observed on the mesh in the slurry filtering experiment) cannot be considered a quantitative determination. Hence, the calculated oxide collection values should be considered "best available estimates."

The following significant maintenance factor should be considered when comparing the two types of cold traps. In the boiling-coolant trap, at least one toluene valve must be located in the shielded vault and operated remotely. It is available for maintenance only after a reactor shutdown. With the forced-convection-cooled unit all service coolant valves are located outside the vaults in an accessible area.

E. CONCLUSIONS

The type of economizer described herein is not suitable for use with a cold trap in a reactor system, due to oxide plugging when the sodium is saturated. Reactor sodium is sometimes saturated, after maintenance or modification programs, when low system temperatures (300-400°F) are being maintained with electric heaters. It is at this time, prior to high temperature power operation, that the cold trap is needed to purify the sodium. If the reactor is operated with excessive oxygen concentration, oxide will precipitate in branch lines containing stagnant sodium. It is not economical design to provide the piping with enough heaters to keep their temperature above sodium saturation temperature under such abnormal conditions.

The advantage of the boiling-coolant cold trap is constant coolant temperature somewhat above the freezing point of sodium. As a result of this feature, minimum sodium temperature is held constant for normal variations in sodium flow rate. All other comparisons favor the forced-convection-cooled trap. Its trapping rate is at least twice that of the boiling-coolant trap and its capacity is four times that of the toluene trap tested at the SRE, under comparable conditions. Considering traps of the same size, the heat transfer rate of the forced-convection-cooled trap exceeds that of the boiling-coolant trap by a factor of three and the overall heat transfer coefficient by a factor of two and one-half. Finally, the service coolant valves of the forced-convection-cooled trap are located in a nonradioactive area, where they are always accessible for maintenance.

The significance of the 0.02-lb-oxygen/hr trapping rate, in terms of the time required to clean a 50,000-lb sodium system, is shown graphically in Figure 10 — the saturation temperature can be reduced from 350 to 250°F in less than one day.

III. HOT TRAP

A. DESCRIPTION OF HOT TRAP

The extraction operation using zirconium to getter oxygen from sodium is conducted in a hot trap. Figure 15 is a diagram of the SRE hot trap. The zirconium inserts are mounted in a removable cartridge. Sodium enters at 1165°F, having been preheated in an economizer, and then passes through the zirconium coils and out the discharge line. A discharge temperature of 1200°F is maintained by the 30 kw furnace. The sodium flow rate is 6 gpm. The cartridge is supported on a base ring which prevents sodium from bypassing the zirconium. A tetralin cooling jacket freezes the sodium in the annulus between the insulation plug and the 16-in. pipe wall. The top seal is a ring joint flange. The insert cartridge is linked to the blind flange insulation plug assembly to facilitate removal.

The zirconium for the trap was rolled to 0.004-in. thick, 6-in. wide strips. Half of the strip was corrugated to 0.19-in. pitch and 0.045-in. depth. Alternate

