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Mass Transfer of Oxygen
in Sodium Cold Traps

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Mass Transfer of Oxygen
in Sodium Cold Traps*

by

Charles C. McPheeters

*This report is derived from a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Engineering Science of Materials from the Graduate School of the University of New Mexico.

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ABSTRACT

Low temperature precipitation of sodium monoxide is a method of removing oxygen from solution in liquid sodium commonly called cold trapping. Sodium monoxide precipitation is assumed to be a heterogeneous process because of the strong effect of surface area on the rate of precipitation. Growth of crystals from a super-saturated solution is said to proceed according to the equation

$$\frac{dm}{dt} = kA(C - C_e) \quad (1)$$

where dm/dt is the rate of oxygen accumulation on the crystal, k is an over-all mass transfer coefficient including a diffusion step and a surface deposition step, A is the crystal surface area, C is the oxygen concentration in the bulk stream, and C_e is the equilibrium oxygen concentration at the temperature of the crystal.

Mass transfer coefficients were calculated by measuring the rates of oxygen concentration changes during cold trapping runs and by correlating these rates with the surface area available for precipitation. The mass transfer coefficient was found to be a function of both Reynolds number and temperature. The effect of Reynolds number on the coefficient indicated that the process was diffusion controlled. Arrhenius plots of the coefficients indicated that the activation energy for precipitation

was approximately 3 kcal/mole. This activation energy is in fair agreement with that for diffusion of oxygen in sodium which is approximately 2.4 kcal/mole. The mass transfer coefficients calculated were of the order of 10^{-5} g O/cm²-h-ppm.

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ABBREVIATIONS AND SYMBOLS

A	Effective surface area for precipitation or dissolution, cm^2 .
a	Dimensionless exponential constant.
A_b	Pre-exponential factor for backward reaction.
A_f	Pre-exponential factor for forward reaction.
A_o	Area constant which is a function of the cold trap temperature gradient, cm^2 .
A_r	Pre-exponential factor in the Arrhenius equation.
b	Dimensionless exponential constant.
C	Solute concentration in the bulk solution adjacent to the area of precipitation or dissolution, ppm.
(c)	Indicates the crystalline form of a compound.
C_e	Equilibrium solute concentration at the temperature of the solution, ppm.
C_i	Solute concentration at the crystal-liquid interface, ppm.
C_m	The effective mean oxygen concentration in the sodium in the cold trap, ppm.
C_{mx}	The effective mean saturation oxygen concentration in the cold trap, ppm.
C_o	The initial oxygen concentration in the sodium system, ppm.
C_{out}	The oxygen concentration in the sodium at the cold trap exit, ppm.
C_s	The oxygen concentration in the system at any time, ppm.
C_x	The equilibrium oxygen concentration as a function of distance along the cold trap based on the temperature distribution, ppm.

ABBREVIATIONS AND SYMBOLS (Continued)

D	Diffusivity of oxygen in sodium, g-mole/cm-sec.
d	Hydraulic diameter of the flow passage, cm.
E	Activation energy, cal/mole.
E_b	Activation energy for the backward reaction, cal/mole.
E_f	Activation energy for the forward reaction, cal/mole.
gpm	Gallons per minute.
K	Equilibrium constant for a reversible reaction.
k	Overall mass transfer coefficient, g/cm ² -h-ppm.
k'	Reaction rate constant, g/cm ² -h-ppm.
k'_b	Reaction rate constant for the backward reaction, g/cm ² -h-ppm.
k'_d	Diffusion limited mass transfer coefficient, g/cm ² -h-ppm.
k'_f	Reaction rate constant for the forward reaction, g/cm ² -h-ppm.
k_r	Reaction rate limited mass transfer coefficient, g/cm ² -h-ppm.
M	Total sodium mass in the system, g.
m	Mass deposited on a crystal growing from solution, g.
(Na)	Indicates a compound in solution in sodium.
ppm	Parts per million by weight.
R	Gas constant, cal/mole-°K.
Re	Reynolds number.
Sc	Schmidt number.

ABBREVIATIONS AND SYMBOLS (Continued)

Sh	Sherwood number.
T	Absolute temperature, °K.
t	Elapsed time, h.
v	Sodium velocity, cm/sec.
W	Mass flow rate of sodium, g/h
x	Distance from the sodium entrance along the flow path in the cold trap, cm.
α	Coefficient indicating the fraction of the oxygen removed in a single pass through the cold trap.
β	Dimensionless constant.
γ	Emperical constant relating the difference between the actual concentration and the equilibrium concentration at the cold trap exit to the effective mean difference inside the cold trap.
δ	Emperical constant relating system oxygen concentration to the effective surface area in the cold trap, cm ² .
ΔC_p	The difference between the heat capacities at constant pressure of the reactants and the products of a chemical reaction, cal/mole-°C.
ΔH	The enthalpy of reaction, cal/mole.
ΔS	The entropy of reaction, cal/mole-°K.
η	The viscosity of liquid sodium, poise.
ρ	The density of liquid sodium, g/cm ³ .

I. INTRODUCTION

Systems which require efficient transfer of heat or transfer of large quantities of heat through small surface areas require a heat transfer fluid of high thermal conductivity, high heat transfer coefficient, and low viscosity. Such fluids as gases, water, and some organic fluids have the advantage of low viscosity; however, their thermal conductivity is low, and with the exception of the gases, their high temperature performance is poor.

Due to the limitations of the above fluids, attention was focused on liquid metals as heat transfer fluids. Of the liquid metals available, sodium has the most desirable combination of properties such as high thermal conductivity, low viscosity, good surface wetting characteristics, and a large temperature range between its melting point (97.8°C) and its boiling point (877.5°C).³¹

Sodium has been used extensively as a heat transfer fluid in nuclear reactors, experiments requiring high heat fluxes, and other miscellaneous applications.³¹ Certain metals are subject to corrosion by sodium, and the rate of corrosion is a strong function of the impurity concentration in the sodium. An impurity which has a great effect on the corrosion rate is oxygen. Experimental results in the United Kingdom,²³ and in the United States at General Electric Company,²⁶ have shown that as the oxygen concentration in sodium is increased the corrosion rate of stainless and ferritic steels increases approximately linearly. Refractory metals exposed to sodium containing 10 ppm or more of oxygen react with

the sodium oxide to form surface films of the refractory metal oxide.⁹ Oxygen is also taken into the refractory metal lattice.

