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TO: J. B. Williams*

COPIES TO: R. J. Beeley W. J. Hallett* A. C. Williams*
 R. W. Dickinson* J. A. Leppard*
 J. J. Droher* J. E. Mahlmeister
 L. E. Glasgow A. E. Miller*

SUBJECT: Investigation of Sodium Leak Plugging

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I STATEMENT OF PROBLEM

Investigate the possibility of stopping sodium leaks, at temperatures up to 1200°F, by reacting the leaking sodium with a gas such as CO₂ or O₂ present in the surrounding atmosphere. The success of such a plugging mechanism would make it possible to reduce the likelihood of having equipment shutdowns due to sodium leaks, for instance a leak in the shell of a calandria core.

II. SUMMARY AND CONCLUSIONS

1. Results obtained in this experiment indicate little likelihood of success in stopping reactor sodium leaks by this plugging mechanism at temperatures above about 600°F. It is probable that this statement is true in general for oxygen containing atmospheres, because it appears that for the plugging process the rate controlling factor is the chemical reaction rather than the rate of oxygen diffusion to the sodium surface.

2. Sodium leak plugging tests were conducted in an oxygen atmosphere over the following ranges of independent variables: circular hole size, 0.006-0.0135-in.; oxygen partial pressure, 4.1-10.1 psi; and leakage differential pressure drives, 5-25 psi. Test results indicated the plugging characteristics to be virtually independent of the oxygen concentration

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in the surrounding atmosphere. The experimental results were correlated on the basis of an "effective film force" to yield the following relation which gives the maximum hole size for which leaking sodium can be plugged for a given sodium temperature (within the 400-600+ °F range) and leak driving difference:

$$d = 4.5 \times 10^9 T^{-3.92} \Delta P^{-1},$$

where d is the hole diameter in inches, T is in °F, and ΔP is in psi.

3. A single test was conducted with CO₂ as the gaseous reactant. The resulting plugging performance was slightly better than was obtained with O₂, but was not sufficiently promising to justify continued testing.

4. Equations were set up for the solution of the chemical kinetics-heat transfer problem by means of an analog computer. Approximate values for the sodium oxygen reaction velocity constant and energy of activation were derived from data presented in British reports. Solutions of this problem would have been of value in connection with oxide film thickness-strength studies; however, they were not carried out since the plugging mechanism appeared not to have merit for the proposed application. The equations and recommended values of constants are included for possible reference.

III. DISCUSSION

A. Background

In connection with sodium fire hazard studies a moderate amount of experimental data has been obtained regarding sodium-oxygen reactions; however, some of the reports on the subject make only a limited presentation of data. Findings reported by the English⁵ indicate that under a certain set of conditions a small pool of sodium contained in a reaction vessel was elevated to a temperature of 1020°F without an ignition occurring. This gave hope of the possibility that leaks might be plugged by the rapid formation of an oxide film or membrane of sufficient tenacity to stop a flow of sodium. The experiment reported herein was concerned with this particular aspect of the sodium-gas reaction.

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Other results of the British experiments clearly showed that hydrogen or water vapor present in the oxygen in adequate amount has a catalytic effect on the sodium oxygen reaction. However, at levels of moisture (or hydrogen) content $< 2 \times 10^{-5}$ mm Hg no reaction was evident; it was under these conditions that the 1020°F temperature mentioned above was reached without ignition. The English in their kinetics studies also found the reaction rate to depend upon the partial pressure of oxygen in the surrounding atmosphere.

The reaction of carbon dioxide with sodium results in the formation of sodium carbonate and carbon. In a sodium fire study here at AI,⁷ the application of gaseous carbon dioxide to a burning sodium surface was found to have no effect. Other than the AI report, no information was found in the literature on the carbon dioxide-sodium reaction as it relates to plugging or film formation.