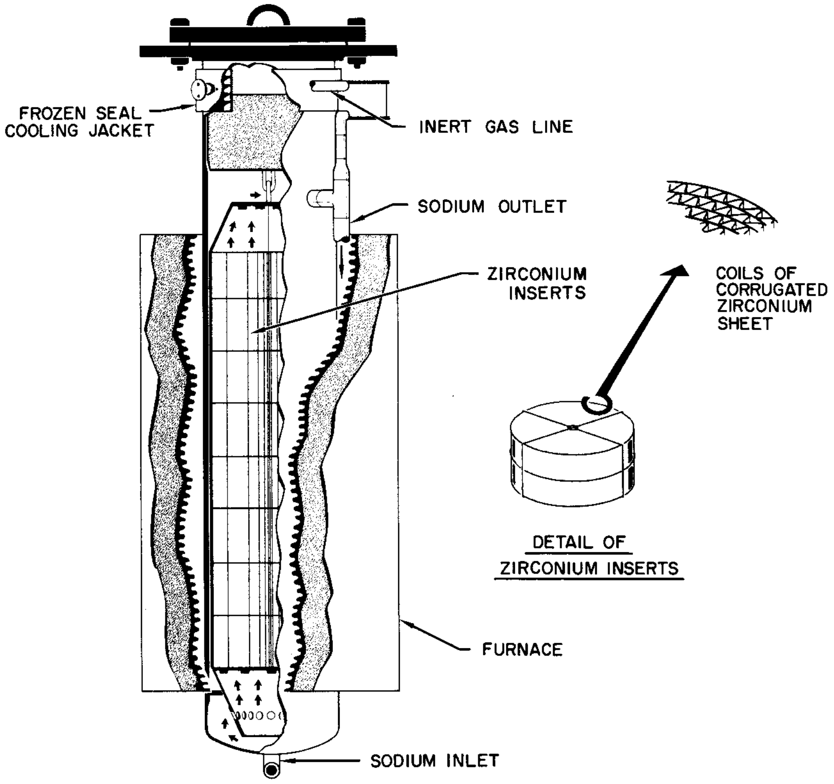


Figure 15. Hot Trap

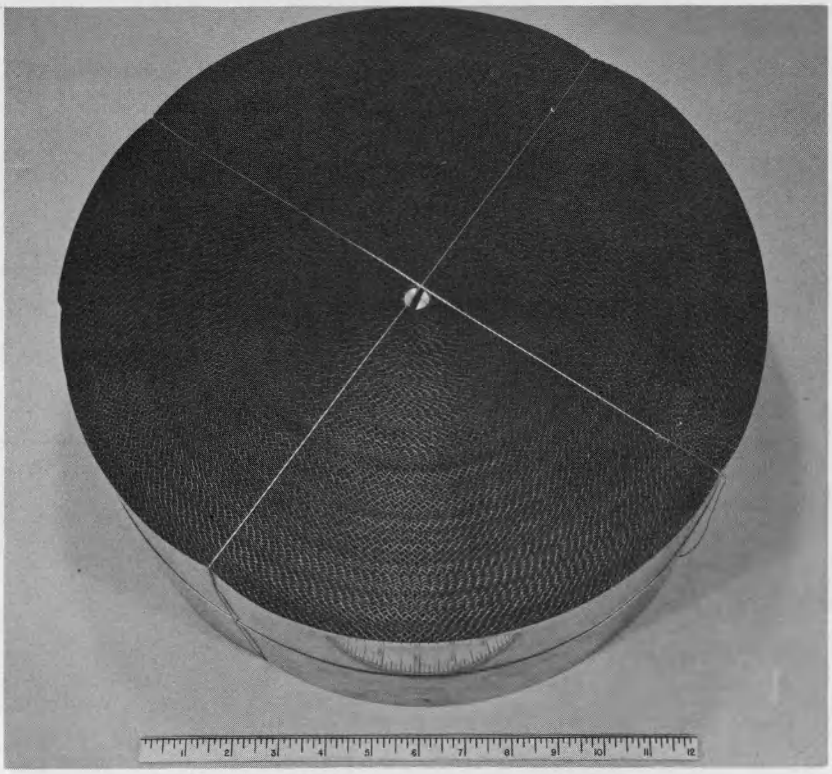


Figure 16. Zirconium Coil

corrugated and flat sheets were then rolled together to form 14-in. diameter coils, one of which is shown on Figure 16. There are eight of these coils in the trap; total area is 4300 ft^2.

B. PROCEDURE

The trapping rate was determined as described in Section II. The calculation of the ultimate capacity of the hot trap, based on the reaction equation, is shown in Appendix C. Extraction during the period of predictable rate has been calculated in Appendix D using the equation $w = kt^{1/2}$, relating oxidative weight gain to time, which is based on data obtained from sodium-zirconium laboratory test facilities.[2] The theoretical oxygen concentration in a hot trapped sodium system has been calculated in Appendix E using methods of chemical thermodynamics and has been based on published data for sodium, zirconium, and oxygen systems.

There is no direct method for determining oxygen concentration of sodium when the level is below the limit of a plugging meter. An indirect method has been used to evaluate the effectiveness of the hot trap in maintaining system oxygen levels at a very low concentration. The oxidation of zirconium specimens exposed in the materials evaluation facility in the primary sodium system of the reactor has been compared with samples exposed in both cold-trapped and hot-trapped experimental systems outside of the reactor.

C. RESULTS

Hot trap data are shown in Table II

TABLE II

HOT TRAP DATA

O_2 Trapping Rate (lb/hr)	0.009
O_2 Capacity, Ultimate (lb)	96.4
Operating Parameters	
Sodium flow rate (gpm)	6
Inlet temperature (°F)	1165
Outlet temperature (°F)	1200

The hot trap controls saturation temperature lower than the limit of detection of a plugging meter (225°F). The theoretical equilibrium concentration in a hot-trapped sodium system has been calculated to be less than 7×10^{-6} ppm.