High sodium purity, then, is required for successful operation of sodium systems. Many methods of purification have been developed including filtration, hot trapping with refractory metals, reaction and precipitation of impurities with reactive liquid metals, and low-temperature precipitation of impurities having a positive temperature dependence of solubility.¹⁶ These methods are sometimes used in combination and they can be used to purify the sodium before loading into the system; however, it is of great importance to purify the sodium continuously to remove impurities introduced during system operations. Only the low-temperature precipitation method of purification will be considered in this study.

The method of low temperature precipitation of impurities is commonly called cold trapping. A cold trap is a section of a sodium system which receives either part or all of the system flow and in which the sodium is cooled, precipitation of impurities (including oxides) occurs, and the purified sodium is reheated and returned to the main part of the system.

It is the purpose of this research to determine the mechanisms involved in cold trap performance, and the mass transfer coefficients for collection of oxygen. From these data and a suitable mathematical model, the rate of cleanup of sodium systems and the resulting distribution of solid sodium oxide in the cold trap can be predicted.

II. LITERATURE SURVEY

Early investigations³⁸ concerned with the use of sodium as a heat transfer medium indicated two major problems arising from the presence of oxygen as an impurity dissolved in the sodium. These problems included increased corrosion of structural material with increased oxygen content and plugging of cold pipe sections as a result of Na_2O precipitation. The cold trap is a simple, economical method of controlling oxygen concentration in sodium systems, and it removes oxygen by utilizing the temperature dependence of the solubility of sodium monoxide in sodium. At low temperatures, the sodium monoxide solubility is low, and excess sodium monoxide will precipitate if the sodium temperature is lower than the saturation temperature.

The solubility of sodium monoxide in sodium has been determined several times.^{6,24,29} The most recent solubility relationship (Fig. 1) was determined by Rutkauskas²⁸ using a vacuum distillation technique.¹⁵ This recent work was probably more accurate than the previous studies because the detection limit for oxygen in sodium was of the order of 1 part per million by weight (ppm) as opposed to 10 to 20 ppm in some of the earlier work.

Oxide removal from a sodium system is accomplished by cooling a bypass stream of sodium, promoting precipitation of the sodium monoxide and separation of the oxide from the liquid metal. Two possible mechanisms for this process were proposed by Voorhees³⁸: (1) liquid phase precipitation resulting in discrete particles suspended in the

Fig. 1. Oxygen solubility in sodium as a function of temperature.

liquid, or (2) deposition of the oxide on relatively cool solid surfaces. Tests were run on six cold traps of slightly different designs to determine the feasibility of removing oxygen from sodium by cold trapping. All of these cold traps consisted of a regenerative heat exchanger for reducing the sodium temperature to cold trapping temperatures, a cooled settling chamber and a filter. Although it was shown that cold traps can remove oxygen from sodium, the mechanisms involved were not determined.

Some of the experimental work done with sodium cold traps was directed toward performance testing of prototypes of designs to be used on nuclear reactor coolant circuits,^{8,18,22} and operating experience has been obtained on large sodium systems.^{7,10} Gray et al¹² reported experimental work aimed at determining the performance characteristics of cold traps in terms of the rate at which they remove oxygen from a flowing sodium system. Cleanup curves showing reduction of oxygen concentration as a function of time were determined at three flow rates. Increase in flow rate caused a decrease in over-all cold trap efficiency. At very low flow rates (long residence times), the efficiency was high; however, the system turnover time was prohibitively long. An optimum residence time of approximately 5 minutes was determined for maximum system cleanup rate in that system.

Various experimental programs have also been conducted to determine the nature of sodium oxide deposits in cold traps. Hinze¹³ determined the apparent density of sodium oxide deposits on stainless

steel wire mesh in a sodium cold trap to be approximately 0.02 lb/in.³. Billuris⁵ performed two types of experiments to determine the nature of sodium oxide deposits. The first of these was a plug growth experiment in which a cold finger was inserted in a sodium container, and oxide was allowed to deposit on the cold surface. The resulting deposit was hard and granular with agglomerated needle-like crystals of Na₂O. The second type of experiment involved running cold traps containing various types of packing material including wire mesh, loosely knitted wire mesh, Raschig rings (short tube sections), wire screen with 1/4 in. openings and no packing at all. These cold traps were run in sodium containing high oxygen concentrations until the cold trap plugged or gave some definite indication that it was loaded with oxide. The oxide distribution in these traps was determined. Of those traps tested, the loose wire packing performed best. Some conclusions were that the inlet oxygen concentration determined the point in the temperature gradient where nucleation started and that the packing helped support and retain the oxide deposit.

Subbotin et al.³³, Russian investigators, considered the cold trap to consist of three effective zones: a cooling zone, a precipitation zone, and a filtration zone. Experiments showed equal distribution of oxide deposits in these three zones. By assuming incomplete removal of oxides with one pass through the cold trap, and using mass balance around the sodium system, Subbotin arrived at the equation

$$\frac{C_s - C_e}{C_o - C_e} = e^{-\alpha \frac{W}{M} t} \quad (1)$$

where C_s = concentration of oxygen in the sodium, ppm.
 C_e = final concentration of oxygen, ppm.
 C_o = initial oxygen concentration, ppm.
 W = sodium flow rate, g/h.
 M = sodium mass in the system, g.
 t = time, h.

and α is a coefficient correcting for incomplete removal of oxides in the trap.

While this analysis does recognize the possibility of cold trap efficiencies less than 100%, it does not attempt to express possible mechanisms occurring within the cold trap. The time required for removal of oxide from a system with a cold trap of < 100% efficiency was said to be

$$t = 5 \frac{M}{\alpha W} \quad (2)$$

McPheeters and Williams¹⁹ derived an equation similar to the Russian work except the term α was replaced by $1/(W/kA + 1)$ which related incomplete mass transfer during one pass through the cold trap to the mass transfer coefficient, k , the flow rate and the surface area, A . This analysis was done for dissolution of oxygen from a cold trap, and a value for $k(\text{dissolution}) = 1.04 \times 10^{-6} \text{ g/cm}^2\text{-h-ppm}$ was determined experimentally.

In general, the experimental work that has been done to date has been concerned primarily with empirical testing of particular cold trap designs which were intended for use in specific applications. Little has been done to determine the mechanisms involved in precipitation, and at least one question concerning these mechanisms is whether the precipitation process is primarily a surface phenomenon or homogeneous-nucleation in the liquid phase. In the homogeneous-nucleation case, the oxide would nucleate throughout the liquid phase and would then have to be filtered or settled out of the flowing sodium stream. In the completely heterogeneous case the oxide would precipitate only on solid surfaces, and no filtration or settling would be necessary.