B. General Approach

The objective of this investigation was to determine what gaseous reactant content in an atmosphere surrounding a sodium system is required in order to plug a sodium leak through a crack of postulated size. Attainment of this objective included studies of the strengths of plugs at various temperatures. For application of this information to a reactor system it would also be desirable to conduct a survey of sizes of cracks which have occurred in operating systems; this would provide a statistical foundation for the postulation of a crack size.

The plan of action called first for studying the plugging of round holes to determine functional plugging relationships dependent upon temperature, hole size, and reactant gas partial pressure. Following this, plugs at high temperature were to be subjected to strength tests. Results of the foregoing were then to be tested for applicability to rectangular holes. As it developed, the results of the first phase gave unfavorable results for the plugging mechanism and the program was terminated.

C. Experimental Apparatus and Procedure

The apparatus used in this experiment is pictured in Figure I. Each 3/4-in. diameter capsule (SS 304 - 16 mil wall thickness) containing sodium was centered in the 6-in. diameter reaction vessel directly opposite a 2½ x 4-in. window in such a manner that the circular leak hole could be clearly observed. Positioned around the capsule was a clamshell heater whose power supply was controlled by a Variac. Passing through the flange of the reaction vessel were tube connections for the helium cover gas, the vent, vacuum line, and services for argon, air, and reactant gas. Also penetrating the flange were power supply leads and leads connecting the thermocouple on the capsule bottom to a Pyrotest potentiometer. In the reactant gas and air supply line was a Drierite drying unit (containing P_2O_5) guaranteed to reduce moisture to an amount corresponding to -110°C dewpoint. Pressure in the reaction vessel was measured by a compound gage, and a mercury manometer was used to determine differences in pressure of the capsule cover gas and the reactant vessel atmosphere.

The test capsules were filled with sodium in a glove box, then drilled under a flow of purge gas after which the hole was quickly sealed with tape. Following this, the capsules were mounted in the test fixture and, while the capsule (and chamber) were continuously flooded with argon, the sealing tape was removed and the vessel tightly closed. Then, to bring the atmosphere to a "superdry" condition, the vessel was evacuated to 1 in. Hg absolute after which it was charged with air from the drier until the pressure in the vessel rose to 5 psig. The assembly was again evacuated and the dilution procedure repeated ten times, thus reducing the moisture content to less than 2×10^{-5} mg/liter of dry air. Next the oxygen was passed through the drier and admitted to the chamber until its total partial pressure was as desired.

The capsule was rapidly (within about 3 min.) heated to about 400°F with the pressure of the sodium and the surrounding atmosphere being equal. At this point the desired pressure difference was

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established, after which rapid heat addition continued until conclusion of the run. The various combinations of leak hole size, oxygen partial pressure, and ΔP included in the test program are tabulated in Table I.

Table I
Summary of Experimental Runs
Plug Failure Temperature, °F (ΔP Shown in parenthesis)

Oxygen partial Pressure, psi	Leak Hole Size, inch		
	0.006	0.009	0.0135
4.1	(5) 605 (15) 500	(5) 525	(5) 440
7.1		(5) 530 (15) 520 (25) 535	
10.1	(5) 520 (15) 555	(5) 550	(5) 436 (15) 405
CO ₂ partial pressure, 5 psi			(5) 549

Runs were usually terminated when there was complete failure of the plug, and the measures taken at those times were to drop the ΔP to zero and flood the vessel with argon.

After the capsule assembly cooled to room temperature, the oxide formation around the leak hole was cleaned away (under a flow of inert gas) and polished with emery paper. Then the chamber was quickly sealed, and another run was conducted. The initial quantity of sodium in each capsule was in general sufficient to permit three runs per capsule. A single test was conducted in the same general fashion with CO₂ as the vessel atmosphere.

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It is recognized that the procedure described above does not produce precisely the conditions that one would expect to be associated with all leaks which might occur in a reactor sodium system. It is possible that during preparation and installation of the capsule for the experiment a protective film of foreign material might form over the exposed sodium surface. Also an oxide film might begin to form during the rapid heating of the specimen; however, sodium-oxygen reaction rates are apparently not fast at the lower temperatures. In spite of these potential introductions of extraneous plugging devices, it is considered that the information obtained indicates fairly clearly what might be expected in the way of temperature-plug strength characteristics under the conditions which might be associated with an actual leak.