Polished zirconium coupons have been exposed to SRE primary sodium in the materials evaluation facility. The weight gain of samples recently removed from the facility was less than one-half that estimated on the basis of their time at temperature history, assuming the sodium to be cold trapped to 10 ppm. Analysis of the data shows the oxidation to be consistent with exposure to sodium of lower oxygen concentration than is attainable by cold trapping. Visual examination of the coupons showed only a slight tarnish. These data indicate that the hot trap is effective in minimizing formation of zirconium oxide film on the moderator sheathing.[6]

D. DISCUSSION

While the reactor was being designed, the results of development programs indicated a need to prevent the growth of a fatigue-sensitive zirconium oxide film on the moderator cans. Studies of the effect of sodium on the mechanical properties of zirconium[7] showed that the fatigue life of zirconium exposed in sodium of very low oxygen concentrations was twice that of samples exposed to sodium containing 10 ppm oxygen, when the specimens were cycled through the yield point. Analog computer studies of post-scram core temperature transients and prototype moderator can tests[8] indicated that the moderator cans will undergo some plastic yielding after emergency reactor shutdowns if convective flow is not controlled. A concurrent program had demonstrated the effectiveness of a zirconium gettering device for scavenging oxygen from sodium to such low concentrations[9] that oxide film would not form on the moderator sheathing even at 1000°F. Since it was established that the maintenance of very low oxygen concentrations by use of the gettering device would result in a doubling of the fatigue life of sodium-exposed zirconium stressed beyond the yield point, the hot traps were included in the reactor design.

It has been reported that initial reactor transient tests showed that there was an adequate factor of safety in the moderator can design.[3] The installation of post scram convective flow control equipment has reduced the magnitude of temperature cycles, and hence the stresses that are imposed on the moderator cans. Since actual reactor operating conditions differ from the analog predictions, it is possible that the requirement for a hot trap gettering device may not be valid. The effect of oxide film formation on the fatigue life of zirconium with stress below the yield point is currently under investigation. This work will indicate the degree of improvement that can be expected in zirconium performance due to very low oxygen concentrations under existing operating conditions in the system. Hot traps are being operated pending the outcome of this investigation.

The oxidative weight gain of zirconium exposed in sodium can be described by the equation $w = kt^{1/2}$, where w is the weight gain per unit surface area in time t, and k is a constant dependent on temperature. From the values of this constant, 0.025 $mg/cm^2\text{-}hr^{1/2}$ at 1000°F and 0.078 at 1200°F (based on 10 ppm oxygen in sodium), it is apparent that this chemical oxidation reaction is strongly temperature dependent.[2] The values of k given above are for vapor-blasted zirconium, which has a relatively rough surface. These values are 170% of the k determined for chemically polished strip, the value used in Appendix D. The difference is attributed to the greater actual surface area of the vapor-blasted material. The apparent surface area based on length, width, and thickness measurements was used in the experimental determinations of the rate coefficient, k.

Hot traps were sized so that oxygen would be absorbed preferentially on the hot trap zirconium rather than on the moderator cans in the ratio of ten to one.[10] The zirconium oxide formed is very stable; the equilibrium partial pressure of oxygen over zirconium oxide at 1200°F has been estimated to be 10^{-52} atmospheres, compared to a pressure of 10^{-33} atmospheres over sodium oxide (Appendix E).

Figure 17 shows the effect of initial hot trap operation on sodium saturation temperature. Prior to time zero, the cold trap was valved out of the system after the plugging temperature had been reduced below 250°F. Then the hot trap was started, and at the same time system sodium temperatures were increased as a result of reactor startup. This caused an increase in saturation temperature as residual oxide was dissolved out of diffusion cold traps in the piping system. At 141 hr, oxide solution was essentially complete, and the saturation temperature decreased as shown. The chord of this curve between 8 and 10 ppm has a slope which corresponds to an oxygen removal rate 0.009 lb/hr (Appendix A). After such a startup period, the hot trap maintains saturation temperature below the limit of detection.

During the operation of an SRE plugging meter, 225°F is the lowest practical temperature before freezing of sodium in the piping becomes imminent, and hence is the lower limit of detection. If there has been no change in the flow rate of the sodium stream when a temperature of 225°F is reached, the test is terminated.

The temperature-oxygen solubility curve[1] has been extrapolated to 275°F at 8 ppm oxygen, to permit the calculation of trapping rates. Extrapolation below this point has not been made for any of the calculations in this paper. However, Cashman and Salmon[11] have extrapolated the curve to the freezing point. This extrapolation should be valid, since a continuous straight line with negative slope is expected on a plot of log solubility against the reciprocal of absolute temperature from thermodynamic considerations.