The problem of determining the effect of surfaces on reaction rates can be solved by varying the surface-to-volume ratio and observing the effect of these changes on the resulting reaction rates. If this effect has an influence, the reaction is not homogeneous.¹ Lauben¹⁷, in experiments with packless cold traps, has shown that low surface areas are very inefficient in oxide removal. Cold traps containing large surface areas have been shown to be up to 100 per cent efficient in removing oxygen.⁵ These experiments show that precipitation is heterogeneous. Heterogeneous growth of crystals was considered by Noyes and Whitney²⁵ to be essentially a diffusional process. Furthermore, they considered the process of dissolution to be the reverse of crystallization, and the rates of both processes were governed by the

difference in concentration between the solid surface and the bulk fluid. As presented by Mullin²¹ and similarly by VanHook³⁷, an equation for crystallization was proposed in the form:

$$\frac{dm}{dt} = k A(C - C_e) \quad (3)$$

where

m = mass deposited in time, t .

A = surface area of the crystal.

C = solute concentration in the solution (super-saturated).

C_e = equilibrium saturation concentration.

k = the over-all mass transfer coefficient.

More recent work by Berthoud³ and Valetton³⁶ proposed a two-step mechanism in crystal growth. The first step is a diffusion process with the rate of mass transfer given by

$$\frac{dm}{dt} = k_d A(C - C_i) \quad (4)$$

where

k_d = diffusion mass transfer coefficient, and

C_i = solute concentration at the crystal interface.

The second step involves a first order reaction at the surface, the rate of which was given by the equation:

$$\frac{dm}{dt} = k_r A(C_i - C_e) \quad (5)$$

where

k_r = the rate constant for the surface reaction.

Since it is very difficult to measure interfacial concentrations, it is convenient to combine Equations 4 and 5 to form the over-all rate

equation

$$\frac{dm}{dt} = kA(C - C_e) \quad (6)$$

where

$$\frac{1}{k} = \frac{1}{k_d} + \frac{1}{k_r} \quad (7)$$

It will be noted that Equation 6 is the same result obtained in Equation 3; however, a better definition of the over-all mass transfer coefficient, k , has been provided by the more recent work.

The rates of chemical processes are very sensitive to temperature changes. The well-known formulation of the dependence of reaction rates on temperature is¹

$$k' = A_r e^{-E/RT} \quad (8)$$

In Equation 8, which is known as the Arrhenius equation, k' is the specific rate constant at some temperature, T is the absolute temperature, R is the gas constant, A_r is known as the frequency factor or the pre-exponential factor, and E is the activation energy. Benson¹ has demonstrated the physical significance of the frequency factor and the activation energy in a reversible chemical reaction which proceeds to a final state of dynamic equilibrium. The equilibrium constant, K , is related to the forward reaction rate constant and the back reaction rate constant by

$$K = \frac{k'_f}{k'_b} \quad (9)$$

Furthermore, the frequency factors for the forward and back reactions are related to the entropy of reaction by

$$\ln A_f - \ln A_b = \frac{\Delta S}{R} \quad (10)$$

and the difference between the forward and back reaction activation energies is equal to the enthalpy of the reaction

$$E_f - E_b = \Delta H \quad (11)$$

Equation 8 is the approximate form of the Arrhenius equation, and it applies over a restricted range of temperatures and to data of limited accuracy. The validity of Equations 8, 10, and 11 depend on the assumption that the change in ΔC_p is negligible over the temperature range. The small temperature range and limited accuracy of this experiment warrants the use of these approximate forms of the Arrhenius equation.

III. MECHANISM OF COLD TRAP OPERATION

Cold trap designs include a region of decrease in sodium temperature, a cool, isothermal region, and a region of increase in sodium temperature. In the cold trap at all points with the temperature below the saturation temperature of the sodium, precipitation of Na_2O will occur.³⁸ The location of the beginning of precipitation is determined by the temperature distribution in the cold trap and the saturation temperature of the incoming sodium. The precipitation process is considered here as a process consisting of two steps. The first step consists of mass transfer from the bulk sodium to a very thin layer of sodium adjacent to a solid surface or to a sodium monoxide crystal. This layer is supersaturated to some degree with oxygen. The second step involves deposition of sodium monoxide molecules from the supersaturated layer onto growing crystals or other solid surfaces. Equations 4, 5, and 6 and the accompanying discussions describe the rates of these two processes and the over-all rate resulting from combination of the two steps.

Since one of the steps is a diffusion step, the rate of agitation and the hydraulic diameter of the flow path should have a strong effect on the over-all mass transfer rate. The effect of flow rate (or Reynolds number) was considered in this experiment; however, a constant hydraulic diameter was used.

The presence of wire mesh or other foreign objects in the cold trap increases the precipitation surface area, provides favorable sites

for nucleation, and decreases the hydraulic diameter. Sodium flowing into the cold trap is cooled, and at some point its temperature reaches the saturation temperature. Near this point, sodium oxide precipitates, and the concentration of oxygen in that segment of sodium is reduced. Precipitation occurs along the path of the sodium until the temperature rises and the sodium again attains a temperature equal to its new, lower saturation temperature. At a later time, the sodium entering the cold trap has a lower oxygen concentration, thus it progresses further along its path before precipitation occurs; furthermore, the oxide that was initially deposited is now at a higher temperature than the saturation temperature of the sodium. The initially deposited sodium oxide redissolves in the incoming stream and is redeposited further along the flow path. As a result of this dissolution-redeposition process, the sodium oxide is ultimately transferred to the coldest portion of the cold trap.

The rate at which oxygen is removed from sodium in a cold trap is given by the equation

$$\frac{dm}{dt} = kdA(C - C_x) \quad (12)$$

as defined earlier in Equation 6. Where the units of k are $\text{g O/cm}^2\text{-h-ppm}$ and

C = oxygen concentration in the sodium as a function of position in the cold trap, ppm.

C_x = equilibrium concentration as a function of the temperature at any position, ppm.

A = effective surface area, cm².

m = oxygen mass deposited, g.

t = time, h.

The rate of removal is also given in terms of the rate of change of oxygen concentration in the system, C_s, by

$$\frac{dm}{dt} = - M \frac{dC_s}{dt} \times 10^{-6} \text{ g O/g Na-ppm} \quad (13)$$

where

M = sodium mass in the system, g.

The oxygen concentration difference between the entrance and exit of the cold trap defines the rate of oxygen removal according to the following equation:

$$\frac{dm}{dt} = W(C_s - C_{out}) \times 10^{-6} \text{ g O/g Na-ppm} \quad (14)$$

Where

W = sodium flow rate through the cold trap, g/h.