D. Description of Typical Plugging Process

The usual sequence of events occurring as the test capsules were heated was as follows:

- 1) Nothing happened up to temperatures in the 500°F range.
- 2) A beginning of sodium activity with the (slow) formation of a series of hemispherical bubbles, each of which seemed to dissolve as a thin film of sodium and flow away from the hole. The flowing film oxidized and remained fixed to the surface, leaving the appearance of a number of dark circular waves concentric with the hole.
- 3) At higher temperatures, a film formed over the bubble surface allowing it to grow in size rather than disappear as in (2) above. As the bubble continued to grow fissures opened in the skin allowing fresh sodium seepage. In most runs a small fire would finally break out, and after it was extinguished, the remaining plug had a cauliflower-like appearance.

E. Analysis of Results

Two possible modes of cracking and sodium leakage seem plausible. One mode involves initial formation of a hairline crack with gradual propagation occurring until finally, after development of a high load condition, the crack opens sufficiently wide for significant

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sodium flow to take place. The other possible mode is the occurrence of a sudden fracture large enough to permit sodium to leak. In the first type there is small sodium communication with surrounding atmosphere for a time before the leak event occurs, and this is somewhat analagous to conditions prevailing during this experiment. This is the sort of crack considered to be by far the most likely to occur.

In the second of the two kinds of cracks described above, the sodium reaction rate is of great importance. It was originally planned to study analytically the formation of film thickness as a function of time for comparison with experimental film strength results; however, the plugging process was found not to be sufficiently promising to justify performance of calculations at this time. Nevertheless, included in the Appendix for possible future reference are the heat transfer and chemical kinetics equations for analog solution to determine film thickness as a function of time. Also given are suggested values for the sodium-oxygen reaction velocity constant and energy of activation, based on analysis of the British experimental results.

Turning to the results of this experiment, the film formation process is first considered. The film strength (which should be proportional to thickness), appeared to be almost independent of oxygen partial pressure in the chamber, as may be seen in Figure 2. According to the kinetic theory of gases⁸ for a given temperature and pressure, the coefficient of diffusivity of oxygen should vary only slightly with composition. This is consistent with what one might infer on a gross basis from the results of this experiment. The diffusivity coefficient varies in proportion to $\frac{T^{3/2}}{P}$, and the English experiments conducted over a range of pressures (pure oxygen atmosphere) indicated a reaction rate dependence upon oxygen content. This suggests that for situations such as ours the rate controlling process is not the chemical reaction alone, but also the rate of diffusion of the oxygen to the surface. However, because of the reaction characteristic curves found in the British kinetics studies, Appendix I considers only the parabolic

reaction rate law and gives no treatment of the diffusion problem.

If the exposed sodium surface at the leak hole is hemispherical as shown in the profile of Figure 3, a static force balance yields

$$\Delta P = P_s - P_a \approx \frac{2F}{r},$$

in which F is regarded as an effective film force. By measuring the temperature for the various runs at which the plug failed (i.e., showed evidence of becoming liquid) it was possible to obtain an idea of the film strength as a function of temperature through the use of the above equation. Appearing on Figure 4 is a plot of all points from this experiment, thus representing various r , ΔP , and oxygen partial pressures. Also included in the Figure is a single point reported by the British.⁹ Consistent with our observations from Figure 2 regarding the lack of dependence on oxygen content, we may, using Figure 4, represent the film force solely as a function of temperature -

$$F = 1.12 \times 10^9 T^{-3.92},$$

where T is in °F. This may be substituted in the force balance expression to yield an equation giving the size of hole that one may expect to plug for a given T and ΔP , for oxygen partial pressures in the range 4 - 10 psi.

$$d = 4.5 \times 10^9 T^{-3.92} \Delta P^{-1},$$

where d is the hole diameter in inches, T is in °F, and ΔP is in psi. The single test conducted with CO_2 involved a 0.0135 in. hole and a 5 psia CO_2 pressure. With a P of 5 psi, the plug failure occurred at 549°F, which compares with 440°F for the O_2 test under similar conditions.