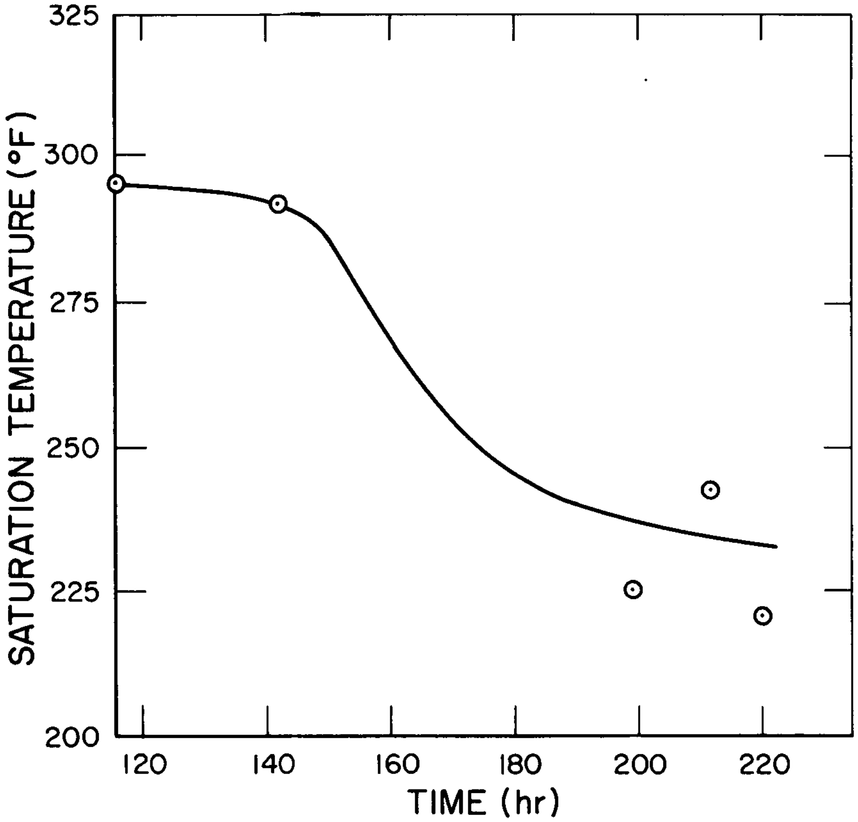


Figure 17. Hot Trap Performance

It should be noted that reference has been made to the solubility curve only for the purpose of calculating trapping rates. At Atomics International during four years of sample exposures in dynamic sodium test facilities, the behavior of materials in sodium at various temperatures up to 1200°F has been correlated directly with saturation temperature.

The capacity reported for the hot trap, 96.5-lb oxygen, is the ultimate capacity based on the assumption of complete conversion of zirconium to its oxide. The rate equation $w = kt^{1/2}$ was experimentally determined for relatively short exposures, compared to the exposure necessary to react all the zirconium foil in the trap. The validity of this equation has been demonstrated for exposures to 4,000 hr for zirconium based alloys. The equation should be valid as long as the oxide film remains intact, since oxygen diffusion through this film controls the rate of reaction which is described by $w = kt^{1/2}$. There has been no indication of cracking or spalling of this film on any of the exposed samples examined. It has been calculated that the zirconium in the hot trap will react with 25-lb oxygen in 4,000 hr (Appendix D); this is only 26% of the ultimate capacity. Therefore, in the absence of long term rate data, accurate predictions of the time to reach even 30% of the theoretical capacity cannot be made.

While the extraction of oxygen during the first 4,000 hr of trap operation has been calculated to be 25 lb (Appendix D), the rate constant used in this calculation was determined when an oxygen concentration of 10 ppm was maintained in the sodium. In a reactor application such as the SRE, oxygen content will be but a fraction of 10 ppm during most of the hot trap operation, so the applicable rate constant will be less than 0.0454. Thus, the capacity of the trap for the period of predictable rate is really somewhat less than the 25 lb calculated.

The trapping rate in an SRE hot trap has been calculated on the basis of experimentally determined behavior of the gettering material in Appendix D. The derivative of the equation, $w = kt^{1/2}$, evaluated at 150 hr, is 0.016 lb oxygen/hr. This predicted rate is about twice the rate determined experimentally at the SRE after the first 150 hr of operation, 0.009 lb oxygen/hr. The following factors make the actual rate one-half the rate predicted on the basis of material studies:

1) The original experimental work was done on chemically polished zirconium. The strip used in the SRE trap had a thin oxide film resulting from the manufacturing process. Due to this initial oxide film, the condition of the gettering strip was represented by a point somewhat out on the parabolic curve, rather than at the origin as the calculation in Appendix D assumes. Therefore, all the actual trapping rates would be less than those calculated.

2) After 150 hr of operation, the oxygen content of the sodium flowing through the trap was being depleted. The inlet concentration was 9.3 ppm (from Figure 17 and Reference 1), but the outlet concentration was only 5.4 ppm (Appendix F). Therefore, the actual rate constant, k, was less than 0.0454 mg/cm^2-hr$^{1/2}$, which had been determined in sodium containing 10 ppm oxygen. The rate constant, and hence the trapping rate, were decreasing throughout the length of the vessel.