C_{out} = oxygen concentration in the cold trap exit
sodium, ppm.

Equation 12 could be integrated with respect to distance, x, along the cold trap; however, such an integration would be extremely difficult since C_x, the equilibrium concentration at the surface, is a function of the temperature gradient, and C, the oxygen concentration in the sodium, is a function of the temperature gradient as well as the geometry of the cold trap and the system concentration. Average values of C and C_x are used to obtain the equation

$$\frac{dm}{dt} = kA(C_m - C_{xm}) \quad (15)$$

where C_m = the effective mean value of the oxygen concentration of the sodium in the cold trap, ppm.

C_{xm} = the effective value of the equilibrium concentration in the cold trap, ppm.

The mean concentration must be approximated by some measurable concentrations external to the cold trap because of the difficulty of estimating or measuring concentrations as a function of distance along the flow path. We can approximate the mean concentration difference, $C_m - C_{xm}$, in terms of the concentration difference at the cold trap exit, $C_{out} - C_e$, by

$$C_m - C_{xm} = \gamma(C_{out} - C_e), \quad (16)$$

where γ is a constant factor which is a function of the cold trap geometry and the temperature gradient. If C and C_x decreased linearly along the cold trap, γ would be 1/2; however, a computer simulation⁴ of the concentration gradient in this cold trap indicates that for sodium flow rates of 1.0 gallon per minute (gpm), γ should be approximately 0.8, and for flow rates less than 1.0 gpm, γ should be approximately 1.0. Here γ is assumed to be constant, while in reality it probably varies during a cold trap run.

Substituting Equation 16 into 15 and combining with Equations 14 and 13 to eliminate C_{out} and dm/dt , we obtain

$$-M \frac{dC_s}{dt} = kA\gamma \left(C_s + \frac{M}{W} \frac{dC_s}{dt} - C_e \right) \times 10^6. \quad (17)$$

The surface area on which precipitation occurs does not remain

constant during a period of oxide removal from the system. The effective precipitation surface area decreases as the system oxygen concentration decreases. An empirical relationship between effective surface area and system concentration was determined from temperature gradient measurements. Saturation concentrations as a function of cold trap position were determined from these temperature measurements and the solubility of oxygen in sodium. These concentrations were plotted vs the surface area below the point of measurement. Figure 2 shows the relationship between system concentration and the effective surface area. Equation 18 was determined from plots such as that shown in Fig. 2.

$$A = A_0 + \delta \ln(C_s - C_e) \quad (18)$$

where A_0 and δ are constants defined by the temperature gradient in the cold trap.

Substituting Equation 18 into 17 and rearranging, we obtain the differential equation

$$\left(\frac{(M/\delta\gamma) \times 10^{-6}}{kA_0/\delta + \ln(C_s - C_e)} + \frac{M}{W} \right) \frac{dC_s}{C_s - C_e} + dt = 0. \quad (19)$$

Integrating and applying the initial value condition that $C_s = C_0$ at $t = 0$, we obtain the final equation

$$\frac{W \times 10^{-6}}{\delta k \gamma} \ln \left[\frac{A_0/\delta + \ln(C_s - C_e)}{A_0/\delta + \ln(C_0 - C_e)} \right] + \ln \left(\frac{C_s - C_e}{C_0 - C_e} \right) = - \frac{W}{M} t \quad (20)$$

Fig. 2. The effect of concentration on effective precipitation surface area.

The dissolution process is simpler than the precipitation case because the surface area from which material is being transferred remains relatively constant. Oxide which was deposited in the cold trap during previous cold trapping operations has been redistributed and deposited in the coldest portion of the trap. In the cold region of the trap no temperature gradient exists and all portions of the oxide are dissolving at the same temperature. A layer of sodium saturated with oxygen at the cold trap temperature forms around the oxide crystals, and the oxygen diffuses from this layer into the sodium stream. The rate of mass transfer is given by Equation 6. In the dissolution case, C_e and A are constant. Although mass is leaving the wall, the positive direction of mass flow is to the wall. The rate of mass transfer is related to the rate of change of concentration in the system by Equation 13 and to the concentration change across the cold trap by Equation 14. Since C_e is constant, the average driving force for dissolution is approximately

$$1/2(C_s + C_{out}) - C_e. \quad (21)$$

Substituting Equation 21 in Equation 6 and combining with Equations 13 and 14 to eliminate dm/dt and C_{out} , we obtain the differential equation

$$\frac{dC_s}{C_s - C_e} = - \frac{W}{M} \left(\frac{2kA}{2W \times 10^{-6} + kA} \right) dt \quad (22)$$

which, on integration and substitution of the initial condition that at $t = 0$, $C_s = C_0$, we obtain the particular solution

$$\ln \left(\frac{C_s - C_e}{C_o - C_e} \right) = - \frac{W}{M} \left(\frac{2 kA}{2 W \times 10^{-6} + kA} \right) t \quad (23)$$

The above analysis is also applicable to precipitation in an isothermal cold trap. In this case, C_e and A are constant and no oxide redistribution occurs.

IV. EXPERIMENTAL

Sodium systems which serve to transfer heat from the core of a nuclear reactor to a steam generator consist of a closed forced-convection flow circuit. Purification of the sodium is accomplished by bypassing part of the flow through a purification section. In view of this general arrangement, the sodium system used in this test was a closed, forced-convection circuit with partial flow through the cold trap.

The cold trap test loop (Fig. 3) consists of the following components:

1. A large volume ballast tank to provide a reasonable time delay for impurity removal and thermal inertia.
2. An electromagnetic sodium pump.
3. A vacuum distillation analytical sampler.^{2,15}
4. A plugging meter.^{11,32}
5. A cold trap section which was removable and which was provided with a NaK alloy cooling circuit. The cooling circuit consisted of an expansion tank, a NaK to air heat exchanger, an electromagnetic pump, a flowmeter, and a diffusion cold trap.
6. Two electrochemical liquid metal oxygen meters,^{20,35} one upstream from the cold trap section and one downstream.
7. An expansion tank which contained the main system heat input and an impurity addition device.
8. Two sodium system flowmeters, one of which was located

Fig. 3. Isometric view of cold trap test loop.

immediately upstream from the cold trap and the other was located in the plugging meter section.

9. The system was provided with a valving and piping arrangement so that the cold trap section could be isolated from the large tank section while maintaining pumped flow through the cold trap section.