Based on results of these capsule tests, it is considered unlikely that leaking sodium at temperatures above about 600°F can be stopped by reaction with oxygen. One test indicated that better results might be obtained with carbon dioxide; however, the latter did not offer sufficient promise to justify continued testing.

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Nomenclature

A	energy of activation
C	sodium specific heat
d	hole diameter
F	effective film force
h	heat transfer film coefficient
ΔH	heat of sodium-oxygen reaction
k	reaction velocity rate constant
k_o	parabolic law reaction coefficient
k_a	air thermal conductivity
P_s	sodium pressure
P_a	vessel atmosphere pressure
ΔP	leak during pressure difference
r	leak hole radius
r_1	coordinate of inner surface of film
R	universal gas constant
T	temperature
T_a	absolute temperature
T_c	vessel atmosphere temperature
ϵ	coefficient of emissivity
ρ	sodium density
δ	Boltzman constant

APPENDIX

Equations for Sodium Oxide Plug Formation

To determine the approximate oxide film thickness on the surface of sodium issuing through a circular leak hole it is necessary to carry out simultaneously a solution of the chemical kinetics and heat transfer problems. As discussed in Section III, E, it is assumed that the speed of chemical reaction is the rate controlling mechanism in the Na-O₂ reaction, and it was found that the reaction process may be described by the corrosion or parabolic rate law. The reaction velocity constant is assumed to depend on temperature in accordance with Arrhenius's equation. It is assumed that the exposed sodium presents a hemispherical surface and, in addition, spherical symmetry is assumed. Thus the chemical reaction is described by

$$\rho^2 (r - r_1)^2 = k_0 t \exp(-A/RT_a). \quad (1)$$

A heat balance accounting for the heat of reaction and radiation and convection heat transfer to the gaseous atmosphere gives, after (1) is differentiated with respect to time and used in making a substitution for $\frac{dr_1}{dt}$

$$\frac{dT}{dt} = \frac{3\Delta H k r_1^2}{2\rho^2 C r^3 (r-r_1)} \exp(-A/RT_a) - \frac{3h}{C\rho r} (T-T_c) - 3\frac{\sigma\epsilon}{C\rho r} T_a^4 \quad (2)$$

The various terms are as defined in the nomenclature. Analysis of two reaction data curves* plotted in the English reports^{5,6} results in the following values which are probably accurate within an order of magnitude, for the constant, k, and the energy of activation.

$$k_0 = 4 \text{ gm}^2 \text{ Na/Cm}^4 \text{ sec.}$$

$$A = 13,600 \text{ cal/mol}$$

* Data in the curves were for sodium temperatures of 104 and 270°C and moisture contents of .01 and .0005 mg/litre, respectively.

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The velocity rate constants corresponding to 104 and 270°C are, respectively

$$k_{104} = 0.43 \times 10^{-7} \text{ gm}^2 \text{ Na/Cm}^4 - \text{sec.}$$

$$k_{270} = 1.1 \times 10^{-5} \text{ gm}^2 \text{ Na/Cm}^4 - \text{sec.}$$

Because of the assumption that spherical symmetry exists, the heat transfer film coefficient for the sodium surface in still gas equals k_a/r ,¹⁰ where k_a is the thermal conductivity of the surrounding atmosphere. A value of 0.80 is suggested for the emissivity ϵ , and the heat of reaction ΔH equals -104 Kcal/mole.¹¹ Solution of the problem is probably best handled on an analog computer; however, as mentioned previously, the solution was not carried out due to the lack of promise of the plugging mechanism. The problem setup is presented above for possible future reference.

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Figure 1
Experimental Apparatus

Figure 2

Temperature at Plug Failure vs Oxygen Partial Pressure

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Figure 3
Profile of Leak Hole and Plug