E. CONCLUSIONS

The hot trap performance graph, Figure 17, shows that the hot trap decreased the saturation temperature of the 50,000-lb sodium system from 290 to 225°F, the lower limit of detection for a plugging meter, in 75 hr. The hot trap maintains the sodium saturation temperature below the limit of detection. Although the oxygen concentration is too low to measure, the calculation showing that the equilibrium concentration in a hot trapped system is less than 7×10^{-6} ppm demonstrates as quantitatively as possible the exceptional performance of a zirconium gettering device.

Evidence from the materials evaluation facility, although indirect, indicates that only a slight amount of oxidation is occurring on the moderator cans.

The actual oxygen extraction rate was found to be approximately one-half the rate predicted from studies of chemically polished specimens exposed in sodium containing 0.001 wt % oxygen. These rates will decline with time since the rate function is parabolic.

APPENDIX A
TRAPPING RATE CALCULATION

The sample calculation is for the boiling-coolant cold trap.

The concentration range 8 to 10.5 ppm has been selected as the basis for calculation. From the upper curve of Figure 10:

Point	1	2
Saturation temperature (°F)	295	275
Concentration (ppm)	10.5	8
Time (hr)	24	38

The system contains 50,000 lb of sodium.

$$\text{Trapping Rate} = \frac{\Delta w_{O_2}}{\Delta \theta} = \frac{\left[(10.5 - 8)\ \frac{\text{lb } O_2}{10^6 \text{ lb Na}}\right]\left[5 \times 10^4 \text{ lb Na}\right]}{(24 - 38)\text{ hr}}$$

$$= -\,0.0089 \frac{\text{lb } O_2}{\text{hr}}$$

Data are given in Table III.

TABLE III

TRAPPING RATE DATA

	Boiling-Coolant Cold Trap	Forced-Convection-Cooled Cold Trap	Hot Trap
Reference Curve	Figure 10, upper	Figure 10, lower	Figure 17
Point 1			
Saturation temperature (°F)	295	295	293
Concentration (ppm)	10.5	10.5	10.3
Time (hr)	24	8	143
Point 2			
Saturation temperature (°F)	275	275	275
Concentration (ppm)	8	8	8
Time (hr)	38	14	156
Rate (lb oxygen/hr)	0.009	0.02	0.009

APPENDIX B
COLD TRAP CAPACITY CALCULATION

1. Apparent Density of Sodium Oxide in Filter Mesh

Cylinder of mesh containing sodium and sodium oxide was cored. Analysis of core material using the butyl bromide method:[12]

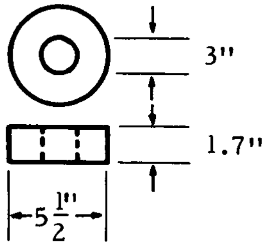
Sodium metal (wt %)	22
Sodium oxide (wt %)	78

The remaining torus was weighed before and after removal of sodium and oxide from the steel mesh. Weight of sodium and sodium oxide = 343 gm (by difference)

$$\text{Torus volume} = h\,\pi\,(r_o^2 - r_i^2)$$

$$= 1.7\,\pi\left[\left(\frac{5.5}{2}\right)^2 - \left(\frac{3}{2}\right)^2\right]$$

$$= 28.3\ \text{in.}^3$$



$$\text{Apparent density} = \frac{\left[78\ \frac{\text{lb oxide}}{100\ \text{lb (Na + oxide)}}\right]\left[\frac{343\ \text{gm (Na + oxide)}}{28.3\ \text{in}}\right]}{453.6\ \frac{\text{gm}}{\text{lb}}}$$

$$= 0.0208\ \frac{\text{lb Na}_2\text{O}}{\text{in.}^3\ \text{mesh}}$$

$$= \frac{0.0208\left(\frac{\text{lb Na}_2\text{O}}{\text{in.}^3\ \text{mesh}}\right)\left(32\ \frac{\text{lb O}_2}{\cancel{\text{lb mole}}}\right)}{\frac{124\ \text{lb Na}_2\text{O}}{2\ \cancel{\text{lb mole}}}}$$

$$= 0.00536\ \frac{\text{lb O}_2}{\text{in.}^3\ \text{mesh}}$$

since $4\,\text{Na} + \text{O}_2 \longrightarrow 2\,\text{Na}_2\text{O}$.