Flow through the system followed a path from the pump to a pipe cross where flow was divided to go to the vacuum distillation analytical sampler, to the plugging meter and to the cold trap. Flow through the distillation sampler was returned to the main stream between the expansion tank and the ballast tank. Flow through the plugging indicator was returned to the ballast tank. Flow to the cold trap passed through the main system flowmeter, through oxygen meter number 1, through the cold trap, the expansion tank, oxygen meter number 2, and returned to the ballast tank. Sodium was drawn from the ballast tank to the electromagnetic pump.

The main criterion involved in designing the cold trap was that it should be simple so that mathematical treatment could be accomplished with relative ease. Normal cold trap design generally involves the use of wire mesh packing to provide many nucleation sites for oxide crystals; however, packing was not used in this cold trap design because it would have interfered with the simplicity of the surfaces provided for nucleation. A second consideration in the design was recovery of some of the heat lost in cooling the sodium.

The resultant cold trap design used in this test is shown in Fig. 4. Sodium entered the annulus at the top, flowed downward and lost heat to the sodium in the central tube and to the NaK in the cooling jacket. Precipitation was initiated near the point at which the sodium temperature was equal to the impurity saturation temperature. The cooled and partially purified sodium flowed up the central tube and regained heat from the incoming sodium.

Hot NaK from the jacket flowed through an expansion tank to a NaK to air heat exchanger. The air flow was provided by a 150 cfm blower, and it was controlled by a pneumatically operated system of louvers. A thermocouple located on the NaK piping immediately downstream from the heat exchanger actuated an air pressure controller which in turn controlled the louver position.

The temperature-controlled NaK flowed past a diffusion type cold trap, (which was used to lower the oxide content of the NaK to prevent plugging of the piping) through an electromagnetic pump, through a flowmeter and back to the lower entrance to the cold trap cooling jacket.

The total volume of the cold trap was 387 in.³ and the total internal surface area was 800 in.². The temperature of the internal bulk sodium was measured with six thermocouples in a thermocouple well located in the annulus.

A description of the analytical devices discussed earlier is provided below:

Fig. 4. Cutaway view of experimental Cold Trap Number 1.

1. Vacuum Distillation System

The vacuum distillation technique was developed by Humphreys¹⁵ and also by Thacker³⁴ in 1957. The technique involves sampling the sodium system, removal of the sodium from the sample cup by evaporation at high temperature (350°-400°C) under vacuum and analyzing the residue for sodium content. The residue is assumed to be Na₂O, and the sodium content of the residue is used to calculate the oxygen content of the original sample. Improved vacuum distillation samplers were designed by Walker³⁹ and later by Rutkauskas²⁸ and the principle was proven by Bergstresser² who added known quantities of oxygen to a sodium system and recovered the known concentrations. This method of analysis was used successfully on a routine basis during these tests. The results of the vacuum distillation analyses were used to calibrate the on-line instruments, i.e., the plugging meter and the oxygen meters. The distillation sampler used during these studies was designed by Rutkauskas²⁷ and is shown in Fig. 5.

2. Plugging Meter

Operation of the plugging meter or plugging indicator depends on the positive temperature dependence of the solubility of oxygen in sodium. The plugging meter consists of a flowmeter, a sodium cooler, and an orifice plate or slotted valve seat. Sodium flows through the orifice plate while it is slowly cooled. The temperature of the orifice and the sodium flowrate are monitored

Fig. 5. Full flow sodium distillation sampler.

continuously. As the sodium temperature at the orifice reaches the impurity saturation temperature, precipitation occurs in the orifice, and the flow rate drops. The temperature at which a decrease in flow is first noted is called the plugging temperature and can be related to the impurity concentration in the sodium.

The plugging meter used in these tests (Fig. 6) had an orifice plate containing four small holes tangent to a large central hole. During plugging runs, the large hole was plugged with a tapered stem, and after each run, flow was restored by removing the stem and allowing the oxide to redissolve.

3. Electrochemical Oxygen Meters

The electrochemical oxygen meters used in these tests (Fig. 7) were developed by United Nuclear Corporation.^{20,35} The oxygen meter is an electrochemical cell with a solid ceramic electrolyte which conducts primarily by oxygen ion migration. A reference electrode consisting of a Cu-Cu₂O compacted and sintered powder mixture is used, and the other electrode is sodium containing dissolved Na₂O. The emf produced by the cell is proportional to the log of the oxygen activity in the sodium. Presumably, this activity is derived from Na₂O concentration; however, other compounds containing oxygen could contribute to the oxygen activity and therefore to the cell emf.

Fig. 6. Plugging meter.

Fig. 7. Electrochemical oxygen meter.

The performance of the cold trap tested in this experiment was determined by observing changes in system concentration as a function of time. Test runs were conducted by making rapid changes in cold trap temperature and measuring the oxygen concentration at short time intervals until the system concentration reached the new equilibrium value. The preparation for a run involved equilibration of the system for a period of at least four days at the initial concentration. To start a run, the air cooler louver control was reset to a new control temperature. The temperature transient time from a minimum cold trap temperature of say 260°C to 170°C was of the order of 15 minutes. Therefore, the effect of the initial temperature transient on the determination of time-zero was negligible.

Oxygen concentration determinations were made at periods of 30 minutes to 1 hour intervals with the plugging meter and the oxygen meters. The required time interval for sampling with the vacuum distillation sampler was 1.5 to 2 hours. Data were taken at short time intervals for 16 hours after the start of each run. Thereafter, data were accumulated at longer time intervals until the system reached equilibrium at the new cold trap temperature. High flow rate runs resulted in very rapid reduction in oxygen concentration because of increased mass transfer coefficients and decreased system turnover time. At 1.0 gpm the time required to reach equilibrium was of the order of 24 hours.

The final or equilibrium concentration was determined from the

cold trap temperature and the LASL solubility relationship.²⁸ Using this value for C_e , the dimensionless concentration,

$$\frac{C_s - C_e}{C_o - C_e}, \quad (24)$$

was determined for each data point. The log of dimensionless concentration was then plotted vs the number of system turnovers, $\frac{W}{M}t$, and the shape of this curve was correlated with the theoretical curve. The mass transfer coefficient was calculated at a value of the dimensionless concentration of 0.2 with Equation 20.

V. RESULTS

Fourteen cold trap test runs were completed during this experimental program. The tests covered a range of sodium flow rates from 0.1 to 1.0 gpm and a range of minimum cold trap temperatures from 142°C to 233°C. In addition to tests in which oxide precipitation occurred, two oxide dissolution test runs were conducted to determine the dissolution mass transfer coefficients. Table 1 is a summary of the runs showing the conditions of flow rate, temperature, initial and final oxygen concentrations and the calculated mass transfer coefficient, k . Runs 1-1, 1-3, and 1-5 produced insufficient data for proper analysis.