2. Effective Trapping Volume

In the boiling-coolant trap, all oxide was collected in the sodium annulus.

$$\text{Annular area} = \pi\left(r_o^2 - r_i^2\right) = \pi\left[\left(\frac{12}{2}\right)^2 - \left(\frac{8}{2}\right)^2\right] = 63\ \text{in.}^3$$

$$\text{Volume} = hA$$

	Height of Oxide (in.)	Volume (in.^{3})
SRE trap	2	126
Prototype trap	4	252

In the forced-convection-cooled trap, the upper 3 in. of the sodium annulus was observed to contain oxide.

$$V\ \text{annulus} = 3\ \pi\left[\left(\frac{12}{2}\right)^2 - \left(\frac{6}{2}\right)^2\right] = 254.5\ \text{in.}^3$$

The crown also contained oxide, but the depth of deposition could not be determined because the sodium in the crown and central tube burned during disassembly. Deposition 2-in. deep was assumed, based on the slurry filtering experiment.

$$V\ \text{crown} = 2\ \pi\ 3^2 + 6\ \pi\left[\left(\frac{6}{2}\right)^2 - \left(\frac{2}{2}\right)^2\right] = 207.6\ \text{in.}^3$$

The upper 2 in. of mesh in the middle section of the central tube was assumed to contain oxide, the lower section of mesh was assumed to be clean.

$$V\ \text{middle section} = 2\ \pi\ 3^2 = 56.6\ \text{in.}^3$$

For the forced-convection-cooled trap

$$\sum V = 518.7 \text{ in.}^3$$

3. Cold Trap Capacity

Trap capacity = (apparent density) (effective volume)

$$= 0.0208\left(\frac{\text{lb } Na_2O}{\text{in.}^3 \text{ mesh}}\right)(518.7 \text{ in.}^3 \text{ mesh})$$

$$= 10.8 \text{ lb sodium oxide}$$

for the forced-convection-cooled trap.

APPENDIX C
ULTIMATE HOT TRAP CAPACITY

All of the 275 lb of Zr in a hot trap theoretically is available for gettering oxygen in accordance with the equation

$$Zr + O_2 \longrightarrow Zr\ O_2.$$

Hence, the ultimate capacity of the trap is

$$\frac{275 \text{ lb Zr}}{91.22 \, \frac{\text{lb Zr}}{\text{lb mole}}} \qquad \frac{32 \text{ lb } O_2}{\text{lb mole}} = 96.5 \text{ lb oxygen}$$

APPENDIX D

GETTERING MATERIAL BEHAVIOR

For a given temperature it has been determined (Reference 2) that

$$w = kt^{1/2}$$

where

$$w = \frac{\text{oxidative weight gain}}{\text{unit area}}$$

and

$$t = \text{time.}$$

Hot trap design was based on the behavior of smooth, chemically polished Zr. For exposures in Na containing 10 ppm O_2 at 1200°F, it has been determined that

$$k = 0.0454 \frac{\text{mg}}{\text{cm}^2 \ \text{hr}^{1/2}}.$$

Prediction of oxygen extracted in 4000 hr:

$$W = wA = kt^{1/2} A$$

$$= \frac{\left(0.0454 \dfrac{\text{mg}}{\text{cm}^2 \ \text{hr}^{1/2}}\right) (4000 \ \text{hr})^{1/2} \ (4300 \ \text{ft}^2) \left(929 \dfrac{\text{cm}^2}{\text{ft}^2}\right)}{4.536 \times 10^5 \ \dfrac{\text{mg}}{\text{lb}}}$$

$$= 25.2 \text{ lbs.}$$

Trapping rate prediction:

$$w = kt^{1/2}$$

$$\frac{dw}{dt} = \frac{k}{2t^{1/2}}$$

$$\left(\frac{dw}{dt}\right)_{t=150} = \frac{\left(0.0454 \frac{mg}{cm^2\ hr^{1/2}}\right)\left(4300\ ft^2\right)\left(929\ \frac{cm^2}{ft^2}\right)}{(2)\ (150\ hr)^{1/2}\left(4.536 \times 10^5\ \frac{mg}{lb}\right)}$$

$$= 0.0163\ \frac{lb}{hr}$$

t (hr)	$t^{1/2}$ (hr)	$\frac{dw}{dt}$ (lb/hr)
1	1	0.2
150	12.25	0.016
4000	63.25	0.0032

APPENDIX E

EQUILIBRIUM OXYGEN CONCENTRATION IN A HOT TRAPPED SYSTEM

Assumptions: No oxygen leakage into sodium system. System temperature is 1200°F.

Ref (13) $$\tfrac{1}{2}\mathrm{Zr(s)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightleftharpoons \tfrac{1}{2}\mathrm{ZrO_2(s)} \qquad \Delta F^{o} = -\ 110\ \mathrm{kcal} \qquad \ldots(1)$$

Ref (14) $$K_{eq} = \frac{(a_{ZrO_2})^{1/2}}{(a_{Zr})^{1/2}\,(a_{O_2})^{1/2}}$$

Standard state for oxygen is taken as ideal gas at 1 atmos.

$$a = \frac{p}{p^{o}}$$

$$K_{eq} = \frac{(1)^{1/2}}{(1)^{1/2}\,(p_{O_2}/1)^{1/2}} = \frac{1}{(p_{O_2})^{1/2}}$$

$$\Delta F^{o} = -\ RT\ \ln K$$

$$R = 1.987\ \frac{\mathrm{cal}}{^{\circ}\mathrm{K}}, \qquad 2.3\ R = 4.57\ \frac{\mathrm{cal}}{^{\circ}\mathrm{K}}$$

$$-100{,}000\ \frac{\mathrm{cal}}{^{\circ}\mathrm{C}} = -\left[4.57\ \frac{\mathrm{cal}}{^{\circ}\mathrm{K}}\right]\left[925\,^{\circ}\mathrm{K}\right]\left[\log\frac{1}{(p_{O_2})^{1/2}}\right]$$

$$(p_{O_2})^{1/2} = 10^{-26} \qquad\qquad p_{O_2} = 10^{-52}\ \mathrm{atmos.}$$

This is the partial pressure of oxygen over ZrO_2 at 1200°F.

Ref (13) $2Na(\ell) + \frac{1}{2}O_2(g) \rightleftharpoons Na_2O(s) \quad \Delta F^o = -69 \text{ kcal}$ ...(2)

$$K = \frac{a_{Na_2O}}{(a_{Na})^2\ (a_{O_2})^{1/2}} = \frac{(1)}{(1)^2\ (p_{O_2}/1)^{1/2}} = \frac{1}{(p_{O_2})^{1/2}}$$

$$\Delta F^o = -RT\,\ell n\ K$$

$$-69{,}000 \text{ cal} = -\left[4.57\ \frac{\text{cal}}{°K}\right]\left[925\,°K\right]\left[\log \frac{1}{(p_{O_2})^{1/2}}\right]$$

$$(p_{O_2})^{1/2} = 10^{-16.3}$$

$$p_{O_2} = 10^{-32.6} \cong 10^{-33} \text{ atmos.}$$

This pressure is designated p^*.

$$Na_2O(s) \rightleftharpoons 2Na(\ell) + \frac{1}{2}O_2(g) \qquad \Delta F_3^o = -RT\,\ell n\, \frac{(1)\ (p_{O_2})^{1/2}}{1} \qquad \text{...(3)}$$

Now this

$$p_{O_2} = p^* \text{ from Equation (2).}$$

Considering liquid Na_2O dissolved in Na (note: Na_2O is a solid at the hot trap operating temperature)

$$Na_2O(\ell) \rightleftharpoons 2Na(\ell) + \frac{1}{2}O_2(g) \qquad \Delta F_4^o = -RT\,\ell n\, \frac{(1)\ (p_{O_2})^{1/2}}{a_{Na_2O}} \qquad \text{...(4)}$$

Equation (3) - (4) = (5)

$$Na_2O(s) \rightleftharpoons Na_2O(\ell) \qquad \Delta F_3^o - \Delta F_4^o = - RT \ln \left[\left(\frac{p^*}{p_{O_2}} \right)^{1/2} a_{Na_2O} \right] \quad \ldots (5)$$

However

$$\Delta F_3^o - \Delta F_4^o = \Delta F^o \text{ for fusion}$$

$$\Delta F_{fusion} = \Delta H_{fusion} - T \Delta S_{fusion}. \quad \ldots (6)$$

Assume that ΔH, and ΔS are independent of temperature.

Ref (15) $\Delta H_{fusion} = 10 \frac{kcal}{mole}$,

Ref (15) $\Delta S_{fusion} = 8.4 \frac{cal}{mole\ °K}$,

and $\Delta F_{fusion} = 10 - \left(925°K\right) \left(8.4 \frac{cal}{mole\ °K}\right) \left(\frac{kcal}{1000\ cal}\right)$

$$= 10 - 7.76 = 2.24 \text{ kcal}.$$

Substituting in Equation (5)

$$2.24 = - \left[4.57 \right] \left[925 \right] \left[\log \left(\frac{p^*}{p_{O_2}} \right)^{1/2} a_{Na_2O} \right]$$

$$\log \left[\left(\frac{p^*}{p_{O_2}} \right)^{1/2} a_{Na_2O} \right] = - 0.53$$

$$\left(\frac{p^*}{p_{O_2}} \right)^{1/2} a_{Na_2O} = 10^{-0.53} = \frac{1}{10^{0.53}} = \frac{1}{3.38} = 0.296 \cong 0.3$$

p^* over solid Na_2O has been determined. p_{O_2} over Na_2O in solution is fixed by p_{O_2} in the hot trap.