It was found during these tests that the plugging indicator produced the most consistent oxygen concentration data. The oxygen meters responded to changes in oxygen concentration; however, their change was sluggish and erratic. The distillation sampler was used as the standard for oxygen concentration measurements. Although the plugging indicator gave consistent results, the plugging temperatures did not agree with saturation temperatures determined from the distillation sampler and the oxygen solubility curve. This situation necessitated the calibration of the plugging indicator against the distillation sampler. With oxygen concentrations near 30 ppm, the plugging temperature was 10°C lower than the saturation temperature, and with oxygen concentrations near 10 ppm, plugging temperatures were 20°C lower than the saturation temperature. Figure 8 shows the

Table 1
Operating Parameters for Cold Trap Tests

Run No.	Minimum Cold Trap Temp. (°C)	Flow Rate (gpm)	Initial O ₂ Concentration (ppm)	Final O ₂ Concentration (ppm)	Mass Transfer Coefficient (g/cm ² -h-ppm x 10 ⁶)
1-2	213	1.05	4.4	14.0	8.4*
1-4	180	1.0	41.0	5.7	27.6
1-6	186	0.95	42.0	6.9	28.4
1-7	180	0.25	58.0	5.7	4.5
1-8	142	0.5	42.0	2.2	14.3
1-9	160	0.5	48.0	3.3	16.6
1-10	171	0.1	43.0	4.4	1.26
1-11	196	0.1	46.2	9.1	1.23
1-12	146	0.1	50.0	2.3	1.35
1-13	195	0.25	47.0	8.8	2.67
1-14	233	1.0	3.0	28.7	18.0*

*These runs consisted of dissolution of sodium oxide from the cold trap to increase the oxygen concentration in the system.

calibration curve of the plugging indicator for Runs 1-1 through Run 1-6. The solubility curve is also shown in this figure for reference. After Run 1-7, it was noted that plugging indicator calibration curve had shifted. This shift was due to a change in the operating flow rate used during plugging determinations made after Run 1-7. The calibration curve for Runs 1-7 through 1-14 is shown in Fig. 9 with the solubility curve shown for reference. In these calibrations the

Fig. 8. Plugging indicator calibration curve for Runs 1-1 through 1-6. The oxygen solubility curve is shown for reference.

Fig. 9. Plugging indicator calibration curve for Runs 1-7 through 1-14. The oxygen solubility curve is shown for reference.

solubility curve and the distillation analyses were assumed to be correct. This assumption was based on agreement between the minimum cold trap temperature, the distillation analyses and the solubility curve during steady state operation of the sodium system.

It should be noted here that workers in the sodium technology field have previously equated the two terms "plugging temperature" and "saturation temperature". However, it was found that below 30 ppm oxygen concentration, the plugging temperature was lower than the saturation temperature in all cases.

Figures 10, 11, 12, 13, and 14 show the results from cold trap test Runs 1-6, 1-9, 1-13, 1-10, and 1-14, respectively. The data points represent experimental oxygen concentration data accumulated during the test runs, and the curves are plots of Equation 20 using the calculated k values. Figure 10 (Run 1-6) is representative of the series of 1.0 gpm precipitation runs. The temperature profile resulting from this flow rate was such that the correlation shown in Fig. 2 between effective surface area and the system oxygen concentration was good. The model fit the 1.0 gpm case very well over about $1\frac{1}{2}$ orders of magnitude in dimensionless concentration. Figure 11 (Run 1-9) is representative of the 0.5 gpm flow rate series of tests. These tests were conducted with a temperature gradient which resulted in a less adequate area correlation than in the 1.0 gpm runs. The model fit the data well over one order of magnitude in dimensionless concentration. Figure 12 (Run 1-13) is representative of the 0.25 gpm

Fig. 10. Results from Run 1-6. The curve is a plot of Equation 20 with $k = 28.4 \times 10^{-6} \text{ g/cm}^2\text{-h-ppm}$.

Fig. 11. Results from Run 1-9. The curve is a plot of Equation 20 with $k = 16.6 \times 10^{-6}$ g/cm²-h-ppm.

Fig. 12. Results from Run 1-13. The curve is a plot of Equation 20 with $k = 2.67 \times 10^{-6} \text{ g/cm}^2\text{-h-ppm}$.

Fig. 13. Results from Run 1-10. The curve is a plot of Equation 20 with $k = 1.26 \times 10^{-6} \text{ g/cm}^2\text{-h-ppm}$.

Fig. 14. Results from Run 1-14. The curve is a plot of Equation 23 with $k = 18.0 \times 10^{-6} \text{ g/cm}^2\text{-h-ppm}$.

runs. The correlation of the experimental data with the model was good in the range of dimensionless concentration from 1.0 to 0.2.

Figure 13 (Run 1-10) is representative of the 0.1 gpm runs, and the correlation of the data with the model was good in the range of dimensionless concentration from 1.0 to 0.3.

Figure 14 (Run 1-14) represents the dissolution runs which involved an increase in oxygen concentration. The change in dimensionless concentration was linear on a log scale as a function of the number of system turnovers as predicted by Equation 23.

VI. DISCUSSION

The observed decrease in the range of applicability with decreasing flow rate could be due to any of three causes: First the area correlation fails at the lower flow rates because the temperature profile becomes very steep at the cold trap inlet and flat through the rest of the cold trap. Second, dissolution of oxide precipitated early in the runs and reprecipitation in cooler regions of the cold trap was not considered in the mathematical treatment. Third, the rapid drop in temperature at the cold trap inlet probably lead to homogeneous nucleation of Na_2O crystals.

The mass transfer coefficient, k , was a function of temperature according to the Arrhenius equation (Equation 8). Figure 15 is a plot of k vs $1/T^\circ\text{K}$ where T is the minimum cold trap temperature. An increase in the mass transfer coefficient with increasing temperature occurred for both the precipitation and the dissolution processes. The activation energy for precipitation was 3.0 kcal/mole, and that for dissolution was 19.0 kcal/mole. The strong effect of flow rate on the precipitation mass transfer coefficient suggests that the process was diffusion controlled. If the process were precipitation rate controlled, no flow effect would be seen.

The activation energy for diffusion of sodium monoxide in sodium was reported as 2.43 kcal/mole³⁰ which is in reasonably good agreement with the activation energy observed for the diffusion controlled sodium monoxide precipitation process. The dissolution

Fig. 15. Arrhenius plot showing the mass transfer coefficient, k , as a function of $1/T \text{ } ^\circ\text{K}$.

process was not diffusion controlled because the activation energy is much too high to be attributed to diffusion.