$$a_{Na_2O} = 0.3\left(\frac{p_{O_2}}{p^*_{O_2}}\right)^{1/2} = 0.3\left(\frac{10^{-52}}{10^{-33}}\right)^{1/2} = \frac{0.3}{3.16}\,10^{-10}$$

$$= 0.095 \times 10^{-10} \cong 10^{-11}$$

The activity coefficient, γ, is the activity divided by mole fraction

$$\gamma = \frac{a}{N}$$

In general,[16] the deviation from ideality of molten metal — salt solutions is such that $\gamma > 1$,

then

$$\frac{a}{N} > 1,\ N < a,\ \text{and}\ N < 10^{-11}$$

$$\text{Concentration} < \frac{\left(10^{-11}\,\frac{\text{moles } Na_2O}{\text{moles Na}}\right)\left(16\,\frac{\text{g } O_2}{\text{mole } Na_2O}\right)\left(10^{6}\right)}{23\left(\frac{\text{g Na}}{\text{mole Na}}\right)\qquad\left(10^{6}\right)}$$

$$< 7 \times 10^{-6}\ \text{ppm.}$$

APPENDIX F

HOT TRAP OXYGEN CONCENTRATION

The oxygen concentration of the hot trap outlet stream at 150 hrs is:

$$\text{Na feed} = \left(6\ \frac{\text{gal}}{\text{min}}\right)\left(60\ \frac{\text{min}}{\text{hr}}\right)\left(6.7\ \frac{\text{lb Na}}{\text{gal}}\right) = 2410\ \frac{\text{lb Na}}{\text{hr}}$$

$$O_2\ \text{feed} = \left(2410\ \frac{\text{lb Na}}{\text{hr}}\right)\left(9.3\ \frac{\text{lb } O_2}{10^6\ \text{lb Na}}\right) = 0.022\frac{\text{lb } O_2}{\text{hr}}$$

Material balance for O_2 (basis is 1 hr operation):

Feed	0.022 lb
Extracted	0.009
Outlet	0.013

Hence concentration of outlet stream will be

$$\frac{\left(0.013\ \text{lb } O_2\right)\left(10^3\right)}{\left(2410\ \text{lb Na}\right)\left(10^3\right)} = 5.4\ \text{ppm.}$$

REFERENCES

1. I.L. Gray, R.L. Neal, and G.B. Voorhees, "Control of Oxygen in Sodium Heat Transfer Systems," Chem. Eng. Prog. Symposium Series 53, 20, 1957

2. R.L. Carter, R.L. Eichelberger, and S. Siegel, "Recent Developments in the Technology of Sodium Graphite Reactor Materials," Proceedings of the International Conference on the Peaceful Uses of Atomic Energy (Geneva, 1958) A/Conf 15/P/705

3. F.E. Faris, L.E. Glasgow, et al., "Operating Experience With the Sodium Reactor Experiment," Proceedings of the International Conference on the Peaceful Uses of Atomic Energy (Geneva, 1958) A/Conf 15/P/452

4. M. Nathan, "Performance of the SRE Prototype Cold Trap Assembly," (unpublished memorandum, Atomics International, Canoga Park, California, 1956)

5. W.H. Bruggeman, "Purity Control in Sodium-Cooled Reactor Systems," AIChE Journal 2 (1956), p 153

6. Atomics International Staff, "Unclassified Technical Progress Report, January-February, 1959," NAA-SR-3579, p I-B-9

7. J.C. Bokros, "Effect of Sodium on the Mechanical Properties of Zirconium," NAA-SR-1867 (1957)

8. J.A. Leppard, "Zirconium Moderator Reflector Can Development for the SRE," NAA-SR-2006 (1957)

9. L.E. Glasgow and V.R. DeMaria, "Sodium Graphite Quarterly Progress Report," April-June, 1956, NAA-SR-1690 (September 15, 1956)

10. R.L. McKisson, and R.L. Eichelberger, "Evaluation of Predicted SRE Hot Trap Performance," (unpublished memorandum, Atomics International, Canoga Park, California, 1956)

11. T.J. Cashman, and O.N. Salmon, "Solubility of Sodium Monoxide in Liquid Sodium," KAPL 1653 (1956)

12. L. Silverman, and M. Shideler, "Determination of Oxygen in Sodium and in Sodium-Potassium Alloy by the Butyl Bromide Method," Anal. Chem. 27, (1955), p 1660

13. A. Glassner, "The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500° K," ANL 5750

REFERENCES

14. F. H. Getman and F. Daniels, Outlines of Theoretical Chemistry, 6th Ed. Chapter XIX

15. L. Brewer, and J. Margrove, "Vaporization of Alkali Metal Oxides," UCRL 1864

16. Supplied by S. Yosim, Atomics International, in a conversation with R. B. Hinze, Atomics International