The difference between the activation energy of dissolution and the activation energy of precipitation is the enthalpy of solution of Na_2O in sodium. The enthalpy of solution obtained from recent solubility data was 16.0 kcal/mole.²⁸ From this data, the activation energy for the precipitation rate controlled process should be approximately 3.0 kcal/mole.

Since the proposed model did not fit the 0.25 and 0.10 gpm runs, the data from these runs were not expected to be very reliable. As can be seen in Fig. 15, the data points from the low flow rate runs do not fit a curve of consistent or easily explainable slope.

In diffusion controlled crystal growth, the rate of mass transfer is a function of the viscosity, η , and the density, ρ , of the solution, the relative velocity, v , between the solution and the crystal, the diffusivity, D , of the solute molecules in the liquid, and the hydraulic diameter of the flow passage, d . The relationship between these quantities can be written in the form of a dimensionless equation containing three dimensionless groups.

$$\frac{kd}{D} = \beta \left(\frac{\rho v d}{\eta} \right)^a \left(\frac{\eta}{\rho D} \right)^b \quad (25)$$

where the groups $\frac{\rho v d}{\eta}$, $\frac{\eta}{\rho D}$, and $\frac{kd}{D}$ are the Reynolds (Re), Schmidt (Sc) and Sherwood (Sh) number respectively.²¹ Also, a , b and β are dimensionless constants. Experimental work by Hixson and Knox¹⁴ on

investigation of growth rates of copper sulfate and magnesium sulfate single crystals determined the exponential constants, a and b, to be 0.6 and 0.3, respectively. Substitution of these constants and the appropriate physical constants ($\eta = 0.0045$ g/sec-cm, $D = 0.35 \times 10^{-5}$ g mole/cm sec,³⁰ $\rho = 0.904$ g/cm³ and the units of k are g mole/cm²-sec) into Equation 25 results in

$$k = 157 \beta (v)^{0.6}. \quad (26)$$

Figure 16 is a plot of k vs v with $\beta = 2.49 \times 10^{-12}$. The data points were taken from the curves in Fig. 15 at a common temperature of 170°C. The data points from the low flow rate runs appear to be too low to fit the $v^{0.6}$ vs k curve. The poor fit at low flow rates is probably due to the same reasons stated earlier plus the possibility of diffusion through completely stagnant films of significant thickness at the very low sodium velocities.

At very high flow rates the diffusional mass transfer coefficient would no longer be controlling, and the surface reaction rate constant would control. Further increase in the flow velocity would then have no effect on the mass transfer coefficient. However, the increased sodium velocity would tend to erode the deposited oxide away. An optimum sodium velocity could be determined which would result in high mass transfer coefficients with minimum erosion of the oxide.

Fig. 16. Effect of sodium velocity on the mass transfer coefficient at 170°C.

VII. CONCLUSIONS

The data obtained in this experiment can be classified in two groups: The relatively high sodium velocity runs resulted in data which fit the mathematical model quite well. The low sodium velocity runs (0.25 and 0.1 gpm runs) resulted in data which fit the model very poorly. Comparison of the mass transfer data from each flow regime indicates that the low velocity data produced apparent mass transfer coefficients which are probably lower than the true coefficients. The mass transfer coefficients calculated from the higher velocity data are probably correct; however, further experimental work will be necessary to verify these numbers.

The precipitation process was in all cases diffusion limited. This conclusion is verified by the dependence of the mass transfer coefficients on velocity and the close agreement between the precipitation activation energy and the diffusion activation energy. The dissolution process was reaction rate limited as verified by the high activation energy.

The precipitation mass transfer coefficient is a function of both temperature and Reynolds number. The mass transfer coefficient increased with increasing temperature with an activation energy of 3 kcal/mole, and it increased with increasing Reynolds number proportional to $(Re)^{0.6}$. At common temperatures and flow rates, the dissolution mass transfer coefficient was lower than the precipitation mass transfer coefficient, and the activation energy for dissolution was 19 kcal/mole.

VIII. RECOMMENDATIONS

Only one cold trap design was tested in this experiment, and that design was a packless cold trap. Cold traps which have been used on large systems in the past have, in generally, contained wire mesh or some other forms of material suitable for retaining or supporting the oxide crystals. The flow characteristics are undoubtedly different in a packless cold trap from those in a packed cold trap. Since the flow characteristics are very important in mass transfer, packed cold traps should be tested and the mass transfer coefficients measured under these flow conditions. Aside from the flow effects, the packing would prevent breaking away of the oxide during oxide deposition. Oxide breakaway would result in apparent mass transfer coefficients lower than the true coefficients.

Cold traps should be tested at very high Reynolds numbers to determine whether or not the mass transfer coefficients are much greater under these conditions. As discussed previously, the coefficients could be much higher, and if these high coefficients could be attained, cold traps could be designed which would perform much more efficiently than the cold traps currently being used.

A computer simulation of cold trap operation should be developed. Such a simulation would not be limited by some of the assumptions made in the analytical development. The cold trap could be divided into many finite nodes. The nodes at temperatures above the saturation temperature would be ineffective, and those cooler than the saturation

temperature would precipitate oxide according to the rates expressed by Equation 6. Sodium system piping and mixing tanks could be simulated in the computer program.

Computer determinations of mass transfer coefficients as a function of temperature, Reynolds number and geometry would provide values which could be used to design cold traps for sodium systems of any size, required cleanup rate and oxide holding capacity.

IX. BIBLIOGRAPHY

1. Benson, Sidney W., The Foundations of Chemical Kinetics, McGraw-Hill Book Co., Inc., New York, Toronto, London, 1960.
2. Bergstresser, K. S., Waterbury, G. R., and Metz, C. F., "Determination of Trace Amounts of Oxygen Added to Metallic Sodium," Report LA-3343, Los Alamos Scientific Laboratory, August 1965.
3. Berthoud, A., "Theorie de la Formation des Faces d'un Crystal," J. Chim. Phys. 10, 624 (1912).
4. Biery, J. C., Personal Communication, Los Alamos Scientific Laboratory, December 1967.
5. Billuris, G., "Experimental Investigations of the Removal of Sodium Oxide from Liquid Sodium," Report GEAP-3328, General Electric Atomic Power Equipment Dept., January 18, 1960.
6. Bogard, A. D. and Williams, D. D., "Solubility of Sodium Monoxide and of Sodium Hydroxide in Metallic Sodium," Report NRL-3865, 1951, Naval Research Laboratory.
7. Bray, J. A., "Experience on the Removal of Impurities from Liquid Metal Systems by Cold Trapping," European Atomic Energy Society Symposium on Liquid Metals, September 1963.
8. Cygan, R., "HNPF Cold Trap Evaluation," Report NAA-SR-4382, Atomics International, a Division of North American Aviation, Inc., 1959.
9. Davis, M. and Draycott, A., "Compatibility of Reactor Materials in Flowing Sodium," Report IGR-TN/C-857, 1958, Culcheth Laboratory, Lanchester, Great Britain.
10. Faris, F. E., Glasgow, L. E., Johnson, D. H., Campbell, R. W., and Owens, J. E., "Operating Experience with the Sodium Reactor Experiment," Proceedings of the 2nd United Nations International Conference on the Peaceful Uses of Atomic Energy held in Geneva, Sept. 1-13, 1958, Vol. 9, Nuclear Power Plants, Part 2, A/Conf./15, p. 452.
11. Gray, I. L., Neal, R. L., and Voorhees, B. G., "Inexpensive Way to Control Oxygen in Sodium Heat Transfer Systems," Nucleonics, Vol. 14, No. 10, October 1956.

12. Gray, I. L., Neal, R. L., and Voorhees, B. G., "Control of Oxygen in Sodium Heat Transfer Systems," Liquid Metal Technology, Part I. Vol. 53, 1957.
13. Hinze, R. B., "Control of Oxygen Concentrations in Large Sodium Systems," Report NAA-SR-3638, Atomics International, a Division of North American Aviation, Inc., December 1, 1959.
14. Hixson, A. W. and Knox, K. L., "Effect of Agitation on the Rate of Growth of Single Crystals," Ind. Eng. Chem. **43**, 2144 (1951).
15. Humphreys, J. R., AICHE Nucl. Engr. Sci. Congress, CEP Symp. Ser. 53, (20) 7, 1957.
16. Jackson, C. B., Liquid Metals Handbook, Sodium (NaK) Supplement, TID-5277, July 1, 1955, Atomic Energy Commission-Department of the Navy, Washington, D. C.
17. Lauben, G. N., "Packless Cold Trap Evaluation," Report NAA-SR-MEMO-9920, Atomics International, a Division of North American Aviation, Inc., 1964.
18. McDonald, J. S. and Perez, F., "Heat and Mass Transfer Analysis of Proposed Experimental Cold Trap Design," Report NAA-SR-MEMO-4578, Atomics International, a Division of North American Aviation, Inc., 1959.
19. McPheeters, C. C. and Williams, J. M., "A Comparison of Three Methods of Oxygen Concentration Measurement in Sodium," IAEA Symp. on Alkali Metal Coolants, Corrosion Studies, and System Operating Experience, Vienna, 1967.
20. Minushkin, B., "Plugging Meter and Continuous Oxygen Meter," Report MTL-3761, United Nuclear Corporation, April 14, 1964.
21. Mullin, J. W., Crystallization, Butterworths, London, 1961.
22. Nathan, M. E. "Performance of the SRE-Prototype Cold Trap Assembly," Report NAA-SR-MEMO-1798, Atomics International, a Division of North American Aviation, Inc., 1956.
23. Nettley, P. T., et al., "Problems in the Selection and Utilization of Materials in Sodium Cooled Fast Reactors," London Conference on Fast Breeder Reactors, May 1966 (British Nuclear Energy Society), Ref. 5B/3.

24. Noden, J. D. and Bagley, K. Q., "Solubility of Oxygen in Sodium and NaK Alloy," Report R&DB(C)-TN-80, United Kingdom Atomic Energy Authority, 1954.
25. Noyes, A. A. and Whitney, W. R., "Rate of Solution of Solid Substances in Their Own Solution," J. Amer. Chem. Soc. 19, 930 (1897) and Z. Phys. Chem. 23, 689 (1897).
26. Rowland, M. C., Plumlee, D. E., and Young, R. S., "Sodium Mass Transfer: XV. Behavior of Selected Steels Exposed in Flowing Sodium Test Loops," Report GEAP-4831, General Electric Atomic Power Equipment Dept., March 1965.
27. Rutkauskas, V. J., "Quarterly Status Report on the Advanced Plutonium Fuels Program, April 1 - June 30, 1967," Report LA-3745-MS, Los Alamos Scientific Laboratory, August 30, 1967.
28. Rutkauskas, V. J., "Determination of the Solubility of Oxygen in Sodium Using the Vacuum Distillation Analytical Technique," Report LA-3879-MS, Los Alamos Scientific Laboratory, 1968.
29. Salmon, O. M. and Cashman, Jr., T. J., "Solubility of Sodium Monoxide in Liquid Sodium," Report KAPL-1653, Knolls Atomic Power Laboratory, 1956.
30. Siegel, S. and Epstein, L. F., "Diffusion of Na_2O in Sodium in the Range 900 to 100°F," Report GEAP-3357, General Electric Atomic Power Equipment Dept., San Jose, California, December 21, 1959.
31. Sittig, Marshall, Sodium Its Manufacture, Properties and Uses, Reinhold Publishing Corp., New York, Chapman and Hall, Ltd., London, 1956.
32. Smith, C. R. F., "Determination of Oxygen in Sodium - A Critical Review of Analytical Methods," Report NAA-SR-MEMO-2061, Atomics International, a Division of North American Aviation, Inc., May 1961.
33. Subbotin, V. I., Kirilov, P. L., and Kozlov, F. A., "The Purification of Sodium from Oxygen and Monitoring of the Oxygen Content in Sodium," USSR Report 701, 1965.
34. Thacker, R., "The Determination of the Oxygen Content in Liquid Sodium," Report IGR-TN/C-609, June 1957, Culcheth Laboratory, Lanchester, Great Britain.

35. "Liquid Metal Oxygen Meter Operating Manual Model TP," Report UNC-5141, United Nuclear Corporation Research and Engineering Center, Elmsford, New York, December 15, 1965.
36. Valetton, J. J. P., "Wachstum und Auflosung der Kristalle," Z. Kristallogr. 59, 135, 335 (1923); 60, 1 (1924).
37. Van Hook, Andrew, Crystallization Theory and Practice, Reinhold Publishing Corp., New York, Chapman and Hall, Ltd., London 1961.
38. Voorhees, B. G. and Bruggeman, W. H., "Interim Report on Cold Trap Investigations," Report KAPL-612, Knolls Atomic Power Laboratory, 1951.
39. Walker, J. A. J., France, E. D., and Edwards, W. T., "The Determination of Oxygen in Sodium," The Analyst, the J. Soc. Analytical Chem. Vol. 90, No. 1077, pp. 727-731, December 1965.